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Synthesis Characterization and DNA Cleavage Studies of Some Transition Metal Complexes Derived from 5-chloro-3-phenyl-*N*'-(tetrazolo[1,5-a]quinolin-4-ylmethylene)-1*H*-indole-2-carbohydrazide.

Mruthyunjayaswamy BHM*, Vivekanand DB and Mahendra Raj K.

Department of Studies and Research in Chemistry, Gulbarga University, GULBARGA- 585 106, Karnataka, INDIA.

ABSTRACT

A series of new coordination complexes of Cu(II), Co(II), Fe(III), Ni(II), Zn(II) and Cd(II), with a new Schiff base 5-chloro-3-phenyl-*N*'-(tetrazolo[1,5-a]quinolin-4-ylmethylene)-1*H*-indole-2-carbohydrazide have been synthesized and characterized by elemental analysis, UV-Visible, IR spectra, ^{1}H NMR spectra, mass spectra, powder X-ray diffraction data, molar conductance, magnetic susceptibility, ESR and TGA. The new Schiff base has been synthesized by the reaction between 5-chloro-3-phenyl-1*H*-indole-2-carboxyhydrazide and tetrazolo[1,5-a]quinoline-4-carbaldehyde. The Schiff base behaves as tridentate ONN donor ligand and forms the complexes of the type ML stoichiometry in case of Cu(II), Co(II), Fe(III), Ni(II), Zn(II) and Cd(II). The Cu(II), Co(II), Ni(II), Zn(II) and Cd(II) complexes have exhibited square pyramidal and Fe(III) exhibited octahedral geometry. The ligand and its metal complexes have been screened for their antibacterial activity against *Klebsiella* and *Pseudomonous aeruginosa,* antifungal activity against *Aspergillus niger* and *Aspergillus flavus* in minimum inhibitory concentration (MIC) by cup plate method respectively and antioxidant activity by free radical scavenging activity using 1, 1-diphenyl-2-picryl hydrazyl (DPPH), with standard drug vitamin-E and DNA cleavage activity. From this study our newly synthesized ligand and some of its complexes have exhibited good antimicrobial, antioxidant and DNA cleavage activities.

Keywords: Schiff base, Metal complexes, antimicrobial activity, antioxidant activity and DNA cleavage activity.

**Corresponding author*

INTRODUCTION

The quinoline skeleton is often used for the design of many synthetic compounds with diverse pharmacological properties such as, anti-inflammatory [1], antimicrobial agents [2], cytotoxic activity [3], antidotal and antibacterial [4], antitumor activity [5], antimalarial activities[6]. Additionally, quinoline derivatives find their use in the synthesis of fungicides, viruses, biocides, alkaloids, rubber chemicals and flavoring agents [7]. They are also used as polymers, catalysts and corrosion inhibitors, preservative as solvent for resin and terpenes. Furthermore, these compounds find applications in chemistry of transition metal catalysts for uniform polymerization and luminescence chemistry [8]. Quinoline derivatives also act as antifoaming agents in refineries [9].

Tetrazoles represents an important class of heterocycles which exhibit a wide range of applications in medicinal as well as synthetic chemistry. The tetrazole group which is considerd as analogue to carboxylic group as a pharmacophore possesses wide range of biological activities. Several substituted tetrazole have been shown to posses antinflammatory, CNS depressent, antimicrobial, anti-aids and antif ertility activities. Compounds containing quinoline, pyrimidine tetrazole, functionally have been reported to exhibit antiinflammatory activity.

The development of resistance to current antibacterial therapy by various pathogens continues to stimulate the research for more effective agents. In addition, primary and opportunistic fungal infections continue to increase rapidly because of the increased number of immunocompranised patients (AIDS, cancer and transplants). The increasing clinical importance of drug resistant bacterial and fungal pathogens has lent additional urgency to antibacterial research and development of new antibacterial compounds.

Antioxidant agents which exhibit the oxidation and have got their own importance in pharmacy and food industry. These agents are used to prevent the oxidation of drugs, food preservatives etc. On the other hand, many tetrazolo[1, 5-a]quinolines play a vital role in biology [10] and yet most potent antifungal agent [11], anti-inflammatory and antibacterial agents [12] and HCV inhibitor [13]. In view of these findings, we have synthesized some metal complexes with a new Schiff base 5-chloro-3-phenyl-*N*'-(tetrazolo[1,5-a]quinolin-4-ylmethylene)-1*H*-indole-2-carbohydrazide which was prepared by the reaction between 5-chloro-3-phenyl-1*H*-indole-2-carboxyhydrazide and tetrazolo[1,5-a]quinoline-4-carbaldehyde.

MATERIALS AND METHODS

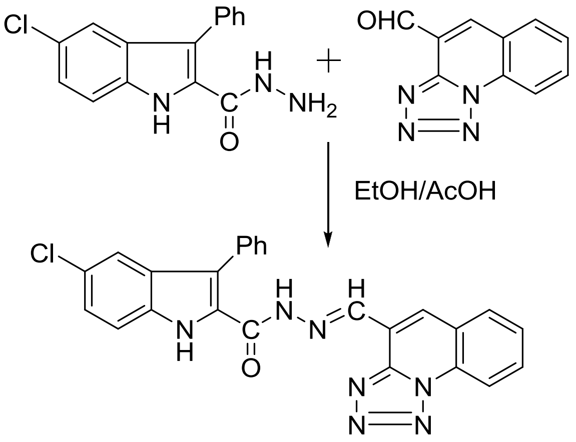
General Remarks

All solvents and reagents were used as obtained from commercial sources with further purification according to standard procedures [14]. Melting points were determined in open glass capillary tubes. Purity of the compounds was checked on TLC. The IR spectra of compounds were recorded on Perkin-Elmer spectrum one spectrophotometer using KBr disc technique. ^{1}H NMR spectra were recorded on Bruker Avance 400 MHz instrument in d_6-DMSO using TMS as an internal standard and mass spectra on a JEOL GC mate and Agilent 6330 ion trap mass spectrophotometer. ESR on Bruker BioSpin GmbH Frequency at 9.432 GHz. Satisfactory C, H, N analysis was recorded for all the compounds.

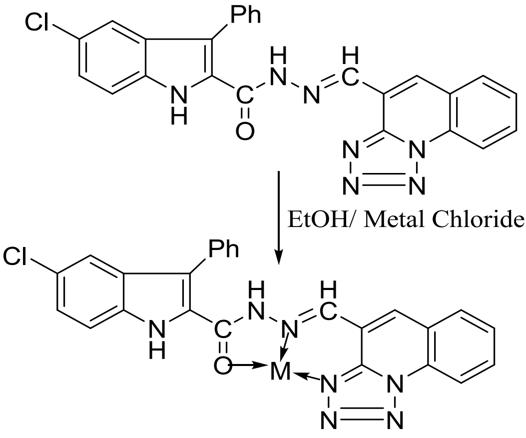
Compounds 2-chloro-3-formylquinolines, tetrazolo[1,5-a]quinoline-4-carbaldehyde and 5-chloro-3-phenyl-1*H*-indole-2-carboxyhydrazides [15-17] were prepared according to reported methods.

Synthesis of ligand HL

An equimolar mixture of 5-chloro-3-phenyl-1*H*-indole-2-carboxyhydrazide (0.285 g, 0.001 mol) and tetrazolo[1,5-a]quinoline-4-carbaldehyde. (0.198 g, 0.001 mol) in ethanol (30 mL) were refluxed in presence of catalytic amount of glacial acetic acid (1-2 drops) for about 6-7 h on water bath. The reaction mixture was cooled to room temperature, the separated Schiff base was collected by filtration, washed with ethanol, dried and recrystallized from 1, 4-dioxane Scheme 1.



Scheme 1: Synthesis of ligand HL



M = Cu(II), Co(II), Fe(III), Ni(II), Zn(II) and Cd(II).

Scheme 2: Synthesis of Metal complexes of ligand HL.

Preparation of complexes of Cu(II), Co(II), Fe(III), Ni(II), Zn(II) and Cd(II) with Schiff base 5-chloro-3-phenyl-*N*'-(tetrazolo[1,5-a]quinolin-4-ylmethylene)-1*H*-indole-2-carbohydrazide

To a hot solution of 5-chloro-3-phenyl-*N*'-(tetrazolo[1,5-a]quinolin-4-ylmethylene)-1*H*-indole-2-carbohydrazide (0.93g, 0.002 mol) in ethanol (25 mL) was added a hot ethanolic solution (10 mL) of respective metal chlorides (0.002 mol). The reaction mixture was refluxed on a steam bath for 4 h and then sodium acetate (0.5 g) was added to it and refluxed for 2 h. It was then poured in to distilled water. The resulting solid complexes were collected by filtration, washed with sufficient quantity of distilled water, then with hot ethanol to apparent dryness and dried in a vacuum over anhydrous calcium chloride in a desiccator (yield 75-80%) Table 1.

Table 1: Physical, Analytical, and Molar conductance data of ligand HL and its complex.

Compounds	Molecular formula	Mol. Wt.	M.P ^{0}C (Yield in%)	Elemental analysis (%) Calcd (Found)					Molar cond (λ_M) ohm^{-1} cm^2 mol^{-1}	μ_{eff} (B.M)	Colour
				M	C	H	N	Cl			
*HL	$C_{25}H_{16}N_7OCl$	465	318-320 (76)	-	64.51 (64.71)	3.44 (3.41)	21.07 (21.16)	7.52 (7.60)	7	-	Yellow
Cu-complex	$Cu[C_{25}H_{16}N_7OCl_3]$	598.54	>350 (79)	10.53 (10.61)	50.12 (49.96)	2.67 (2.69)	16.37 (16.46)	17.54 (17.43)	10	1.58	Greenish brown
Co-complex	$Co[C_{25}H_{16}N_7OCl_3]$	593.93	>340 (80)	9.78 (10.12)	50.51 (50.86)	2.69 (2.73)	16.50 (16.68)	17.67 (17.50)	11	4.18	Brown
Fe-complex	$Fe[C_{25}H_{16}N_7OCl_4]$	625.84	302-304 (75)	8.92 (9.03)	47.93 (47.73)	2.55 (2.58)	15.65 (15.79)	22.36 (22.42)	8	5.88	Yellow
Ni-complex	$Ni[C_{25}H_{16}N_7OCl_3]$	593.69	>330 (78)	9.88 (9.91)	50.53 (50.37)	2.69 (2.72)	16.50 (16.79)	17.68 (17.82)	6	2.73	Greenish Yellow
Zn-complex	$Zn[C_{25}H_{16}N_7OCl_3]$	600.39	>340 (77)	10.89 (10.83)	49.96 (49.85)	2.66 (2.61)	16.32 (16.18)	17.48 (17.59)	6	Dia*	Yellow
Cd-complex	$Cd[C_{25}H_{16}N_7OCl_3]$	647.41	303-305 (80)	17.36 (17.40)	46.33 (46.19)	2.47 (2.45)	15.13 (15.04)	16.21 (16.06)	68	Dia*	Light green

HL=Ligand HL, Dia= Diamagnetic

Antimicrobial activity

Antimicrobial activity was carried out in MIC by the cup-plate method [18]. The *in vitro* antibacterial screening of ligand and its complexes was undertaken against. *Klebsiella* and *Pseudomonas using* nutrient agar media. In brief, molten agar nutrient kept at 45 ºC was poured into petri dishes and allowed to solidify. Then wells of 6 mm diameter were punched carefully using a sterile cork borer and were filled with test solution 25 µL (1000 ppm, 500 ppm, 250 ppm, 125 ppm). The plates were incubated for 24 h at 37 ºC. The diameter of the zone of inhibition for all the test compounds was measured and the results were compared with the standard drugs Amoxycillin and Gentamycin of the same concentration of the test compound under identical conditions.

The antifungal activity of the test compounds were evaluated against *A. niger* and *A. flavus* by the cup plate method cultured on seberose dextrose agar (SDA) medium adapting the procedures as described above. The plates were incubated at 37 ºC for 48 h. The diameter of the zone of inhibition for all the test compounds were compared with standard drug Fluconazole of the same concentration as that of the test compounds under identical conditions.

Since all the test compounds and standard drugs were prepared in freshly distilled DMF, its zone of inhibition was found to be negligible and taken as 0 mm.

Antioxidant activity by DPPH radical scavenging activity

1, 1- Diphenyl-2-picryl hydrazyl (DPPH) radical scavenging activity was measured by spectrophotometric method at 517 nm [19-21]. To a methanolic solution of DPPH (0.1 mmol) and standard compound Vit-E were added separately in different concentrations and an equal amount of methanol (0.05 mL) was added control. After 30 min, absorbance was measured. The percentage of free radical scavenging was calculated by comparing the control and test samples with the fallowing equation.

$$Percentage\,of\ scavenging\ activity = \frac{A_o - A_e}{A_o} \times 100$$

Where A_o corresponds to the absorbance of DPPH without sample and A_e corresponds to the absorbance of sample with complex or ligand. A_o is the absorbance sample containing only DPPH (blank).

DNA cleavage activity

The degree to which the ligand and its complexes could function as DNA cleavage agents was examined using calf-thymus DNA (Cat. No.105850) as a target. The efficiency of cleavage of these molecules was studied by using agarose gel electrophoresis. Nutrient broth media was used (Peptone 10, NaCl 10 and yeast extract 5 g L^{-1}). The electrophoresis of the samples was done according to the fallowing procedure [22].

Briefly, 250 mg of agarose was dissolved in 25 ml of tris- acetate-EDTA (TAE) buffer (4.84 g Tris base, pH 8.0, 0.5 M EDTA L^{-1}) by boiling, when the gel attains ~55 ºC, it was poured into the gel cassette fitted with comb. The gel was allowed to solidify and then carefully the comb was removed. The gel placed in the electrophoresis chamber flooded with TAE buffer. Load 20 µl of DNA sample (mixed with bromophenol blue dye @ 1:1 ratio) was loaded carefully into the wells, along with standard DNA marker with the constant 50 V of electricity for 45 min. Later gel was removed carefully and stained with ethidium bromide (ETBR) solution (10 µg mL^{-1}) for 10-15 min and the bands were observed under UV gel documentation system.

RESULTS AND DISCUSSION

IR spectra of ligand HL and its complexes

The IR spectrum of ligand showed medium intensity bands at 3202 cm^{-1} and 3444 cm^{-1} assigned to indole NH and amide NH functions. These bands were found to appear at about the same region with 3341-3200 cm^{-1} and 3445-3391 cm^{-1} respectively in the IR spectra of all the complexes viz, Cu(II), Co(II), Fe(III), Ni(II), Zn(II) and Cd(II) metal ions, as in the case of ligand indicates the non- involvement of either indole NH or amide NH functions during coordination with the metal ions. Strong intensity band observed at 1656 cm^{-1} in the IR spectrum of ligand is due to C=O amide function which was found to appear in the region 1656-1624 cm^{-1} with medium to weak intensity in all the complexes indicate the coordination of amide carbonyl function to the metal ions. Medium intensity bands observed at 1620 cm^{-1} and 1605 cm^{-1} in case of ligand are due to azomethine function and C=N of tetrazole moiety which have been observed in the region 1623-1604 cm^{-1} and 1605-1565 cm^{-1} with weak intensity, the coordination of azomethine nitrogen and tetrazole nitrogen with the metal ions. The IR regions are purely tentative because of various skeletal vibrations associated with metal and ligand vibrations. The bands of weak intensity in the region 542-531 cm^{-1} in case of all the complexes of the ligand HL are assigned M-O vibrations and the bands in the region 441-436 cm^{-1} to M-N vibrations [23, 24] Table 2.

Table 2: IR Data of ligand HL and its complex.

Compounds	ν_{H2O}	Indole NH	Amide NH	$\nu_{C=O}$	$\nu_{C=N}$ Azomethine	$\nu_{C=N}$ Tetrazole			
*HL	-	3202	3444	1656	1620 m	1605 w	-	-	-
Cu-complex	-	3203	3413	1656	1623 w	1605 w	542	441	353
Co-complex	-	3341	3422	1624	1604 m	1565 w	531	438	342
Fe-complex	-	3203	3444	1652	1621 w	1587 w	542	441	348
Ni-complex	-	3200	3391	1624	1604 m	1582 w	526	436	339
Zn-complex	-	3202	3443	1657	1620 w	1605 w	542	440	357
Cd-complex	-	3203	3445	1652	1621 w	1587 w	542	441	349

*HL=Ligand HL

^{1}H NMR spectrum of ligand

The ^{1}H NMR spectra of the Schiff base HL in d_6-DMSO at room temperature, showed signal at, δ10.44 (s, 1H, CONH), δ9.02 (s, 1H, indole NH), δ8.7 (s,1H, N=CH) and δ7.50-8.6 (m, 13H, ArH) due to protons of amide NH, azomethine NH and aromatic protons respectively.

Mass spectrum of ligand HL

The mass spectrum of ligand HL showed the molecular ion peak at $M^{\dot{+}}$=465, 467 (23%, 8%). This on loss of N_3 radical gave a fragment ion recorded at m/z 423, 425 (17%, 6%). This on loss of H and CN radicals simultaneously gave a fragment ion recorded at m/z 396, 398 (15%, 5%) which on expulsion of C_9H_5N gave a fragment ion recorded at m/z 269, 271 (25, 8%). This on loss of hydrogen radical gave another fragment ion record at m/z 268, 270 (23, 8%). This on loss of NCO species gave a fragment ion peak at m/z 226, 228 (21, 7%). This on loss of hydrogen radical gave another fragment ion recorded at m/z 225, 227 (22, 7%). Further on loss of chloride radical gave a fragment ion peak recorded at m/z 190 (100%) which is also a base peak. Further loss of C_6H_4 species gave a peak recorded at m/z 114 (42%). The fragmentation pattern is depicted in Scheme-3. The above fragmentation pattern is in consistency with its structure. The IR, ^{1}HNMR and mass spectral data of ligand HL confirms its formation by the reaction between 5-substituted-3-phenyl-1*H*-indole-2-carboxyhydrazide and tetrazolo[1,5-a]quinoline-4-carbaldehyde.

Electronic spectra of Cu(II), Co(II), Fe(III), and Ni(II) complexes of the ligand HL

UV- Visible spectra were recorded on Analytik gena-Specord 50 Spectrophotometer using DMF as solvent. Electronic spectral data of the Cu(II), Co(II), Fe(III), and Ni(II) complexes of the ligand HL are given in Table 3.

Table 3: Electronic and EPR spectral data of complex of the ligand HL.

Compounds	Electronic spectral data (in cm^{-1})				E. S. R data				
	ν_1	ν_2	ν_3	ν_4		$g_\perp$	$g_{\parallel}$	g_{av}	G
Cu-complex	14180	16430	18190	-		2.0	2.2	2.1	4.2
Co-complex	10869	17156	20698			-	-	-	-
Fe-complex	18429	20324	23635	-		-	-	-	-
Ni-complex	8216	9952	13608	22350		-	-	-	-

Cu(II) complex

The electronic absorption spectra of the Cu(II) complex were recorded at 300 K. The absorption region assigned 14180 cm^{-1}, 16430 cm^{-1} and 18190 cm^{-1}. These bands corresponds to the transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}(\nu_1)_{,}$ ${}^2B_{1g} \rightarrow {}^2B_{2g}(\nu_2)$ and ${}^2B_{1g} \rightarrow {}^2E_{1g}(\nu_3)$ which is well agreeing with the reported value for square pyramidal geometry of Cu(II) complex as reported in the literature [25, 26] the complex may be considered to possess a square pyramidal geometry.

Co(II) complex

The electronic spectra of Co(II) complex recorded in DMSO solution display three bands at 10869 cm^{-1}, 17156 cm^{-1} and 20698 cm^{-1}. These band may be assigned to the transitions ${}^4A_2 + {}^4E \rightarrow {}^4B_1(\nu_1)$, ${}^4A_2 + {}^4E \rightarrow {}^4E_1$ (ν_2) and ${}^4A_2 + {}^4E \rightarrow {}^4A_2(P)$ (ν_3), respectively the position of these bands suggest an square pyramidal environment around the Co(II) ion which is well agreeing with the reported value [27].

Fe(III) complex

The electronic spectrum of Fe(III) complex displays three bands at 18429 cm^{-1} (ν_1), 20324 cm^{-1} (ν_2), 23635 cm^{-1} (ν_3), which may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$, and ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^4E_g$ transitions, respectively typical of an octahedral geometry. These observed values for Fe(III) complex in its visible spectrum are in agreement with the literature value [28] and there by proved octahedral geometry for the Fe(III) complex of the ligand HL.

Ni(II) complex

The electronic spectra of Ni(II) complex displayed four absorption band in the ranges 8216(ν_1) 9952(ν_2), 13608(ν_3) and 22350(ν_4) the position of these bands indicates that the complex has distorted square pyramidal geometry and these band may assigned to the three spin allowed transitions. ${}^3B_1 \rightarrow {}^3B_2(\nu_1)$, ${}^3B_1 \rightarrow {}^3E^a(\nu_2)$, ${}^2B_1 \rightarrow {}^3A_2(\nu_3)$ and ${}^3B_1 \rightarrow {}^3E^b(\nu_4)$ respectively.

All these observations favor the square pyramidal geometry for Ni(II) complex of the present study [29].

Magnetic susceptibility data

Magnetic susceptibility measurements of the complexes were performed at room temperature. The magnetic moment values for Cu(II) complex is 1.58 BM corresponding to one unpaired electron. The complex may be considered to possess a square pyramidal geometry which is well agreeing with reported value of square pyramidal geometry for Cu(II) complex reported in the literature [25, 26]. The magnetic susceptibility of various Co(II) complexes in the range 4.3-4.6 BM is reported for square pyramidal complexes. In the present investigation the observed magnetic moment value for Co(II) complex is 4.18 BM indicates square pyramidal for the Co(II) complex [30]. For Ni(II) complex at room temperature the magnetic moment shows at 2.73 being within the range known for five coordinate complexes of square pyramidal geometry reported in the literature. For Fe(III) complexes the observed magnetic moment value is 5.88 BM respectively which corresponds to high spin octahedral complex as reported in the literature [27] Table 1.

Molar Conductance

The molar conductance of the complexes was measured in DMF at 10^{-3}M concentration. Measured conductance values of these complexes are too low to account for their electrolytic behavior except Cd(II) complex given in Table 1.

Powder X-ray diffraction (XRD) studies

The compounds were soluble in polar organic solvents (DMSO & DMF). We could not obtain crystal suitable for single crystal studies. In order to test the degree of crystallinity of the synthesized complexes, we obtained the powder XRD pattern of Co(II) complex.

The powder XRD pattern of Co(II) complex have provided the supplementary material. The Co(II) complex showed four reflections in the range 3-80º (2θ), arising the diffractions of X-ray by the planes of complex. All important peaks have been indexed and observed values of inter–planar distance (d) have been compared with the calculated ones. The unit cell calculations were performed for cubic system and the ($h^2+ k^2+ l^2$) values were determined. The absence of forbidden numbers (7, 15 and 23) indicates that the Co(II) complex has cubic symmetry. The experimental values are in good agreements with ($h^2+ k^2+ l^2$) values of primitive type cubic cell with lattice parameter equal to $a = b = c = 14.85$ Å Table 4.

Similar calculations were performed for Ni(II) complex and this complex showed five reflections in the range 5.82-30.09° (2θ). The absence of forbidden numbers (7, 15 and 23) indicates that the Ni(II) complex may belong to cubic system Table 5.

Table 4: Powder X-ray data of Co(II) complex of ligand HL.

Peak	2ϴ	ϴ	Sinϴ	$Sin^2ϴ$	h k l	d		$h^2+k^2+l^2$	a in Å
						Calc.	Obser.		
1	5.956	2.978	0.0519	0.0026	1 0 0	14.836	14.827	1	14.84
2	35.463	17.731	0.3045	0.0927	5 3 0	2.528	2.529	34	14.74
3	48.979	24.489	0.4145	0.1718	8 0 0	1.857	1.858	64	14.85
4	53.692	26.846	0.4515	0.2038	- - -	1.705	1.705	76	14.86

Table 5: Powder X-ray data of Ni(II) complex of ligand HL.

Peak	2ϴ	ϴ	Sinϴ	$Sin^2ϴ$	h k l	Calc.	Obser.	$h^2+k^2+l^2$	a in Å
1	6.20	3.1	0.054	0.0029	1 0 0	14.25	14.23	1	14.29
2	26.97	13.48	0.233	0.0542	3 3 1	3.30	3.30	19	14.43
3	35.56	17.78	0.305	0.0930	4 4 0	2.52	2.52	32	14.27
4	53.76	26.88	0.452	0.2043	6 5 3	1.70	1.70	70	14.24
5	56.10	28.05	0.470	0.2209	6 6 2	1.63	1.63	76	14.27

ESR spectrum of Cu(II) complex of ligand HL

The ESR spectrum of Cu(II) complex was recorded on Bruker BioSpin GmbH at room temperature, on the x-band at 9.43 GHz under the magnetic field strength 4950G. In order to obtain more information about the environment of Cu(II) complex, the X- band ESR spectrum of the polycrystalline Cu(II) complex has been recorded at room temperature. The value of $g_\parallel$ and $g_\perp$ were calculated and presented in the Table 3. The observed ESR spectrum is characteristics of square pyramidal geometry. The 'g' value averaged to overall distortion where calculated using the relation

$$g_{av}{}^2 = \frac{1}{3}(2g_\parallel{}^2 + g_\perp{}^2)$$

G = $(g_\parallel - 2) / (g_\perp - 2)$ which measures the exchange interaction between copper centers in a polycrystalline solid has been calculated. According to Hathaway [31], if the G value is greater than 4, the exchange interaction is negligible, while a value of G less than 4 indicates a considerable exchange interaction between metal ions in the solid complex. In the present case, G =4.29 indicates that there is no exchange interaction in the Cu(II) complex of ligand HL .

The observed $g_\parallel$ =2.2, $g_\perp$= 2.0 and g_{av} 2.1 values of the Cu(II) complex under the present study followed the same trend $g_\parallel > g_\perp > g_e$ which suggest the presence of unpaired electron in d_{x2-y2} orbital giving square pyramidal geometry [32]. The observed G=4.29 for the complexes under present study evidenced the monomeric nature of the complexes [33]. The $g_\parallel > 2.3$ indicates the considerable ionic character $g_{\parallel, < 2.3.}$ In this case the g ‖ = 2.27 which is covalent in nature the environment is essentially covalent. This fact is further supported by the absence of a band corresponding to ΔMs = ±2 transition in the observed ESR spectrum which is characteristic of monomeric complex.

Thermal studies

From TG curve, information related to the thermal stabilities, composition of the initial sample, intermediate compounds that formed and the final residue could be obtained.

Co(II) complex

The TGA study on Co[$C_{25}H_{16}N_7OCl_3$] were carried out in the temperature range 38 ºC to 721 ºC. at an heating rate of 10 ºC/min.

The decomposition studies of the Co(II) complex, Co[$C_{25}H_{16}N_7OCl_3$] has been carried out. In the thermogram of the Co[$C_{25}H_{16}N_7OCl_3$], the first stage of the decomposition represents the weight loss of N_3 at 225 ºC, with weight loss of 7.09%. The theoretical weight loss for this decomposition was 7.07% agreeing well with observed value of 7.09%. The resultant complex underwent further degradation and gave break at 305 ºC with a weight loss of 13.74%, which corresponds to the decomposition of the C_6H_6 species. This practical weight loss 13.74% is in accordance with theoretical weight loss of 13.95%. The complex gave a third break at 408 ºC with a weight loss 23.89%. The theoretical weight loss at this stage is 23.16% agreeing with observed value 23.89% due to decomposition of C_6H_6Cl. Thereafter, compound showed a gradual decomposition up to 721 ºC and onwards. The weight of residue corresponds to cobalt oxide. The thermal decomposition of Co[$C_{25}H_{16}N_7OCl_3$] with probable assignments are given in Table 6.

Table 6: Thermal decomposition of Co(II) complex of ligand HL.

Complex	Stage	Peak temp TG(^{0}C)	Loss of mass (in %)		Probable assignments
			Practical	Theoretical	
Co-complex					[$C_{25}H_{16}N_7OCl_3$]Co
	I	225	7.09	7.07	$\downarrow$ - N_3 [$C_{25}H_{16}N_4OCl_3$]Co
	II	305	13.74	13.95	$\downarrow$ -C_6H_6 [$C_{19}H_{10}N_4OCl_3$]Co
	III	408	23.89	23.16	$\downarrow$ -C_6H_5Cl CoO_2

Ni(II) complex

The TGA study on [$C_{25}H_{16}N_7OCl_3$]Ni were carried out in the temperature range 38 °C to 547 °C. at an heating rate of 10 ºC/min.

The decomposition studies of the Ni(II) complex, $[C_{25}H_{16}N_7OCl_3]Ni$ has been carried out. In the thermogram of the $[C_{25}H_{16}N_7OCl_3]Ni$, the first stage of the decomposition represents the weight loss of N_3 and C_6H_6 species at 227 °C, with weight loss of 21.27%. The theoretical weight loss for this decomposition was 20.04% agreeing well with observed value of 21.27%. The complex underwent further degradation and gave break at 400 °C with a practical weight loss of 54.04%, is in accordance with theoretical weight loss 52.45% which corresponds to the decomposition of the C_6H_5Cl and $C_{10}H_5N$ species.

Thereafter, compound showed a gradual decomposition up to 547 °C and onwards. The weight of residue corresponds to Nickel oxide. The thermal decomposition of $[C_{25}H_{16}N_7OCl_3]Ni$ with probable assignments are given in Table 7.

Table 7: Thermal decomposition of Ni(II) complex of ligand HL.

Complex	Stage	Peak temp TG(^{0}C)	Loss of mass (in %)		Probable assignments
			Practical	Theoretical	
Ni-complex	I	227	21.27	20.04	$[C_{25}H_{16}N_7OCl_3]Ni$ $\downarrow$ $-N_3$ $-C_6H_6$ $[C_{19}H_{10}N_4OCl_3]$ Ni
	II	400	54.04	52.45	$\downarrow$ $-C_6H_5Cl$ $-C_{10}H_5N$ CoO_2

Antimicrobial activity

Table 8: Antibacterial activity of ligand and its complexes.

Compound	1000 ppm		500 ppm		250 ppm		125 ppm	
	Klebsiella	*Pseudomonas*	*Klebsiella*	*Pseudomonas*	*Klebsiella*	*Pseudomonas*	*Klebsiella*	*Pseudomonas*
*HL	16	15	12	10	8	7	6	3
Cu-complex	18	18	12	13	9	8	7	6
Co-complex	10	9	8	7	7	5	3	3
Fe-complex	16	16	14	14	10	9	6	5
Ni-complex	8	8	7	6	5	4	3	2
Zn-complex	17	16	15	14	12	12	7	6
Cd-complex	7	7	5	4	3	3	2	0
DMF(Control)	-	-	-	-	-	-	-	-
Amoxycillin	20	19	18	18	14	13	11	10
Gentamycin	21	20	19	18	15	15	11	10

The antibacterial activity of all the newly synthesized ligand and its complexes were studied by MIC method in a series of dilutions (1000 ppm, 500 ppm, 250 ppm and 125 ppm) by cup-plate method using nutrient agar media. Cu(II) and Zn(II) complex exhibited high activity towards *Klebsiella* and *Pseudomonas in vitro* tests at minimum inhibitory concentration of 125 ppm. HL, Fe(III) and Ni(II) complexes were active at minimum inhibitory concentrations of 250 ppm against *Klebsiella* and *Pseudomonas* when compared with standard drugs Amoxycillin and Gentamycin at 250 ppm. Co(II) and Cd(II) complexes exhibited less activity towards *Klebsiella* and *Pseudomonas in vitro* tests at minimum inhibitory concentration of 1000 ppm. Table 8.

The antifungal activity of the ligand HL and its complexes was studied in a series of dilutions (1000 ppm, 500 ppm, 250 ppm and 125 ppm) by seberose dextrose agar (SDA) method. HL and Ni(II) complex exhibited high activity towards *A. niger* and *A. Flavus in vitro* tests at minimum inhibitory concentration of 125 ppm. Cu(II), and Fe(III) complexes were moderately active at minimum inhibitory concentrations of 250 ppm against *A. niger* and *A. Flavus.* Co(II), Zn(II) and Cd(II) complex showed less activity at 500 ppm when compared with standard drug Fluconazole at 250 ppm Table 9.

Table 9: Antifungal activities of ligand and its complexes.

Compound	1000 ppm		500 ppm		250 ppm		125 ppm	
	A. Niger	*A. Flavus*	*A. Niger*	*A. Flavus*	*A. Niger*	*A. Flavus*	*A. Niger*	*A. Flavus*
*HL	12	12	9	10	5	5	3	2
Cu-complex	10	10	7	6	4	3	2	0
Co-complex	6	6	3	3	2	2	0	0
Fe-complex	7	7	5	5	3	3	2	2
Ni-complex	12	11	10	9	6	5	4	2
Zn-complex	6	5	3	3	0	0	0	0
Cd-complex	5	5	3	2	2	0	0	0
DMF(Control)	-	-	-	-	-	-	-	-
Fluconazole	14	14	10	10	7	7	4	3

Antioxidant activity by DPPH radical scavenging activity

Antiradical activity evaluation for complexes and its ligand was measured in terms of decreases in absorbance at 517 nm of DPPH methanol solution (0.1 mmol) produced by the effect of each complex or ligand as a result of their ability to donate a hydrogen giving place to the reduced form of DPPH radical. The amount of DPPH reduced form was obtained in every established period of time using the fallowing equation.

$$Percentage\,of\ scavenging\ activity = \frac{A_o - A_e}{A_o} \times 100$$

Where A_o corresponds to the absorbance of DPPH without sample and A_e corresponds to the absorbance of sample with complex or ligand. A_o blank sample containing only DPPH; the negative control is methanol and standard Vit-E as a control.

DPPH scavenging activity of ligand and its complexes against vitamin-E as standards were analyzed at 1mg/mL in DMF solution at T = 30 min. This investigation indicates that there is a great possibility of finding potent antioxidants. The Cu(II), Co(II) and Fe(III) complexes have exhibited very good free radical scavenging activity. Ligand HL, Ni(II), Zn(II) and Cd(II) complexes of ligand HL showed less activity compared with Vit-E. The bar graph representation of percentage of free radical scavenging activities is shown in Figure 1.

Further, the calf-thymus (CT) DNA gel electrophoresis experiment was conducted at 37 ºC using our newly synthesized ligand and its complexes, as can be seen from the result at 100 µg mL^{-1} concentration of all the samples showed complete cleavage of DNA as compared to control DNA.

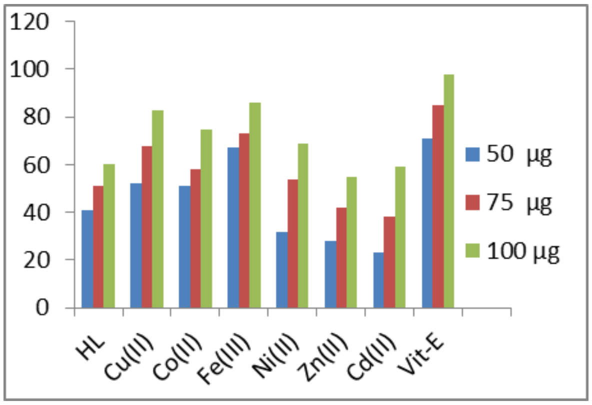


Figure 1: Antioxidant activity of ligand and its metal complexes.

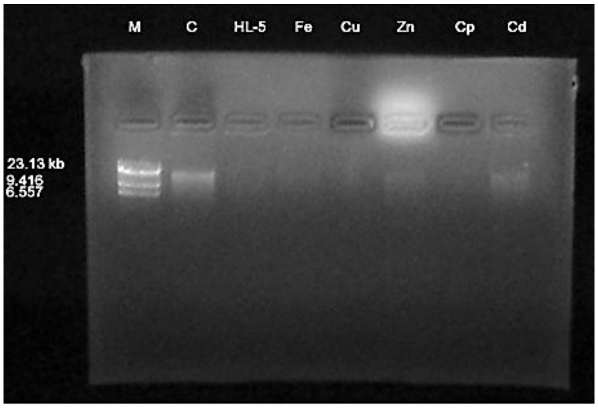


Figure 2: DNA cleavage activity of ligand and its metal complexes.

CONCLUSION

A new ligand 5-chloro-3-phenyl-*N*'-(tetrazolo[1,5-a]quinolin-4-ylmethylene)-1*H*-indole-2-carbohydrazide and its complexes have been synthesized and characterized by IR, ^{1}H NMR, mass, TGA, ESR and Powder-XRD data which concludes that all the complexes are of the type ML_2-stoichiometry and these complexes exhibited octahedral geometry. Some of these complexes have exhibited good antimicrobial, antioxidant and DNA cleavage activities.

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