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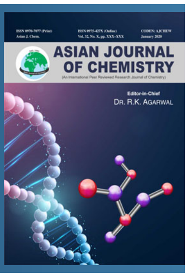

Synthesis, Characterization and Biological Activity of Ni(II), Cu(II) and Fe(III) Complexes Derived from N^2,N^6-*bis*(5-Mercapto-1,3,4-thiadiazol-2-yl)pyridine-2,6-dicarboxamide

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Novel metal complexes of the type [M(L)X] (where M= Cu(II), Ni(II) and Fe(III), L = N^2,N^6-*bis*(5-mercapto-1,3,4-thiadiazol-2-yl)pyridine-2,6-dicarboxamide, X= Cl^-, CH_3COO^-) were synthesized by the reaction of pyridine-2,6-dicarboxylic acid and 2-amino-5-mercepto-1,3,4-thiadiazole. The synthesized ligand was reacted in THF with metal salts (Cu, Ni and Fe) to form complexes. Deprotonated ligand shows tridentate nature and coordinate to metal ion to form pincer cavity. In all, complexes metals were surrounded by three nitrogen atom and other site coordinated by other groups (chloride, acetate). All the synthesized complexes were characterized by spectroscopic techniques like UV-visible, ^{13}C NMR and ^1HNMR, IR spectroscopy, DSC, elemental analysis and molar conductance measurements. The ligand and its metal complexes were tested for antimicrobial activity against bacterial and fungal strains by determining inhibition zone, minimal inhibitory concentration (MIC) and minimal bactericidal concentration (MBC). The complexes showed moderate antimicrobial activity and antifungal activity when tested against bacteria and fungi.

Keywords: Pyridine-2,6-dicarboxamide, Triphenyl phosphite, Pyridine, Antimicrobial activity.

INTRODUCTION

The novel amide based ligands are most important and valuable in coordination chemistry [1-3] and in medicinal chemistry [4,5]. The amide functional organic group found in naturally occurring molecules, polymer, and agrochemicals [6,7]. Such type of ligands in their deprotonated form generates a pincer cavity *via* two *N*-amidate group and an anchoring pyridine ring that strongly hold a metal ion. The amide bond (-CONH-) is one of important constituent of proteins. Due to strong stability towards hydrolysis, they are more prominent and useful in biological chemistry. The amide bonds allow the construction of proteins in biological system. Amide group are versatile for coordination chemistry. It coordinates to metal ion by three nitrogen donor atom, one of pyridine ring and two nitrogen of amide groups. The synthesized pyridine-2,6-dicarboxamide ligand containing this type of linkage behaves as multidendate ligands because they have more than one donor atoms in its structure. Gupta *et al*. [8] have used pyridine-2,6-dicarboxamide ligand appended with pyridine and quinolone ring to synthesize Cu(II) complex. There are so many compounds of amide group containing Cu complexes reported in earlier [9-11]. Ayad *et al*. [12] recently synthesized three different mononuclear copper complexes bearing diprotic macrocyclic ligands. Other Ru(III) complexes were also reported [13,14]. Synthesis of ligands having appended groups thiazole, thiazoline and benzothiazole is also reported [15] and this mode of coordination makes it attractive for their uses in supramolecular structure [16,17]. Several transition metal complexes such as Ni(II) [18-29], Fe(III) [30-35] and Co(III) complexes [36-40] are also reported. Pyridine dicarboxamide ligands are used in asymmetric catalysis [41,42], molecular receptors [43,44]. Many derivatives of pyridine-2,6-dicaboxamide showed antitumor, analgesic and anti-inflammatry activity [45-47]. They are also used in oxidation of hydrocarbon [48]. Noveron *et al*. [49] have synthesized Fe(III) and Co(II) complexes of pyridine-2,6-dicarboxamide based ligands. The metal bound oxygen based compounds have been used in the wide area of oxidation reaction which was promoted by metalloenzymes [50]. To know about their activities, structures and properties of such type of species is rare for finding mechanistic insights about their presence in metalloenzymes and therefore for developing prominent yet selective catalysts [51]. Pyridine-2,6-dicarboxamide based ligands have been significant in stabilizing several metal-bound reactive species, such as terminal alkyl peroxide, terminal hydroxide and terminal superoxide. Importantly, some of these species have been stabilized at room temperature. Ligands containing a pyridine-2,6-dicarboxamide group have been used for the synthesis of several metal compounds containing terminal and bridging hydroxo moieties [52]. Pyridine-2,6-dicarboxamide based ligands shows different catalytic applications of metal complexes. Supported with past few years, several such type of metal complexes have been successfully synthesized and used in organic transformations [53]. For catalytic application metal complexes of pyridine-2,6-dicarboxamide based ligands designed in this manner that the binding site must be present for subsequent catalysis. Kumar and Gupta [34] utilized pyridine-2,6-dicarboxamide based scaffolds containing appended phenyl, naphthyl and anthracenyl groups as the fluorophores for the selective detection of iron. Although, phenyl containing probe showed very low emission intensity, the other two probes shows remarkable sensing abilities both for Fe^{2+} and Fe^{3+} ions. Collective studies of Job′s plot, Benesi-Hildebrand fitting Stern-Volmer plot and detection limit displayed a notable sensing ability of probe for the Fe^{3+} ion as compared to Fe^{2+} ion. In this article, pyridine-2,6-dicarboxamide scaffold with appended thiadiazole group is synthesized and also its Cu(II), Ni(II) and Fe(III) complexes. The ligand and its complexes are characterized and its antimicrobial activity were also evaluated.

EXPERIMENTAL

All reagents of analytical grade were commercially available and used as received. All the solvents were of reagent grade and used without further purification. All reactions were carried out in dried glassware and on oil bath to get constant temperature. The reaction reactivity were monitored by thin layer chromatography plate using silica gel coating. The spot of reactant and product were checked in UV lamp. ^{1}H and ^{13}C NMR spectra were recorded in a Bruker 300 MHz NMR spectrometer. Spectroscopic analysis were carried out at standard temperature. The dilute solution of each compound in $CDCl_3$ and DMSO used for analysis. The chemical shifts are reported in ppm and coupling constant reported in Hertz. ^{1}H NMR chemical shifts are reported relative to residual solvent signals. IR spectra were recorded with Perkin FT-IR spectrophotometer in the 4000-400 cm^{-1} region .The Elemental analyses were perform by using the Elemental GmbH Vario EL-3 instrument. Absorption spectra were recorded using Perkin UV-Visible spectrophotometer. ESI-MS spectra recorded on Shimadzu QP 2010.

Synthesis of H_2L: Pyridine-2,6-dicarboxylic acid (0.334 g, 0.002 mol) and 2-amino-5 mercepto-1,3,4-thiadiazole (0.525 g, 0.004 mol) were taken in 15 mL pyridine and refluxed with stirring for 30 min at 110 ºC. Triphenyl phosphite (1.32 g, 0.0042 mol) was added dropwise to the reaction mixture and the reaction mixture was further stirred at 100 ºC for additional 6 h. The reaction mixture was cooled to room temperature and poured to the ice-cold water. This resulted in the precipitation of a pale-yellow product, which was filtered, washed with water and air dried. Yield 0.66g (76.83%). m.p.: 215 ºC. Anal. calcd/ (found) % for $C_{11}H_7N_7O_2S_4$: C, 33.24 (33.26); H, 1.78 (1.76), N. 24.67 (24.60), S, 32.26 (32.30), O, 8.05 (8.08). MS (ESI CH_3CN, *m/z*): 396.95. FTIR (ATR, cm^{-1}): 3264 (NH), 1685 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): 8.15 (td, J = 17.6, 7.6 Hz, 2H), 7.91 (q, J = 8.3 Hz, 1H), 6.76-7.15 (m, 10H), 11.47 (s, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 184.49, 184.42, 162.14, 161.96, 152.08, 150.93, 149.96, 149.78, 138.90, 138.17, 125.65, 125.49, 77.27, 77.00.

Synthesis of metal complexes

[Cu(L)CH_3COO]: To a THF (10 mL) solution of H_2L (0.397g, 0.001 mmol), $Cu(CH_3COO)_2$ (0.181 g, 0.001 mmol) dissolved in THF (10 mL) was added dropwise while stirring. The resulting bluish green solution was finally stirred for 2 h. The reaction mixture was filtered and the filtrate was left for evaporation. Bluish crystalline compound was appeared after 10 h. This product was filtered washed with diethyl ether and dried. Yield: 0.500 g (87%), m.p.: 256 ºC, MS (ESI methanol, *m/z*): 515.75. FTIR (ATR, cm^{-1}): 3483 (NH), 1678 (C=O). ^{1}H NMR (500 MHz, $CHCl_3$-d_6) δ: 10.49 (s, 10H), 8.32 (s, 2H), 8.03 (s, 1H), 7.02-7.73. ^{13}C NMR (126 MHz, $CDCl_3$) δ: 184.49, 184.42, 162.14, 161.96, 152.08, 150.93, 149.96, 149.78, 138.90, 138.17, 125.65, 125.49, 77.27, 77.00.

[Ni(L)Cl]: To a THF (10 mL) solution of H_2L (0.250 g, 0.0006 mol), $NiCl_2$ (0.149 g, 0.0006 mmol) dissolved in THF (10 mL) was added dropwise while stirring. The resulting green solution was finally stirred for 2 h. The reaction mixture was filtered and the filtrate was left for evaporation. Light green crystalline compound was appeared after 12 h. This product was filtered, washed with diethyl ether and dried. Yield: 0.340 g (85%), m.p.: 274 ºC. MS (ESI, CH_3CN, *m/z*): 487.80. FT-IR (ATR, cm^{-1}): 1622 (C=O). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.37 (s, 1H), 8.21 (s, 1H), 7.32 (d, J = 25.3 Hz, 2H), 7.16 (d, J = 37.7 Hz, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 159.93, 147.66, 144.39, 137.03, 127.50, 126.95, 126.50, 123.53, 123.19, 119.01, 117.09, 112.49, 42.40, 39.50

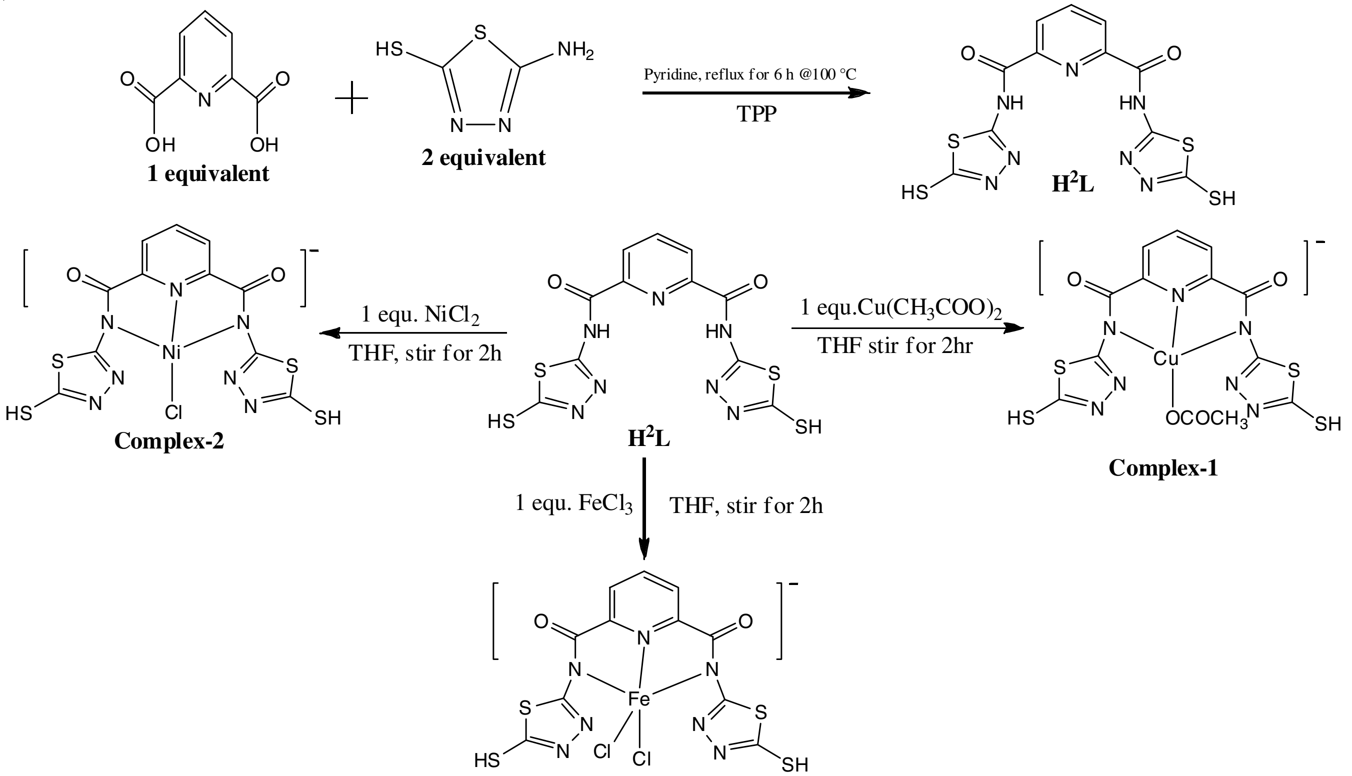
[Fe(L)Cl_2]: To a THF (10 mL) solution of H_2L (0.250 g, 0.0006 mmol), $FeCl_3$ (0.102 g, 0.0006 mmol) dissolved in THF (10 mL) was added dropwise while stirring. The resulting brown solution was finally stirred for 2 h. The reaction mixture was filtered and the filtrate was left for evaporation. Dark brown crystalline compound was appeared after 12 h. This product was filtered, washed with diethyl ether and dried. Yield: 0.288 g (82%), m.p.: 267 ºC. MS (ESI, methanol, *m/z*): 519.50. FT-IR (ATR, cm^{-1}): 1623 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35 (s, 1H), 7.24 (d, J = 6.7 Hz, 12H), 6.92 (t, J = 7.2 Hz, 2H), 6.82 (d, J = 7.6 Hz, 5H), 3.75 (s, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.13, 150.78, 148.16, 138.59, 129.81, 129.52, 129.16, 128.92, 126.49, 126.25, 125.57, 121.82, 121.58, 120.10, 77.51, 77.25, 77.00, 76.75.

Antimicrobial activity: Antimicrobial properties of the ligand and its complexes were studied against the microbes, *Staphylococcus aureus* (Gram-positive), *Escherichia coli* (Gram-negative) and *Candida albicans* and *Aspergillus niger* by agar well diffusion method. A standard inoculums (10^5 CFU/mL) of the microbes was spread on the nutrient agar plates using spreader followed by applying wells of 6 mm diameter filled with all of tested organisms (1 mg m/L). The agar plates containing microbes were incubated for 30-48 h at 35 ºC. The antibiotic gentamycin was employed as the standard drug against bacterial strains *Staphylococcus aureus*, *Escherichia coli*, while nystatin was used as antifungal reference drug against *Candida albicans* and *Aspergillus niger* to be used. The susceptibility was determined on the basis of diameter of the zone of inhibition around the well. All assays were performed at least in duplicate. The dilution test with standard inoculum of 10^5 CFU mL^{-1} was handled to evaluate the minimal inhibitory concentration (MIC) of the ligand test and its complexes. The minimal bactericidal concentration (MBC) was determined by aspirating 0.1 mL of culture medium from each tube on agar plates followed by counting of CFU after 22-24 h of incubation at 35 ºC. The results of MIC and MBC were calculated.

RESULTS AND DISCUSSION

The synthesis and characterization of N^2,N^6-*bis*(5-mercapto-1,3,4-thiadiazol-2-yl)pyridine-2,6-dicarboxamide and its metal complexes are reported. Complexes were synthesized by the reaction of one equivalents of ligand and one equivalent of respective metal salts in THF under stirring (**Scheme-I**). All the synthesized coloured complexes were characterized by elemental analysis, mass, UV-visible, IR spectroscopy and NMR spectroscopy.

IR spectra: The FT-IR data of ligand shows -NH and C=O stretching peaks for the amide linkage were observed at 3482 and 1678 cm^{-1}, respectively. The key IR spectral peaks of the ligand and its metal complexes are given in Table-1. When ligand react with metal ions they form the coordination complexes. The IR spectra of metal complexes C=O stretching at 1628 cm^{-1} (for Cu complex), 1628 cm^{-1} (for Ni complex) and 1628 cm^{-1} ((for Fe complex) were observed. Ligand when coordinated to metal ion, then NH peaks of ligands were diminished due to coordination. FT-IR spectrum of all the metal complexes showed no NH stretching peaks and therefore CO stretching frequency was shifted by 50-60 cm^{-1}. The lowering intensity from 1678 cm^{-1} indicate the formation of coordination complexes. Another peaks of -NH group which occured in 3248 cm^{-1} in ligand found to be absent in each complexes. The deprotonating behaviour suggest that during the complex formation, ligand shows deprotonation and form coordinating site. These features strongly suggest the involvement of the anionic N-amide in the coordination. In IR spectra of the metal complexes, the stretching band was shifted to lower frequencies, because the C=O bond order decreases due to M-N bond formation. The new vibrational band appeared in the range 580-510 and 455-410 cm^{-1} were assigned to ν(M-O) and ν(M-N), respectively. The metal nitrogen bond peaks indicates that during complex formation nitrogen coordinates metal ions. This type of bonding peaks present in IR spectra of all three complexes. The metal oxygen bond present in copper complex, while the metal chloride bond peaks present in the spectra of nickel and iron complexes.



Scheme-I: Synthesis of ligand and metal complexes (**1**, **2**, **3**)

UV-visible spectra: The UV-Vis spectra of the ligand and its metal complexes were recorded in DMF solvent (Fig. 1). In the UV-visible absorption spectra of ligand, two peaks one at 272 nm and other at 342 nm show the π-π* and n-π* transitions, respectively. The UV spectra of complexes shows a charge transfer spectra, which confirmed the coordinate bond formation between the ligand and metal ions. The UV spectra of Cu(II) complexes shows three absorption peaks at 267, 312 and 348 pnm, which correspond to π-π*, n-π* and MLCT transitions, respectively. From these transitions, it is cleared that copper complex possess tetrahedral geometry. The electronic spectrum of Ni(II) complex showed three absorption peaks at 273, 310 and 344 nm which are assigned to π-π* and n-π*, MLCT transition respectively, which confirmed to tetrahedral or square planer geometry. The Fe(III) complex exhibited two absorption peaks at 312 and 395 nm, which are assigned to π-π* and MLCT transition, respectively suggesting a trigonal bipyramidal geometry.

Mass spectra: The mass spectra of a free ligand shows peaks at 396.95. The metal complexes of this ligands peaks were at 515.75 for copper complex, 487.80 for nickel complex and 519.50 for iron complexes. All these results are in agreement of the proposed formulae of the ligand and its metal complexes.

NMR spectra: ^{1}H NMR spectra of ligand showed one broad singlet for the NH at δ 11.47 ppm in $CDCl_3$. Moreover, expected coupling between the protons is also clearly observed. In line with the proton NMR spectrum, the proton decoupled. ^{13}C NMR spectrum of the ligand was also simple and all carbon centres were located easily. The C=O carbon peak was observed at 162.14 ppm. ^{1}H NMR of metal complexes shows absence of NH proton to confirm the coordination of metal ions to ligand. ^{13}C NMR spectra also revealed the coordination of ligand with metal ions. The geometry of nickel complexwas square planer having four coordination number and geometry of copper complex is also four coordinated complexes, while iron complex shows penta-coordinated complex with trigonal bipyramidal geometry.

Biological activity: The antimicrobial activity studies were performed of ligand and its metal complexes. They were found active against bacteria and fungi. They showed activity because these compounds have tendency to form chelate ring. In the antibacterial screening it showed that the ligand were found biologically active against *S. aureus*, *E. coli* while the metal complexes of Cu, Ni and Fe showed more potential activity as compared to ligand. The activity of metal complexes against bacteria were almost similar with standard drug gentamycin. For antifungal activity the standard drug used was nystatin. The metal complexes of Cu, Ni and Fe showed antifungal activity nearer to standard drug taken. All data were given in Table-2.

Conclusion

The synthesis and characterization of N^2,N^6-*bis*(5-mercapto-1,3,4-thiadiazol-2-yl)pyridine-2,6-dicarboxamide and its metal complexes are reported. The metal complexes displayed the migration of amidic N-H protons to the appended heterocyclic rings during the synthesis. Such deprotonated heterocyclic ring create hydrogen bond based cavity adjacent to metal ion and assist in binding of based substrate within the complex cavity.

TABLE-1
IR SPECTRAL PEAKS OF LIGAND AND METAL COMPLEXES

Compounds	ν (cm^{-1})				
	N–H	C=O	M–N	M–O	M–Cl
[H_2L]	3482	1678	–	–	–
[{L}Cu(CH_3COO)]	Diminished	1629	439	583	–
[(L)NiCl]	Diminished	1629	442	–	525
[(L)$FeCl_2$]	Diminished	1628	416	–	480

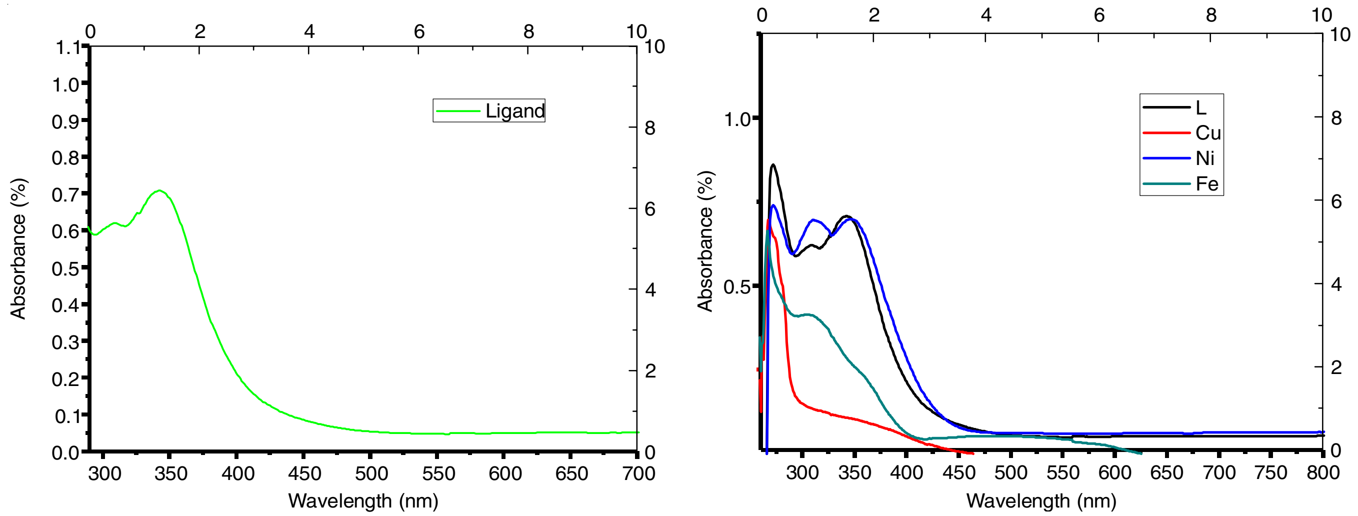


Fig. 1. UV spectra of ligand and complexes

TABLE-2
ANTIMICROBIAL ACTIVITY OF LIGAND AND METAL COMPLEXES WITH STANDARD

Compounds	Conc. (µg/mL)	Bacteria (% Inhibition)		Fungi (% Inhibition)	
		S. aureus	*E. coli*	*C. albicans*	*A. niger*
H_2L (Ligand)	25	18.14	6.80	85.15	53.30
	50	24.42	25.32	90.15	77.22
	100	41.22	98.87	95.29	84.37
Cu-L complex	25	7.70	28.70	85.12	58.29
	50	11.20	72.22	90.19	60.10
	100	18.40	87.12	95.23	72.25
Ni-L complex	25	12.40	36.33	82.15	54.55
	50	28.63	69.52	92.36	66.89
	100	35.65	89.55	94.26	75.66
Fe-L complex	25	19.65	48.45	73.39	48.81
	50	25.70	76.24	75.13	77.75
	100	28.50	86.78	86.27	79.18
Gentamycin	25	7.90	88.74	–	–
	50	10.15	88.35	–	–
	100	16.40	88.17	–	–
Nystatin	25	–	–	84.35	91.30
	50	–	–	93.20	93.57
	100	–	–	97.18	97.43

The biological activity was also evaluated and the results showed that metal complexes are more potent as compared to ligand.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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