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Terpyridine-Metal Complexes: Synthesis, Spectral Studies, DNA Cleavage and Antimicrobial Activity

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A B S T R A C T

Mononuclear transition metal complexes $[Cu(stpy)_2](SO_4)$ (1), $[Ni(stpy)_2](Cl_2)$ (2), and $[Mn(CH_3tpy)_2](ClO_4)_2$ (3) where stpy is the tridentate ligand 4'-(thiophenyl-2,2':6',2''-terpyridine and CH_3tpy is 4'-methylphenyl-2,2':6',2''-terpyridine have been synthesized. Spectral techniques such as UV-Vis, FT-IR and ESI-MS were employed to characterize the compounds. The compounds showed a broad ligand to metal charge transfer transition in the 338-352 nm range, according to the electronic spectra. DNA cleavage studies have been carried out in Copper and Manganese complexes. Interestingly both the complexes were able to cleave DNA. The antimicrobial exercises of the ligands and their complexes have additionally been done.

***Key words*:** DNA cleavage, Terpyridine, Copper, Manganese, Antimicrobial

Multiple life-sustaining processes are required by organisms, including metabolic routes for the conversion of food to energy, transport pathways for the removal of undesired byproducts, and reproductive mechanisms for the generation of new cells. Proteins are involved in the majority of biological activities. Metal ions are essential for the structure and function of approximately 30% of all proteins [1]. Enzymes are proteins that catalyze biological reactions, while metallo-enzymes are those that employ metals. Metal ions are found at the active areas of a substantial percentage of newly identified enzymes and proteins. As a result, metals are increasingly being recognized for their roles in biological processes [2]. Because the ultimate goal of every biological activity is to understand its function, and function is inextricably linked to geometric structure, the growing crystallographic database of protein structure assumes increasing importance. Terpyridine motifs and their complexes have previously piqued the interest of materials chemists due to their potential uses in a variety of domains, including photovoltaic devices, DNA binders, sensors, photosensitizers, molecular chemistry, medicinal chemistry, and MOF fabrication. Furthermore, their complexes with transition metals, in particular, can result in distinctive photoluminescence, catalysis, sensing characteristics, and potentially beneficial tumor-inhibitory actions [3-5]. A donor-acceptor system has been shown to be an effective method for adjusting the optical characteristics of organic–inorganic hybrid materials [6-7]. Transition metal complexes also have a number of advantages, including long-lived luminous excited states and high photochemical strengths [8]. Furthermore, as far as fluorescence probes go, the core-functionalization of terpyridine units with electron-donating/withdrawing substituents has not been fully established. The photophysical and oxidation-reduction characteristics of free terpyridines and their metal complexes can be modified using electron-accepting and -donating substituents, according to the research [9]. As a result, a wide range of substituents with varied electron-releasing or -accepting behaviour were added on the p-position of the terpyridine rings to gain a better understanding of the structure–activity link (absorption and emission qualities). Furthermore, the terpyridine moiety has recently sparked interest, not only because of its intriguing molecular topologies in the design and synthesis of polymers for coordination, but also because it has potent antimicrobial activity, which could serve as a useful benchmark for more effective antimicrobial drug design [10]. Increased lipophilicity can cause the cell permeability barrier to break down, preventing normal cell functions. Bidentate or tridentate ligands with higher lipophilicity exhibited better anti-microbial activity than monodentate ligands, and two different types of ligands in complexes had more anti-bacterial activity than a single ligand, as stated by the concept of similarity and inter-miscibility [11]. It would be motivated by the need to understand the structure–property relationship between complex structures and antimicrobial characteristics, which could provide theoretical guidance for developing and synthesizing complexes with valuable biological activities. We set out to synthesize and characterize 4'-substituted terpyridine 4'-(thiophen-2 -yl)- 2, 2':6',2" – terpyridine and 4'-(methylphenyl)- 2, 2':6',2" terpyridine, as well as their coordination compounds with bivalent transition metal ions, in light of these fascinating properties and applications of metal complexes of derivatives

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of 2, 2':6',2'' – terpyridine, and their coordination compounds with bivalent transition metal ions. We also ventured to study the electrochemical properties and biological properties (anti – microbial and DNA cleavage activities) of the newly synthesized compounds.

MATERIALS AND METHODS

Starting materials for terpyridine ligand synthesis, such as thiophen-2-carboxaldehyde, tolyl aldehyde, and 2-acetyl pyridine, were acquired from Sigma-Aldrich Chemicals and used as received. SD Fine Chemicals in India provided common reagents such as ammonium acetate, glacial acetic acid, hydrochloric acid, ammonia solution, and sodium hydroxide. The newly synthesized ligands and metal(II) complexes were analyzed for carbon, hydrogen, and nitrogen content in a Euro Vector CHN analyzer at the Centralized Instrument Facility Centre, CLRI, Chennai. A Shimadzu FT-IR 8000 spectrophotometer was used to record the FT-IR spectra of the ligands and their metal ion complexes as KBr pellets in the 400 - 4000 cm^{-1} range. A Perkin-Elmer Lambda 35 spectrophotometer was used to measure the UV-visible spectrum properties of the ligands and metal (II) complexes. The conductance values for the current metal (II) complexes were measured in a digital conductivity bridge, Systronics Direct Reading Conductivity Meter 304 with a dip type conductivity cell, at room temperature in 10^{-3} M DMF solutions.

Preparation of ligands

Preparation of 4'-(1H-thiophen-2-yl)-2,2':6',2''-Terpyridine (Thiophene terpyridine) (Stpy)

Adapting a technique from the literature [12], 4'-(1H-thiophen-2-yl)-2,2':6',2"-terpyridine was synthesized. Using a mortar and pestle, 2-acetylpyridine (4.488 mL) and thiophene-2-carboxaldehyde (1.836 mL) were mixed. The grinding was kept going until an orange-red powder appeared (within 10 minutes). The powder was mixed with a 2.24 g ammonium acetate slurry in 100 mL glacial acetic acid and heated to reflux for 3 hours. With the addition of water, the crude product was precipitated out. To obtain white powder, the product was filtered, washed with water and cold methanol, then column chromatographed using a 1:1 methanol-dichloromethane system. Yield: 1.23 g, 82%, Analysis Calculated for $C_{19}H_{13}N_3S$: C, 76.24; H, 4.38; N, 14.04%; Found: C, 75.21; H, 4.36; N, 14.05%.

Preparation of 4'-(4-Methylphenyl)-2,2':6',2''-Terpyridine (Tolyl Terpyridine) (Metpy)

The above explained method was adopted to prepare 4'-(4-methylphenyl)-2,2':6',2''-terpyridine but by using *p*-tolyl carboxaldehyde (1.92 ml) instead of thiophene-2-carboxaldehyde. Yield: 1.29 g, 84%, Analysis Calculated for $C_{22}H_{17}N_3$: C, 81.71; H, 5.30; N, 12.99%; Found: C, 81.69; H, 5.26; N, 12.97%.

Synthesis of metal complexes

Caution! During handling of the perchlorate salts of metal complexes with organic ligands, care should be taken because of the possibility of explosion.

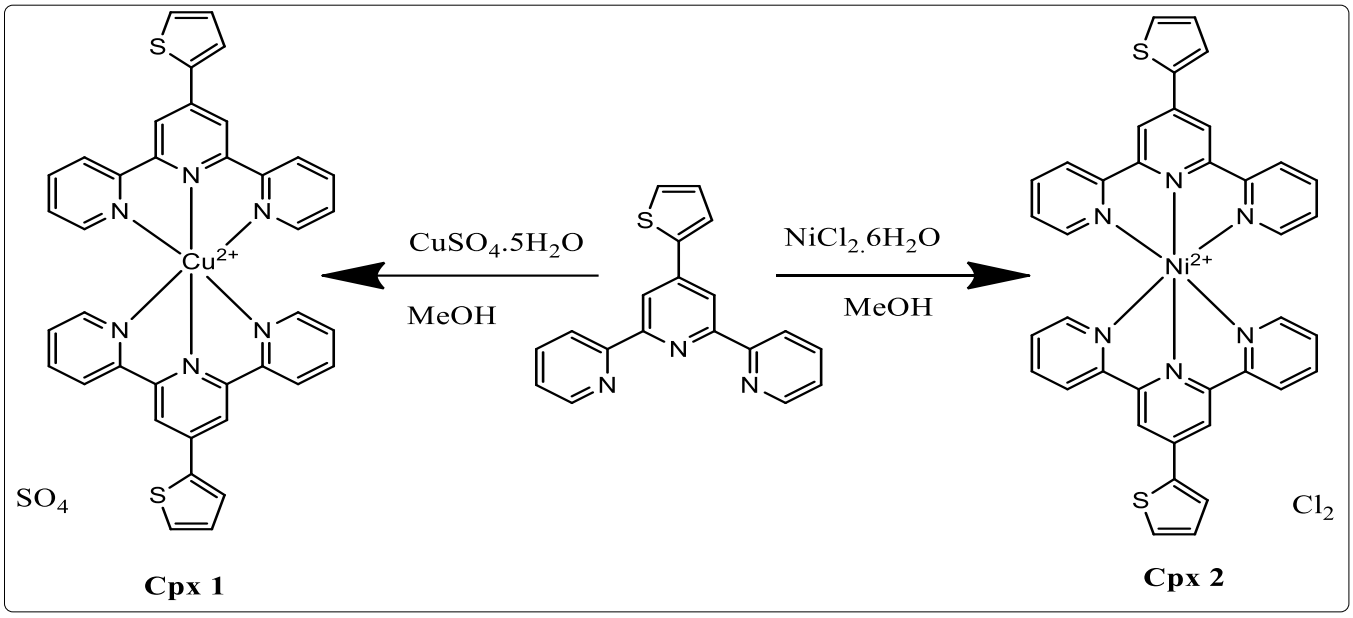

Fig1 Synthetic Scheme for Complex 1 and Complex 2

Synthesis of $[Cu(Stpy)_2]SO_4$ (Cpx 1)

stpy (0.94 g, 2.6 mmol) dissolved in methanol was progressively added to a heated $CuSO_4.5H_2O$ (0.5 g, 1.3 mmol) in methanol solution, and the reaction mixture was refluxed for 15 minutes. The green material that separated when the solvent slowly evaporated was filtered and washed with diethyl ether. Yield: 1.05 g (84 %). Analysis Calculated for $C_{38}H_{26}CuN_6S_2$: C, 65.73; H, 3.77; Cu, 9.15; N, 12.10; S, 9.24%. Found: C, 65.71; H, 3.74; Cu, 9.11; N, 12.08; S, 9.26%.

Synthesis of $[Ni(stpy)_2]Cl_2$ (Cpx 2)

Compound 2 was prepared in high yield by reacting $NiCl_2.6H_2O$ (0.5 g, 1.1 mmol) in methanol with stpy (0.86 g, 2.2 mmol) in methanol. A white solid that separated out was filtered and washed with diethyl ether. Yield: 1.12 g (78 %). Analysis Calculated for $C_{38}H_{26}N_6NiS_2$: C, 66.20; H, 3.80; N, 12.19; Ni, 8.51; S, 9.30 %. Found: C, 66.17; H, 3.71; N, 12.12; Ni, 8.48; S, 9.26%.

Synthesis of $[Mn(CH_3tpy)_2](ClO_4)_2$ (Cpx 3)

This compound was also prepared in a similar manner as that of compound 2 but by using $Mn(ClO_4)_2.6H_2O$ (0.5 g, 1.3 mmol) in methanol in place of $NiCl_2.6H_2O$. Yield: 1.05 g (84%). Analysis Calculated for $C_{44}H_{34}MnN_6$: C, 75.31; H,4.88; N, 11.98; Mn, 7.83%. Found: C, 75.28; H,4.85; N, 11.96; Mn, 7.79%.

Experimental methods of biological studies

DNA cleavage experiment

Using the agarose gel electrophoresis technique, the cleavage of plasmid DNA, pUC 19, by metal complexes was detected. SC pUC19 DNA was used in the studies, which were carried out in aerobic circumstances. Samples were made by collecting 3 litres of SC DNA and 6 litres of the complex from a stock solution in DMSO and diluting them in 10 mM Tris-HCl buffer (pH 7.2) to generate a total volume of 25 litres in the dark at 37°C. At 37°C, the samples were incubated for 1 hour. The reactions were quenched using loading buffer (0.25 percent bromophenol blue, 40% sucrose, and 0.5 M EDTA) before being loaded onto a 0.8 percent agarose gel containing 0.5 mg/mL ethidium bromide. Another set of experiments employing DMSO and histidine was carried out to determine the type of reactive species involved in the cleavage mechanism. The bands were photographed using a UVITEC gel documentation system after running the gels at 50 V for 3 hours in Tris-boric acid-ethylenediamine tetra acetic acid (TBE) buffer.

Antimicrobial assay

Two-gram positive (*Staphylococcus aureus* and *Bacillus subtilis*) and two-gram negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacteria, as well as two fungi (*Candida albicans* and *Aspergillus niger*), were obtained from KMCH, Coimbatore, and used for in vitro antimicrobial screening of test compounds. The Agar Well Diffusion assay was employed as the bioassay. For the study, Mueller Hinton Agar was produced. A sterile cotton swab was used to swab Mueller Hinton agar plates with a suspension of each bacterial species. The test chemicals were then thoroughly soaked on the sterilized filter paper discs. Each infected plate has impregnated dried discs placed on its surface. At 37°C, the plates were incubated overnight. Each substance was tested three times against each organism. As a negative control, methanol was employed. Positive antibacterial controls included standard Gentamycin and Clotrimazole discs. The microorganisms' development was suppressed by the antimicrobial test materials, and a clear, unambiguous zone of inhibition was visible around the disc. The diameter of the zone of inhibition in mm was used to measure the antibacterial activity of the test drugs.

RESULTS AND DISCUSSION

Synthesis of ligands and metal(II) complexes

The tridentate thiophenyl terpyridine ligand (stpy) and tolylterpyridine (CH_3tpy) was prepared according to a known procedure reported already and characterized. The metal(II) complexes with formula $[Cu(stpy)_2](SO_4)$ (1), $[Ni(stpy)_2](Cl_2)$ (2), and $[Mn(CH_3tpy)2](ClO_4)_2$ (3) where stpy is the tridentate ligand 4'-(thiophenyl-2,2':6',2"-terpyridine and CH_3tpy is 4'-methylphenyl-2,2':6',2"-terpyridine has been isolated from methanolic solution containing copper(II) sulfate, nickel(II) chloride and manganese(II) perchlorate respectively as the starting material. All the complexes were obtained in good yield and characterized by using electrical conductance, elemental analysis, UV-Vis and IR spectral techniques. The analytical data obtained for the new complexes given in (Table 1) agreed well with the proposed molecular formulae.

Table 1 Electronic spectral and electrical conductance values of complexes

Compound	UV-Visible λ_{max}, nm	IR cm^{-1}	Molecular weight	Electrical conductance (Scm^2mol^{-1})
$[Cu(stpy)_2]SO_4$ (1)	243, 285, 344	3061, 1604, 1568,1250	694	151
$[Ni(stpy)_2]Cl_2$ (2)	238, 279, 352	3059, 1604, 1569, 1247	689	148
$[Mn(CH_3tpy)_2]\ ClO_4$ (3)	227, 282, 338	3062, 1603, 1548, 1246, 1090	701	153

The synthetic scheme of the present complexes is shown in (Fig 1). Based on electrical conductance measurement, metal(II) complexes are proposed to be 1:2 electrolytes as they measure molar conductance at 151, 148 and 153 Scm^2mol^{-1} respectively in ~10^{-3} M DMF solution. The significant spectral data obtained for the present compounds are collected in (Table 1) and the corresponding UV-Visible spectra of metal complexes is displayed in the (Fig 2).

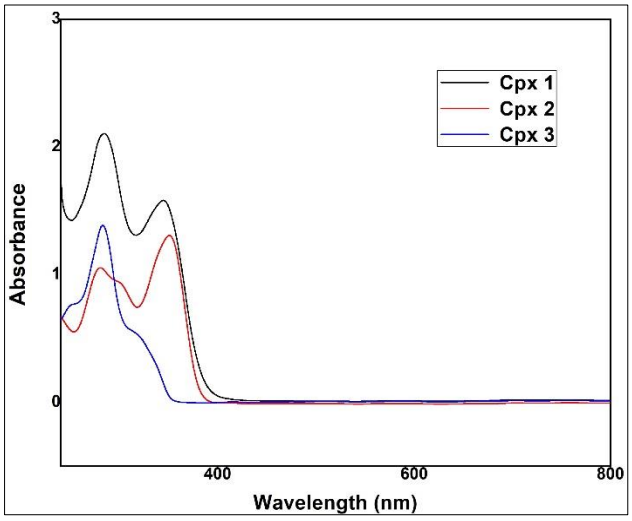

Fig 2 UV-visible absorbance spectrum of complexes

The electronic spectra of both the ligands and complexes in acetonitrile solution showed two bands each in the region of 227-285 nm and a broad band around 350 nm region for complexes alone. The electronic spectra of 1, 2 and 3 showed two types of transitions, the first one appeared at range 227-285 nm which could be assigned to π-π* and n-π* transitions due to transitions involving molecular orbitals located on the ligands. From the spectra it has been observed that the complexes exhibited broad ligand to metal charge transfer transition in the region of 338-352 nm [13]. The C-H stretching vibrational frequencies of thiophenyl and methyl terpyridines are observed at 3054-3074 cm^{-1}. In the spectrum of complex **1**, absorptions in the region 1609-1604 cm^{-1} are attributed to the C=C and C=N ring stretching frequencies of the terpyridyl ligand. These vibrations have not shown appreciable shifting due to coordination but in-plane ring deformation vibration of the pyridyl ligands have shifted to a higher value of 623 cm^{-1} indicating the coordination of the terpyridyl ligand in complex 1 [14]. The very strong absorption found at 1090 cm^{-1} is attributed to the presence of ionic perchlorate in the complex 3.

DNA cleavage studies of metal(ii) complexes

Control experiments suggested that untreated DNA and DNA incubated with complex 1 or 3 or peroxide alone did not show any significant DNA cleavage. However, interestingly in the presence of hydrogen peroxide, both the complexes 1 and 3

were found to exhibit nuclease activity. The cleavage behavior of both the complexes is shown in (Fig 3). As shown in (Fig 3), at a higher concentration of 100 µM, the complexes showed complete cleavage. It is believed that when the present redox active manganese complexes were interacted with DNA in the presence of hydrogen peroxide as an oxidant hydroxyl radical might be produced. These hydroxyl radicals are responsible for cleavage of DNA. In order to establish the reactive species responsible for the cleavage of DNA, experiment in the presence of histidine and DMSO were carried out. On adding the standard hydroxyl radical scavenger DMSO to the reaction mixture of the complex and DNA, the DNA cleavage activity of 1 and 3 decreased significantly. Interestingly, addition of histidine did not affect the cleavage activity of 1 or 3. This suggested that singlet oxygen species were not involved in this reaction. This conclusively shows the involvement of the hydroxyl radical in the observed nuclease activity of complexes 1 and 3 in the presence of peroxide.

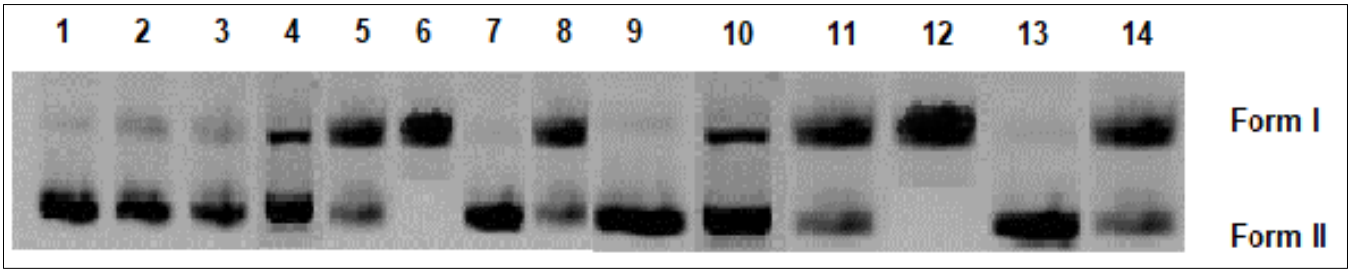

Fig 3 Cleavage of pUC19 DNA by Complexes 1 and 3

DNA was incubated with complex for 60 min in Tris buffer (pH 7.2) at 37˚C. Lane 1, DNA control; lane 2, DNA + peroxide (100 µM); lane 3, DNA + 1 (24 µM) alone; lane 4, DNA + 1(24 µM) + peroxide (100 µM); lane 5, DNA + 1 (60 µM) + peroxide (100 µM); lane 6, DNA + 1 (100 µM) + peroxide (100 µM); lane 7, DNA + 1 (100 µM) + peroxide (100 µM) + DMSO (10 mM); lane 8, DNA + 1(100 µM) + peroxide (100 µM) + Histidine (10 mM); lane 9, DNA + 3 (24 µM) alone; lane 10, DNA + 3 (24 µM) + peroxide (100 µM); lane 11, DNA + 3 (60 µM) + peroxide (100 µM); lane 12, DNA + 3(100 µM) + peroxide (100 µM); lane 13, DNA + 3 (100 µM) + peroxide (100 µM) + DMSO (10 mM); lane 14, DNA + 3 (100 µM) + peroxide (100 µM) + Histidine (10 mM).

Antimicrobial activity

By using the agar disc diffusion method, the antibacterial activity of both the ligands (L1 and L2) and their metal(II) complexes were investigated, and the findings are given in (Tables 2-3). The zone of inhibition created by a test medication is used to determine its antibacterial activity in vitro. The greater the diameter of the zone, the more microbial growth is inhibited. The growth inhibitory actions of the test compounds appear to increase as the concentrations of the test chemicals rise. When the activities of the ligand and its complex against *S. aureus* are compared, the following sequence emerges: 1 > 2 > L2 > L1 ~3. It's worth noting that these molecules are more active than ordinary gentamycin.

Table 2 Antibacterial activity of ligands and their metal(ii) complexes

Test drug	Zone of inhibition (mm)															
	S. aureus				*B. subtilis*				*K. pneumonia*				*P. aeruginosa*			
	25 µg/mL	50 µg/mL	75 µg/mL	100 µg/mL	25 µg/mL	50 µg/mL	75 µg/mL	100 µg/mL	25 µg/mL	50 µg/mL	75 µg/mL	100 µg/mL	25 µg/mL	50 µg/mL	75 µg/mL	100 µg/mL
Stpy (L1)	12	14	18	20	10	12	14	16	16	18	20	22	12	14	17	20
CH_3tpy (L2)	14	17	20	23	16	18	21	25	12	14	16	18	14	16	18	20
$[Cu(Stpy)_2]SO_4$ (1)	25	28	32	36	22	26	30	34	20	22	25	28	22	25	27	30
$[Ni(Stpy)_2]Cl_2$ (2)	25	28	30	33	25	28	32	36	20	24	27	30	24	27	32	35
$[Mn(CH_3tpy)](ClO_4)_2$ (3)	14	16	18	20	14	16	18	20	14	16	18	20	16	18	20	22

Zone size less than 15 mm – Least active; 16 – 20 mm– moderatively active; Above 20 mm – highly active

Table 3 Antifungal activity of ligands and their metal(ii) complexes

Test drug	Zone of inhibition (mm)							
	A. niger				*C. albicans*			
Stpy (L1)	16	18	20	17	10	12	14	16
CH_3tpy (L2)	16	18	20	22	16	18	20	22
$[Cu(Stpy)_2]SO_4$ (1)	14	16	18	20	18	20	22	25
$[Ni(Stpy)_2]Cl_2$ (2)	20	22	24	26	20	22	25	28
$[Mn(CH_3tpy)_2](ClO_4)_2$ (3)	14	16	18	20	16	18	20	22

Zone size less than 15 mm – Least active; 16 – 20 mm– moderatively active; Above 20 mm – highly active

The following is the order of antibacterial activity of test medicines against *B. subtilis*: L2 > 3> L1 > 2 > 1. The activity of *K. pneumonia* diminishes in the following order: 2 > 1 > L1 > 3 > L2. When the test medications are tested against *P. aeruginosa*, compound 2 > 1 > 3 > L1 > L2 is found to have the most activity. As can be observed, the compounds examined are sensitive to the bacteria employed, and all of the compounds tested are significantly more active than gentamycin, the standard antibacterial treatment. The antifungal activity data in (Table 3) show that increasing the concentrations of the test

medications increases their effectiveness against the test fungus (*A. niger* and *C. albicans*). In addition, when compared to standard drug viz. clotrimazole., the test medications are less sensitive to fungus. The activities of test drugs against *A. niger* decrease in the order: 2 > L2 > 1 ~ 3 > L1. The sensitivities of test drugs to *C. albicans* are found to decrease in the order: 2 > 1 > 3 ~ L2 > L1. Zones of inhibition ranging from 10 to 25 mm were seen in the newly synthesized drugs. In comparison to the free ligands, the metal(II) complexes demonstrated dramatically improved antibacterial activity against microbial strains, according to comparative tests. Tweedy's chelation theory and the overtone notion can explain the complexes' increased antibacterial action.

CONCLUSION

Physico-chemical techniques were used to construct and analyze mononuclear copper and nickel(II) complexes with NNN-donor 4'-(1H-thiophen-2-yl)-2,2':6',2''-terpyridine bases, as well as manganese(II) complexes containing 4'-(4-methylphenyl)-2,2':6',2''-terpyridine. In the 340-350 nm range, all three complexes show a significant ligand to metal charge transfer (LMCT) band. Additionally, the copper and manganese(II) complexes had higher DNA breakage activity. Both the ligand and the complexes have improved antibacterial properties. However, because of their chelating properties, the complexes' antibacterial activity has been found to be higher.

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