Synthesis, Characterization and Biological Activity Studies of Thioquinoline Complexes of 3d-Transition Metals

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Keywords : Schiff base, thiosemicarbazide, antifungal activities.

INTRODUCTION

Quinoline derivatives represent the major class of heterocycles, and a number of preparations have been known since the late1980 onwards. The quinoline ring occurs in various natural products, especially in alkaloids[1]. The quinoline skeleton is often used for the design of many synthetic compounds with diverse pharmacological properties[2].

The study of transition metal quinoline complexes is an area of great current interest. Meth Cohn *et.al.*[3] has reported the synthesis of 2-chloro3-formylquinolines which on acid hydrolysis form 2-hydroxy3-formylquinolines. These compounds containing the functional groups –OH / =O and –CHO at the appropriate positions the ring may serve as precursors for the synthesis of ligands and their metal complexes. Further, these precursors may also form Schiff bases, which function as ligands. Schiff bases are known to possess many pharmacological activities such as tuberculostatic, fungicidal, anti-inflammatory, antitumor, antiviral and antimicrobial activities[4].

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These compounds containing the functional groups –OH / =O and –CHO at the appropriate positions the ring may serve as precursors for the synthesis of ligands and their metal complexes. Further, these precursors may also form Schiff bases, which function as ligands. Schiff bases are known to posses many pharmacological activities such as tuberculostatic, fungicidal, anti-inflammatory, antitumor, antiviral, and antimicrobial activities [4].

Many substituted thiosemicarbazone Schiff bases and their metal complexes are reported to exhibit various biological properties like antitumor, antibacterial, antifungal and antiviral

activities. In most of the cases the activity of the ligand is noticeably enhanced after complexation with transition metals[5].

Recently there are interesting studies on combining biologically active quinoline core and thiosemicarbazide moieties through Schiff base formation and their coordination behavior with transition metals. Such complexes were found to exhibit enhanced antimicrobial properties[6].

In the present study we have synthesized Schiff base ligands H_2L^1 by the condensation of 2-thio-3-formylquinoline with thiosemicarbazide and its complexes with Co(II), Ni(II), Cu(II) & Zn(II) metal chloride salts. The complexes were characterized by various spectral and analytical methods and their antimicrobial, antifungal and DNA cleavage activities were investigated.

EXPERIMENTAL

Materials and methods:

The chemicals used were of reagent grade. Purified solvents were used for the synthesis of ligands and complexes. 2-chloro-3-formyl quinoline was synthesized using Vilsmeier Hack reaction. Its thio derivative was prepared by the action of Na_2S in DMF solution, carried out according to the reported method with slight modifications[7].

The metal chlorides used were in the hydrated form. C, H, N, and S analysis was carried out on a Thermo Quest elemental analyzer. Metal and chloride estimations were done following standard procedures. The molar conductivity measurements in dimethylformamide (DMF) were made on an ELICO-CM-82 conductivity bridge. The magnetic susceptibility measurements were made using a Faraday balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. The ^1H NMR spectra were recorded in DMSO-d_6 solvent on a Bruker 300-MHz spectrometer at room temperature using tetramethylsilane (TMS) as internal reference. Infrared (IR) spectra were recorded in KBr matrix using an Impact 410 Nicolet Fourier transform infrared (FTIR) spectrometer. The electronic spectra of the complexes were recorded on a Hitachi 150-20 in the spectrophotometer. The ESR study of the copper complexes was carried out on a Varian E-4X-band electron paramagnetic resonance (EPR) spectrometer, using tetracyanoethylene (TCNE) as the g-marker.

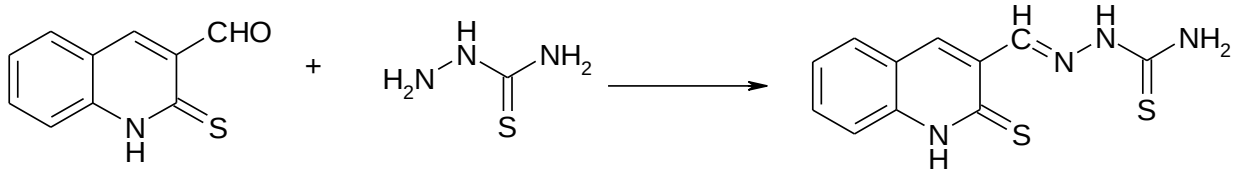
Syntheses:

1. **Synthesis of 3–formylquinoline-2(1*H*)-thione:**

To the solution of 2-chloro-3-formylquinoline (1 mmole) in dry DMF (5 ml), sodium sulphide (1.5m moles, fused flakes) was added (monitored by TLC), the reaction mixture was poured into ice-water (*ca*. 15 ml) and made acidic with acetic acid. The product was filtered off, washed well with water, dried and was pure enough for further use[8]. M.P. 285 - 286^{0}C. Yield 84%.

2. **Synthesis of thiosemicarbazone Ligand:**

Thiosemicarbazide (0.01mol) in ethanol (100ml) was treated with 3–formylquinoline-2(1*H*)-thione(0.01mol). The reaction mixtures were refluxed for 3 - 4 hours. Yellow solids separated were filtered, washed with ethanol 2 - 3 times and dried. Yield 70-80% (Scheme 1).



Reaction Scheme 1. Synthesis of ligand L[1]

3. **Synthesis of complexes:**

Ligand (0.002mol) was taken in 35 - 40 ml of hot ethanol. To this, hot ethanolic solution of metal chlorides (0.002mol) (for multinuclear complexes excess metal salts were added) was added drop wise with stirring at 60 - 65^{0}C. After complete addition of metal salt solution, the reaction mixture was stirred for another 30 - 40 minutes at the same temperature and refluxed for 3 - 4 hours on water bath. The isolated complexes were filtered in hot condition, washed with hot ethanol and dried.

Biological Screening:

Nutrient agar is selected for growing bacterial cultures and for demonstration of antimicrobial activity.

Preparation of plates by cup-bore method: Appropriate quantity of nutrient agar medium were poured into separate sterile Petri plates and allowed to solidify in the laminar air flow. After the perfect solidification of agar medium in the plate, 0.1 ml of bacterial suspension were poured and spread throughout the plate. While spreading special care was taken to spread uniformly all over the plate. With the help of sterilized cork borer uniform wells were bored in agar dish in which known volumes of test solutions were added and allowed to stand at room temperature for stabilization[9].

The bacterial plates were incubated at 37º C for 24 hours in bacteriological incubator. The antimicrobial activity of the compounds were tested against *E. coli* and *Streptococci*, where as antifungal activity was tested against *Chaetomium* fungi. The concentrations used were 50 to 100 µg/ml.

DNA Cleavage activity analysis: was carried out on *E. coli* DNA by Agarose gel electrophoresis method[10]. 10 µg of samples of L^1, CoL^1, NiL^1, CuL^1, ZnL^1 and 100 µg of NiL^1 were used in the study.

RESULTS AND DISCUSSION

The compositional data of synthesized ligand and its complexes are compiled in **Table-1**. The interaction of metal salts with the ligands in 1:2, 1:1 and 2:2 molar ratios in ethanol yielded stable solid complexes. These complexes were non-hygroscopic and in the form of amorphous solids. The metal complexes are soluble in DMSO and DMF, insoluble in ethanol, methanol, and chlorinated hydrocarbons. They melt with decomposition above 300^0C. The Co(III) complex was dark brown, Ni(II) complex was light brown, Cu(II) complex was dark brown and Zn(II) complex was yellowish in color. Attempts to grow single crystals suitable for X- ray structure determination have not been successful due to their low solubility in usual solvents.

Table 1. Elemental analysis data of complexes.

Comp	Empirical Formula	C	H	N	M	Cl	Molar cond. Λ_M
L^1	$C_{10}H_{10}N_4S_2$	45.74(45.86)	3.84(3.65)	21.34(21.45)	--	--	--
CoL^1	$[Co(C_{30}H_{28}N_{12}S_6)]H_2O$	41.76(42.02)	3.51(3.87)	19.49(19.67)	6.84(7.04)	--	58
NiL^1	$[Ni(C_{10}H_{14}N4O_2S_2)Cl]Cl$	28.04(28.78)	3.29(3.59)	13.08(13.84)	14.20(14.46)	16.09(16.86)	105
CuL^1	$[Cu_2(C_{20}H_{28}N_8O_4S_4)]\ Cl_2$	31.58(32.02)	3.71(3.86)	14.74(14.96)	8.36(8.78)	9.08(9.56)	398
ZnL^1	$[Zn(C_{10}H_{12}N_4O_1S_2Cl_2)]$	31.43(31.87)	3.17(2.98)	14.67(14.26)	17.13(17.19)	18.07(18.63)	52.4

Molar conductivity measurements

The molar conductance values of complexes CoL^1 and ZnL^1 in DMSO at concentration 10^{-3} M fall in the range 52 - 58 mho cm^2 mol^{-1} **(Table-1).** These values are less than that expected for 1:1 electrolytes (65 - 90 mho cm^2 mol^{-1}) and hence are non-electrolytic in nature[11]. While NiL^1 complex shows conductance values in the range 90 - 100 mho cm^2 mol^{-1} which indicates the

1:1 electrolyte and CuL^1 complex shows conductance as 398 mho cm^2 mol^{-1} which indicates 2:2 electrolyte nature to this complex[11 - 14].

I.R spectral studies:

The important IR spectral bands of ligand L^1 and corresponding complexes along with assignments are presented in **Table 2.** The IR spectra of ligand and its complex CoL^1 are shown in **Fig. 1**.

The spectrum of ligand shows two bands of medium intensity in the range of 3270 – 3417 cm^{-1} which are assigned to *v*(^{4}NH) and band at 3141cm^{-1} assigned to hydrazine v(^{2}NH) [15, 16]. The possibility of thioamide – thioimidol tautomerism (H-N-C=S ⇔ □C=N-SH) in the ligand have been ruled out, since there is no IR absorption band around 2500-2600 cm^{-1}, which is characteristic of thiol group.

The sharp band around 1665cm^{-1} is assigned to azomethine C=N group [15, 17, 18] in the ligand. This band shifts to lower frequency [19] by ~ 35 - 45 cm^{-1} in all the complexes indicates the coordination through azomethine nitrogen. This is further supported by the shift of band chiefly assigned to the N–N stretch [20]. Coupled vibration among thioamide bands I, II, III, and IV in the fingerprint region are distributed around 1586, 1485, 1348, and 954 cm^{-1} respectively [21- 23]. The appearance of four thioamide bands in the spectra of ligand is another support for the existence of thioketo (thione) form of ligand in the solid state.

In the complex CuL^1 presence of only one band, assigned at higher energy side for ^{4}NH and disappearance of lower energy side band assigned for ^{2}NH around 3200 cm^{-1} in ligand, indicates deprotonation of ^{2}NH proton of ligand during complexation with metal ions via thioenolisation. This fact is supported by the positive shift of thioamide band II and considerable reduction in intensity of thioamide band III & IV (around 1350 & 965 cm^{-1}) which were assigned to the coupled vibration of *v*(C=S). Along with this, appearance of a weak band around 617 – 670 cm^{-1} due to *v*(C-S) confirms the deprotonation of ^{2}NH proton through thioenolization and subsequent coordination to metal through sulfur atom [21, 24].

After complex formation the ^{4}NH band shifted towards higher energy side. In most of the complexes this band is superimposed by uncoordinated water molecule band and hence assignment of this band is difficult. Some intense bands occurring at 3421(NiL^1), 3434(CuL^1) and 3416 (ZnL^1) are assigned for coordinated water molecules.

The spectra are rather complex in the region below 500 cm^{-1}, where the various M-L bond-stretching vibrations are often found in combination with other bands. Non-ligand low frequency bands in the 523 – 500 cm^{-1} regions are assigned to *ν*(M-N) [25, 26].

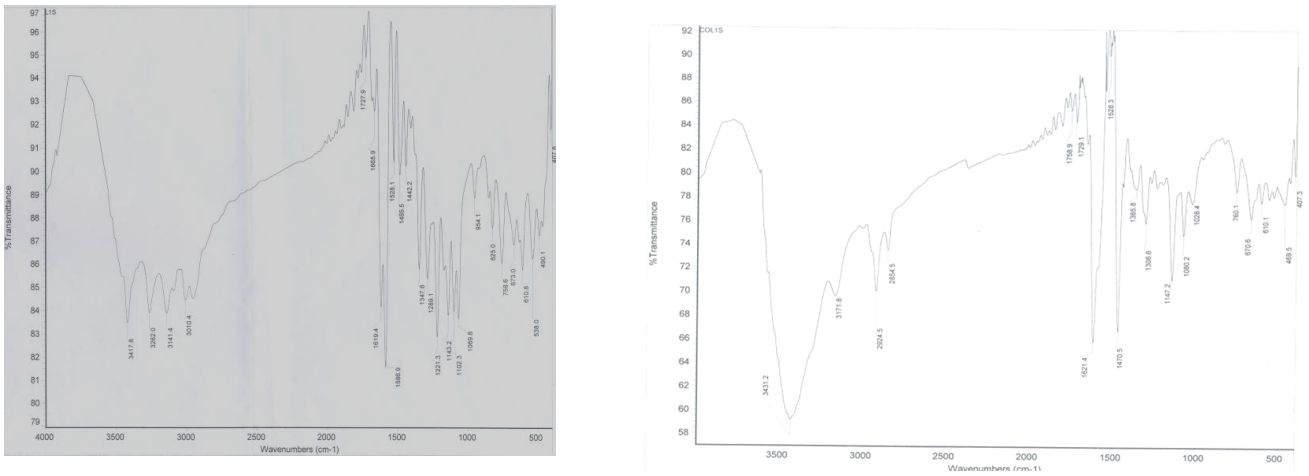


Fig. 1. IR Spectrum of Ligand L^1 (1*H*)-thio-3–formylquinolinethiosemicarbazone and its complex CoL^1

Table 2. IR data of ligand and complexes.

Com	v(OH)	v(^{4}NH)	v(^{2}NH)	*V* C=N	*Thioamide bands*				v(N-N)	v(C-S)	v(MN)
					I	*II*	*III*	*IV*			
L^1	--	3417	3262s	1665	1586s	1485 m	1348 s	954 m	1102 m	--	--
CoL^1	3431	--	3171	1621	1528	1470	1365	1028	1080	610 m	469
NiL^1	3429	--	3134	1625	1625	1487	1371	964	1090	--	467
CuL^1	3434	--	--	1622	1577w	1491	1350	965 w	1062	612	--
ZnL^1	3416	3287 w	3182	1622	1588	1492	1347	963	1068	--	542

Magneto chemistry: The experimentally determined room temperature magnetic moments of all the complexes are given in the **Table 4**.

The Copper (II) complex shows the effective magnetic moment 1.25 B. M. Considerably lower magnetic moment than the spin only value (1.73 B.M) for Cu (II) complex is attributed for the anti-ferromagnetic coupling interaction between metal ions. This value is consistent with the di-nuclear complexes CuL^1, which is further confirmed from the EPR study.

The magnetic moment value of Ni(II) complex gives valuable information regarding its stereochemistry. Naik *et al*., [27] have reported magnetic moment values in the range of 2.62 – 2.91 B.M. for Ni(II) octahedral complexes. Biradar *et al*.,[28] reported 2.5 – 3.4 B.M. for octahedral Ni(II) complexes. In the present investigation the observed magnetic moment value for Ni(II) complex is found to be 2.90 B.M. which are in the range expected for octahedral geometry around Ni(II) ion.

The complex CoL^1 exhibits the magnetic moment 1.84 B.M. indicating the presence of one unpaired electron and forming low spin complex.

^{1}H NMR studies

Chemical shifts of all prominent peaks of ligand and their complexes are tabulated in **Table 3** and spectra represented in **fig. 3.** The spectrum of ligand shows resonances at 7.35 - 8.20, 8.34, 8.77, 11.73 and 13.87 δ ppm. Of these absorptions, a multiplet ranging from 7.35 - 8.20 δ ppm is assigned for aromatic protons. The simple NH_2 group of thiosemicarbazide part in ligand L^1 resonates at 8.34 δ ppm and the azomethine proton is observed as a singlet at 8.77 δ ppm. The hydrazine ^{2}NH protons resonate as singlet at 11.73 δ ppm[29]. This peak disappeared on D_2O exchange. Along with this, the examination of the spectrum of ligand shows no signal around 4 δ ppm, which may be ascribed for S-H proton[30]. Thus appearance of both -NH signal implies that the thiol form (II) is presumably not present in DMSO solution and the ligand exist in thione or keto form (I).

A new singlet around 13.87 δ ppm appeared in the ligand and complex. Due to the resonance the proton bonded to nitrogen in thioquinolone becomes highly acidic. This proton is responsible for the appearance of new deshielded peak at 13.87 δ ppm which clearly indicates the thione form of the ligand. (Fig.-2)

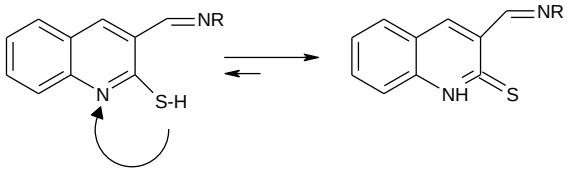


Fig.-2

Comparative study of spectra of zinc complex with its ligand shows very little shifting of peaks on complexation with ligand. The spectrum of zinc complex shows all peaks that were present in their corresponding ligand.

Table 3. NMR data of ligand and Zinc complex.

Comp.	**Ar-H**	**-HC=N**	**Hydrazine NH**	**-NH_2**	**Quin. NH**
L^1	7.35 - 8.20	8.77	11.73*	8.34	13.87
ZnL^1	7.38 - 8.14	8.78	11.72*	8.34	13.88

* Disappeared on D_2O exchange

The fact that the chemical shifts of the azomethine protons change not in an assessable size is caused by the back-donation of the azomethine system for coordination. Since the π electrons of the azomethine group are not affected, the chemical environment of the proton is not changed.

Thus in ZnL^1, azomethine –N, quinoline –S and –S of thiosemicarbazide group are utilized in coordination bond to metal atom.

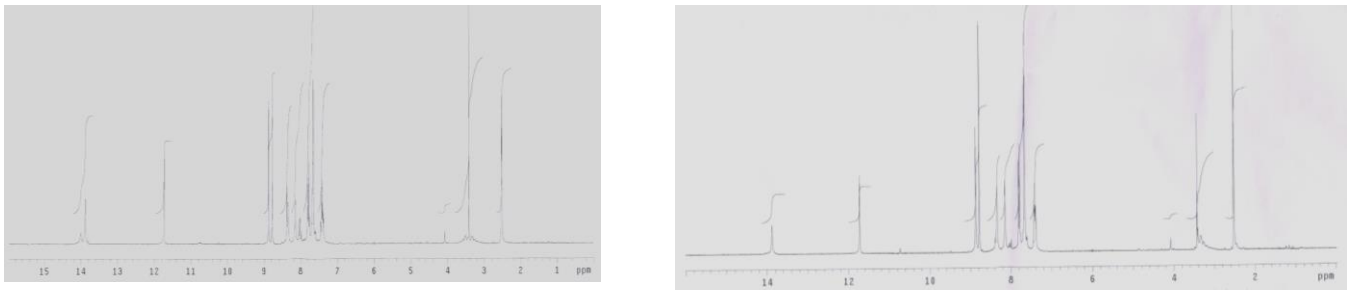


Fig. 3. ^{1}HNMR spectrum of L^1 and ZnL^2

Electronic spectral studies

The electronic spectra of the ligand and its complexes are recorded in Dimeyhylsulphoxide and data are summarized in **Table-4.**

Table 4. Electronic spectra and magnetic moment data.

Compound	λ_{max} **(nm)**	μ_{eff} **(B.M.)**
H_2L^2	356, 371, 420	----
CoL^2	280, 340, 366	1.84
CuL^2	308, 376	1.25
NiL^2	261, 330	2.90
ZnL^2	287, 367	Diamagnetic

The ligand exhibit UV-Visible absorption bands around 220 and 240 – 260 nm. The intense band around 260 nm is assigned to intra ligand $\pi \rightarrow \pi^*$ transition. This band is almost unchanged in the spectra of complexes. The ligand also shows a broad band at 385-420 nm with a shoulder on low energy side, due to $n \rightarrow \pi^*$ transition associated with azomethine linkage. This band in all complexes have shown slight red shift due to the donation of lone pair of electron to the metal and hence the coordination of azomethine functional group.

The third band above 360 nm in all the complexes are assigned to S$\rightarrow$ M(II) ligand to metal charge transfer transition (LMCT) band with molar extinction coefficient ε greater than 15000 l cm^{-1} mol^{-1}. Due to low solubility of some complexes and due to overlapping of LMCT band with d-d absorption bands, d-d bands couldn't be observed and hence ligand field parameters such as Dq, B, β, v_2/ v_1 and LFSE are not calculated.

EPR spectral studies

The solid state X-band EPR spectrum of complex CuL^1 exhibits three g values and the results are presented in the **Table-5** and the spectrum is shown in **Fig. 4.**

Table 6. EPR parameters

Comp.	g_1	g_2	g_3	g_{av}
CuL^1	2.21	2.10	2.03	2.11

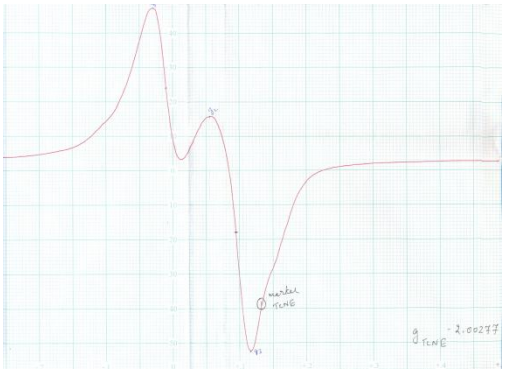


Fig. 4. EPR spectrum of complex: CuL^1

The complex CuL^1 exhibits anisotropic signals giving three g values. These values indicate the distortion in the highest-fold rotation axis. Three lines with different g values (g_1 = 2.21, g_2 = 2.10 and g_3 = 2.03) in this complex not only imply about the magnetic anisotropy but also indicate the rhombic distortion in the complex[31].

Antimicrobial activity studies

Antimicrobial screening of ligand and its complexes were done by cup-bore method as explained earlier and the results are presented in **Table. 7**. "Streptomycin" is used as standard dug to compare the activity of compounds. The potency of compounds was studied by comparing the zones of inhibition with that of standard drug on two bacterial strains. The biological activity was studied against *E. coli and Streptococcus sps bacteria and Chaetomium fungi*.

Table. 7. Antimicrobial activity data

Sl. No.	Compd.	Organisms used			Zone of inhibition
		Bacteria	Bacteria	Fungi	
1	L^1	*Streptococcus sps*			No zone
			E. coli		No zone
				Chaetomium	No zone
2	CoL^1	*Streptococcus sps*			No zone
			E. coli		No zone
				Chaetomium	No zone
3	NiL^1	*Streptococcus sps*			No zone
			E. coli		No zone
				Chaetomium	No zone
4	CuL^1	*Streptococcus sps*			No zone
			E. coli		3 mm
				Chaetomium	6 mm
5	ZnL^1	*Streptococcus sps*			No zone
			E. coli		No zone
				Chaetomium	3 mm

The ligand L^1 and complexes CoL^1 & NiL^1 did not show any activity. However, CuL^1 found active against E. coli and Chaetomium(fungi) where as the complex ZnL^1 shown activity against Chaetomium(fungi) only.

DNA Cleavage activity analysis

DNA Cleavage activity analysis was carried out on *E. coli* DNA by Agarose gel electrophoresis method and the gel picture is shown in Fig.5. Result indicates complete cleavage of DNA for L^1 CoL^1 and NiL^1 except CuL^1. However partial cleavage of DNA was observed with ZnL^1.

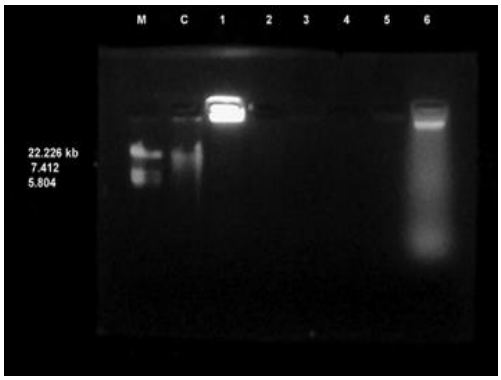
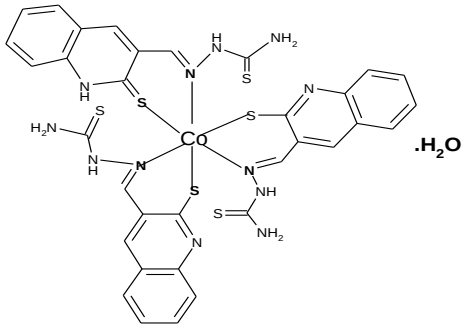


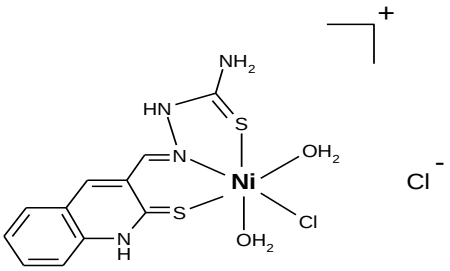
Fig. 5. Gel picture showing the DNA cleavage activity

CONCLUSION

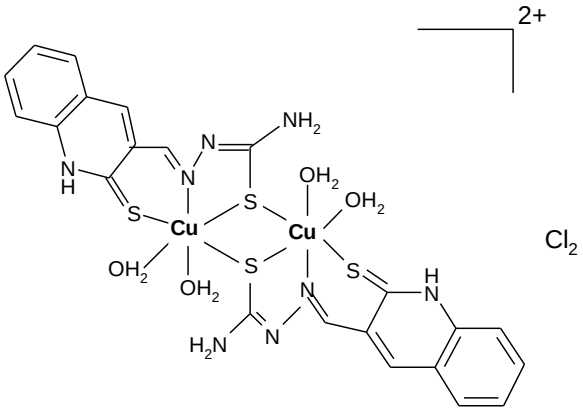
From the results of elemental analysis and various spectral studies, we have proposed octahedral geometry for all complexes. However CuL^1 complex found to be binuclear containing two octahedral sites. Tentative structures for all these complexes are shown below.



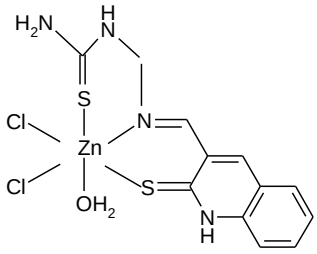
$[Co(L^1)((L^1)^{-1})_2].H_2O$



$[Ni(L^1)(H_2O)_2Cl]Cl$



$[Cu_2((L^1)^{-1})_2(H_2O)_4]Cl_2$



$[Zn(L^1)(H_2O)Cl_2]$

Among two ligands in CoL^1, one behaves as neutral bidentate and other as monobasic bidentate utilizing azomethine –N, and thiolate –S for coordination, to yield mononuclear octahedral complex. NiL^1 shows octahedral geometry involving neutral tridentate ligand coordinating through S, N, S donor atoms, it involves two water molecules and a chloride ion as coordinating sites leading to 1:1 ionic complex. In di-nuclear CuL^1 complex, the ligand behaves as monobasic tridentate coordinating through S, N, S donor atoms where thiolate S acts as bridging donor site. There are two coordinated water molecules leading to distorted octahedral (rhombic) ionic complex with 2:2 ionic ratio. The ligand in ZnL^1 complex acts as neutral tridentates utilizing thione-S, azomethine-N and thione-S of thiosemicarbazide part as donor atoms. There is one coordinated water molecule and two chloride ions to compensate the charge on the metal ion leading to neutral octahedral complex.

The complex CuL^1 found active against E. coli and Chaetomium(fungi) where as the complex ZnL^1 exhibited antifungal activity. Partial cleavage of DNA was observed with ZnL^1 however, except CuL^1 complete cleavage of DNA has been observed for L^1, CoL^1 and NiL^1 compounds.

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