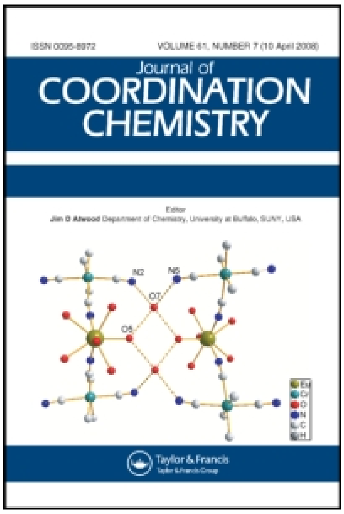

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Synthetic, spectroscopic, fluorescence, and biological investigation of Co(II), Ni(II), Cu(II), and Zn(II) complexes of Schiff bases derived from 3-formyl-2-mercaptoquinolines (Quinol-2-thiones)

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Synthetic, spectroscopic, fluorescence, and biological investigation of Co(II), Ni(II), Cu(II), and Zn(II) complexes of Schiff bases derived from 3-formyl-2-mercaptoquinolines (Quinol-2-thiones)

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Co(II), Ni(II), Cu(II), and Zn(II) complexes have been prepared with Schiff bases derived from 3-formyl-2-mercaptoquinoline and substituted anilines. The prepared Schiff bases and chelates have been characterized by elemental analysis, molar conductance, magnetic susceptibilities, electronic, IR, ^{1}H-NMR, ESR, cyclic voltammetry, FAB-mass, and thermal studies. The complexes have stoichiometry of the type $ML_2 \cdot 2H_2O$ coordinating through azomethine nitrogen and thiolate sulfur of 2-mercapto quinoline. An enhancement in fluorescence has been noticed in the Zn(II) complexes whereas quenching occurred in the other complexes. The ligands and their metal complexes have been screened *in vitro* for antibacterial and antifungal activities by MIC methods with biological activity increasing on complexation. Cu(II) complexes show greater bacterial than fungicidal activities. The brine shrimp bioassay was also carried out to study the *in vitro* cytotoxicity properties of the ligands and their corresponding complexes. Only four compounds have exhibited potent cytotoxic activity against *Artemia salina*; the other compounds were almost inactive for this assay.

Keywords: Quinoline; Coordination; Fluorescent probe; Cyclic voltammetry; Cytotoxicity

1. Introduction

Quinoline has potential as anti-inflammatory, analgesics, anticonvulsant, antibacterial, antipyretic, antihypertensive, and interferon inducing activity [1]. Synthetic applications of 2-chloro-3-formyl-quinoline have been reported by Meth-Cohn *et al*. [2]. Quinoline derivatives with various substituents at C-3 have analgesic, anti-inflammatory, and antipyretic activities [3]. Many Schiff bases derived from 2-chloro-3-formyl-quinoline have been reported for antifungal activities [4] and as potential biodynamic agents [5]. The conversion of aryl quinolines into mercaptoquinolines is of importance in synthesis as starting materials to construct sulfur-containing heterocycles such as thiophene and thiopyrans fused with a quinoline moiety [6]. These functional groups have been utilized to build various pharmaceutically important heterocycles [7–10].

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Schiff bases derived from 3-formyl-2-mercaptoquinoline have also proven to be important pharmaceutical agents [11–16]. Metal complexes of quinoline derivatives have proven their significance in diagnosis of diseases like heart disease, brain disorder, cancer, diabetics and tissue hypoxia, and to detect multi-drug resistance. Use of metal complexes as diagnostic agents is a relatively new area of medicinal research and complexation of biologically-active ligands [17, 18] has received much attention. In the present investigation transition metal complexes of 3-formyl-2-mercaptoquinoline Schiff bases are fairly good biological agents and exhibit excellent fluorescence, making them suitable candidates for fluorescent probes and labeling compounds in medicine and biochemistry. The synthesis, spectroscopic, fluorescence, and biological studies of Co(II), Ni(II), Cu(II), and Zn(II) complexes of Schiff bases derived from 3-formyl-2-mercaptoquinolines (Quinol-2-thiones) are reported.

2. Experimental

2.1. *Materials and methods*

All chemicals were of reagent grade and used without purification. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN elemental Analyzer Model 1106, Carloerba Strumentazione. IR spectra of the ligands and their Co(II), Ni(II), Cu(II), and Zn(II) complexes were recorded on a HITACHI-270 IR spectrophotometer in the 4000–250 cm^{-1} region in KBr disks. Molar conductivity measurements were recorded on an ELICO-CM-82 T conductivity bridge with a cell having cell constant 0.51. Electronic spectra of the complexes were recorded in DMF on a VARIAN CARY 50-BIO UV-spectrophotometer from 200 to 1100 nm. The ^{1}H-NMR spectra of ligands were recorded in $CDCl_3$ on a BRUKER 300 MHz spectrometer at room temperature using TMS as an internal reference. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon (6 KV, 10 Am) as the FAB gas. The accelerating voltage was 10 KV and the spectra were recorded at room temperature with *m*-nitrobenzyl alcohol as the matrix. The mass spectrometer was operated in the +ve ion mode. Thermogravimetric analysis data were measured from room temperature to 1000°C at a heating rate of 10°C min^{-1}. The data were obtained using a Perkin–Elmer Diamond TG/DTA instrument.

2.2. *Synthesis*

2.2.1. Synthesis of 2-chloro-3-formyl-quinoline. This compound was synthesized by reaction of acetanilide with a Vilsmier reaction at 80°C as per the procedure given in the literature [19]. Yellow crystals (ethyl acetate), yield = 92.24%, m.p. = 172–173°C.

2.2.2. Synthesis of N-[2-chloroquinoline-3-ylmethylene aniline] *Schiff base*. A mixture of 1.064 g (0.004 mol) of 2-chloro-3-formyl-quinoline and 0.37 mL (0.004 mol) of aniline in ethanol–acetic acid (20 mL) (2 : 1) was stirred at room temperature for 1 h. After completion of the reaction the solid was filtered, washed with excess cold ethanol, dried, and crystallized from ethanol. Slow evaporation was used to grow crystals of

PQT suitable for diffraction studies in the benzene and ethyl acetate mixture. Similar procedure was followed for **CPQT** and **BPQT** compounds for formation of Schiff bases in equimolar ratios.

PQT: Yellow crystals (benzene + ethyl acetate), yield = 92.24%, m.p. = 162–163°C;
CPQT: Yellow solid (benzene + ethyl acetate); yield: 88.14%; m.p. = 150–152°C;
BPQT: Yellow solid (benzene + ethyl acetate); yield: 86.96%; m.p. = 157–159°C.

2.2.3. Synthesis of ligands. A mixture of Schiff base 2.67 g (0.01 mol) and sodium sulfide 0.84 g (0.01 mol) was refluxed on a water bath for 2 h in ethanol (50 mL). Concentrated HCl (15 mL) was added dropwise to the reaction mixture. The mercapto compound was precipitated out as a yellow solid. The mixture was poured into cold water (500 mL) and the resulting solid was collected by filtration, washed with ethanol, dried, and recrystallized from acetic acid (**PQT**). Similar procedure was followed for **CPQT** and **BPQT** for formation of the mercapto derivative.

PQT: Pale yellow crystalline solid (acetic acid); yield: 78.30%; m.p. = 291–293°C;
CPQT: Pale yellow crystalline solid (acetic acid); yield: 80.13%; m.p. = 282–283°C;
BPQT: Yellow crystalline solid (aqueous acetic acid); yield: 76.86%; m.p. = 286–288°C (figure 1).

2.2.4. Synthesis of Co(II), Ni(II), Cu(II), and Zn(II) complexes. For the synthesis of the metal chelates, hot ethanolic solutions of the respective metal chlorides (0.01 mol) and the Schiff base (0.02 mol) were refluxed for about 4 h on a water bath and the pH of the reaction mixture was adjusted to 7–7.5. During the reflux, the metal chelates separated were filtered, washed successively with ethanol and ether, and finally dried over fused $CaCl_2$ in vacuum.

3. Results and discussion

An effort was made by Khalkamkar *et al.* [20] in growing the single crystal of the ligand. Efforts in growing the single crystals of these complexes were unsuccessful.

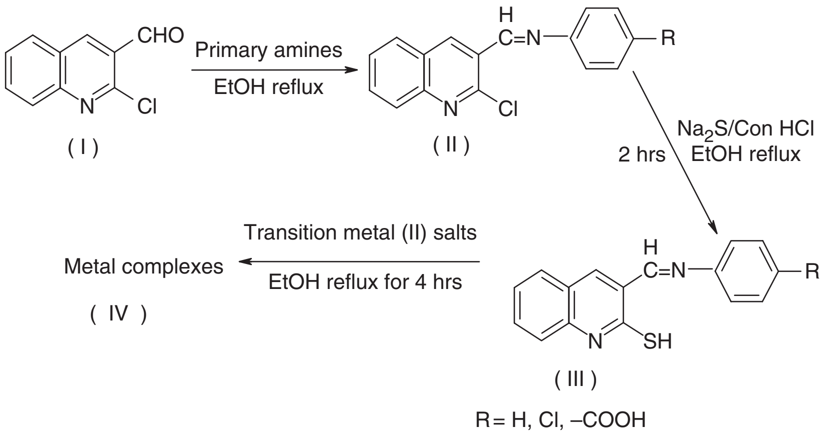

Figure 1. Scheme of the syntheses.

The synthesized complexes are colored and insoluble in water, partially soluble in methanol and ethanol, and totally soluble in DMF and DMSO. The elemental analyses (table 1) are consistent with 1: 2 stoichiometry of the type $ML_2 \cdot 2H_2O$. Conductivity in DMF at the 10^{-3} M concentrations is too low for any dissociation of the complex in DMF and the complexes are nonelectrolytes. The molecular weights of the synthesized complexes could not be determined in nitrobenzene because of their insolubility. In order to establish whether the water present in the synthesized complexes coordinated to metal, weighed complexes were dried over P_4O_{10} in vacuum for 1 h and weighed again with loss in weight being observed. This was confirmed by heating the complex for 2 h at 105°C and the weight loss was considered water of hydration. These observations suggest that water molecules in the Co(II), Ni(II), Cu(II), and Zn(II) complexes are coordinated to the metal.

3.1. *Electronic spectra*

The electronic spectra of Co(II) complexes (table 2) exhibit absorption bands in the region 8000–10,000 cm^{-1} and 18,000–20,000 cm^{-1} corresponding to ν_1 and ν_3 transitions, respectively, which are attributed to the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1); $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) [21, 22]. These bands are characteristic of high spin octahedral Co(II) complexes; ν_2 is not observed because of its proximity to the strong ν_3 transition, but can be calculated [23, 24]. Paramagnetic Ni(II) complexes (table 3) exhibited three bands at 10,487–10,683, 17,534–17,647, and 24,981–25,502 cm^{-1} attributed to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1); $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2); $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) indicating octahedral geometry around Ni(II) [22].

Electronic spectra of Cu(II) complexes (Supplemental material) display three prominent bands. A low intensity broad band in the region 15,198–17,123 cm^{-1} was assignable to $^2T_{2g} \leftarrow {}^2E_g$ transition. Another high intensity band in the region 25,974–26,316 cm^{-1} is due to symmetry forbidden ligand → metal charge transfer and two sharp bands observed at 30,121–33,670 cm^{-1} and 37,879–39,370 cm^{-1} are due to the ligand bands. On the basis of electronic spectra distorted octahedral geometry around Cu(II) is suggested [22].

3.2. *Magnetic data*

The magnetic moments obtained at room temperature are listed in table 1. The Co(II) complexes show magnetic moments in the range of 4.7–5.1 B.M., within the expected range of 4.7–5.2 B.M. [25, 26] for octahedral complexes. The Ni(II) complexes show magnetic moments in the range of 2.81–3.26 B.M. within range of 2.5–3.5 B.M. for octahedral Ni(II) complexes [26, 27]. The magnetic moments of Cu(II) complexes fall in the range 1.63–1.68 B.M. corresponding to one unpaired electron with a slight orbital contribution to the spin only value and the absence of spin–spin interactions.

3.3. *Infrared spectra*

Infrared spectral data of the ligands and their metal complexes are listed in Supplemental material. A high-intensity band at 1610 cm^{-1} for the Schiff bases is

Table 1. Analytical, magnetic, and conductance data of the quinoline derivatives and their transition metal complexes.

Code	Empirical formula	C% Calcd (Found)	H% Calcd (Found)	N% Calcd (Found)	S% Calcd (Found)	Cl% Calcd (Found)	M% Calcd (Found)	Molar condt. $\Omega^{-1}\,cm^{-2}mol^{-1}$	μ_{eff} (B.M.)
PQT	$C_{16}H_{12}NS$	72.48 (72.73)	4.43 (4.55)	10.23 (10.61)	11.98 (12.12)	–	–		–
1	$[Co(PQT)_2(H_2O)_2]$	61.17 (61.64)	3.94 (4.17)	8.64 (8.98)	10.01 (10.27)	–	9.21 (9.46)	8.31	5.08
2	$[Ni(PQT)_2(H_2O)_2]$	61.41 (61.67)	4.02 (4.18)	8.78 (8.99)	10.09 (10.28)	–	9.31 (9.43)	6.08	3.08
3	$[Cu(PQT)_2(H_2O)_2]$	61.04 (61.67)	3.89 (4.14)	8.77 (8.92)	10.03 (10.20)	–	9.88 (10.13)	8.12	1.84
4	$[Zn(PQT)_2(H_2O)_2]$	60.87 (61.01)	3.89 (4.13)	8.72 (8.90)	9.76 (10.17)	–	10.19 (10.4)	7.17	Dia
CPQT	$C_{16}H_{11}NSCl$	63.88 (64.12)	3.92 (4.01)	9.11 (9.38)	10.43 (10.72)	11.67 (11.88)	–	–	–
5	$[Co(CPQT)_2(H_2O)_2]$	55.34 (55.67)	3.19 (3.48)	7.96 (8.12)	9.03 (9.28)	10.02 (10.28)	8.27 (8.54)	7.42	4.74
6	$[Ni(CPQT)_2(H_2O)_2]$	55.38 (55.52)	3.31 (3.47)	7.87 (8.10)	9.06 (9.25)	10.05 (10.25)	8.13 (8.49)	6.33	3.26
7	$[Cu(CPQT)_2(H_2O)_2]$	54.94 (55.14)	3.19 (3.45)	7.81 (8.04)	8.93 (9.19)	9.89 (10.18)	8.86 (9.12)	7.31	1.69
8	$[Zn(CPQT)_2(H_2O)_2]$	59.98 (60.22)	4.79 (5.02)	7.73 (7.81)	7.73 (7.81)	7.73 (7.81)	9.09 (9.11)	7.92	Dia
BPQT	$C_{17}H_{12}NO_2S$	66.06 (66.23)	3.56 (3.89)	8.83 (9.09)	10.07 (10.39)	–	–	–	–
9	$[Co(BPQT)_2(H_2O)_2]$	57.24 (57.55)	3.48 (3.67)	7.63 (7.89)	8.91 (9.03)	–	8.02 (8.31)	8.23	4.86
10	$[Ni(BPQT)_2(H_2O)_2]$	57.19 (57.57)	3.29 (3.67)	7.56 (7.90)	8.79 (9.03)	–	8.06 (8.28)	9.37	2.81
11	$[Cu(BPQT)_2(H_2O)_2]$	56.85 (57.18)	3.28 (3.64)	7.52 (7.85)	8.61 (8.97)	–	8.59 (8.90)	13.89	2.03
12	$[Zn(BPQT)_2(H_2O)_2]$	56.13 (56.40)	3.74 (3.87)	7.70 (7.74)	7.70 (7.74)	–	8.99 (9.04)	14.28	Dia

attributed to the ν(C=N) vibration [28], proof for the formation of Schiff base. Low intensity bands in the region of 700–600 cm^{-1} are assignable to formation of C–S bonds and absorption bands between 2000 and 2500 cm^{-1} indicate S–H bonding [29]. Medium intensity bands in the 1600–1590 cm^{-1} region are regarded as a combination of C=N and C=C stretching vibrations of the aromatic ring. A high-intensity band at 1700–1730 cm^{-1} was assigned to $\nu_{C=O}$(lactone carbonyl) of the COOH group with an additional band around 3100 cm^{-1} for $\nu_{(O-H)}$ of the carboxylic group in **BPQT**.

For the above said complexes we observed the following changes. The medium intensity band around 1610 cm^{-1} due to ν(C=N) in the Schiff bases shifted to 1590–1600 cm^{-1} in the complexes, indicating the azomethine coordinates to the metal through nitrogen. The position of the low intensity band due to C–S in the region 700–600 cm^{-1} is unaltered. Absorption bands between 2000 and 2500 cm^{-1} indicating the S–H bonding in the Schiff bases disappear and a medium to high intensity band in the 350–380 cm^{-1} region in the complexes supports formation of M–S bonds via deprotonation [30]. In addition, the complexes exhibit a broad band at *ca* 3400 cm^{-1}; attributed to symmetric and antisymmetric –OH stretching modes. There was also a medium to high intensity band around 850 cm^{-1} and each of these bands was assigned to coordinated water. The important features of the infrared spectra of all the complexes are the appearance of two strong bands at 350–380 cm^{-1} region are assignable to ν(M–S) and in the region 420–470 cm^{-1} to ν(M–N) vibrations, supporting the coordination of the ligands as bidentate NS chelating agents [30–32].

3.4. ^{1}H-NMR spectra

The Schiff bases exhibit the characteristic resonance at 8.17 ppm due to the azomethine proton. A singlet corresponding to one proton observed at 6.5 ppm is probably due to mercapto (SH). Hydrogen bonding leads to deshielding and increase in frequency of the hydrogen bonded proton. Sharp multiplets of the phenyl protons are found in the region 6.4–7.6 ppm. The peak due to SH at 6.5 ppm in the ligands was not observed in

Table 2. Electronic spectral data of octahedral Co(II) complexes (in DMF solution).

Complex	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_2 (cal) (cm^{-1})	Dq (cm^{-1})	B' (cm^{-1})	β	ν_2/ν_1	LFSE (Kcal mol^{-1})
1	9348	–	19,418	20,088	1083.7	759.3	0.773	2.14	25.03
5	9412	–	19,627	20,304	1091.0	719.1	0.725	2.16	24.86
9	9824	–	19,572	20,247	1087.8	764.0	0.789	2.06	26.08

Free ion value for Co(II) = 971 cm^{-1}; LFSE = 12 Dq.

Table 3. Electronic spectral data of Ni(II) complexes in DMF solution.

Complex	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	Dq (cm^{-1})	*B*' (cm^{-1})	ö	$\nu_2/$ö§$_1$	LFSE (Kcal mol)
2	10,487	17,534	25,502	1067.9	720.9	0.68	1.67	36.48
6	10,546	17,716	24,981	1076.2	694.9	0.65	1.68	36.64
10	10,683	17,647	25,118	1075.4	708.2	0.71	1.66	36.89

Free ion value for Ni(II) = 1041 cm^{-1}; LFSE = 12 Dq.

the Zn(II) complexes, confirming sulfur coordination with the metal. The downfield shift of the methine proton from 8.70 ppm in the ligand spectrum to 9.2 ppm in the complexes indicated participation of azomethine nitrogen in the coordination [33].

3.5. *ESR spectra*

The EPR spectra of the Cu(II) complexes were recorded on a Variant E-4′, X-band ESR spectrometer using cylindrical quartz sample tube at room temperature. Polycrystalline diphenylpicrylhadrazyl (DPPH) was used as "*g*" marker. The ESR spectrum of one representative Cu(II) complex (**7**) was recorded at room temperature (300 K) and at liquid nitrogen temperature (77 K), exhibiting unresolved broad signals giving only one *g* value, i.e. g_{iso} (g_{iso} at 300 K is 2.094 and that at 77 K is 2.114, respectively). The shape of ESR (Supplemental material) indicates that the complexes may have distorted octahedral geometry [34].

3.6. *FAB-mass spectrum*

The FAB spectrum of a representative Co(II) complex (**1**) showed a molecular ion peak M^+ at m/z 623 which is equivalent to its molecular weight $[Co(PQT)_2(H_2O)_2]^+$. The loss of two waters gave a fragment ion $[Co(PQT)_2]^+$ at m/z 587. The fragmentation patterns are observed in the FAB mass spectrum (Supplemental material).

3.7. *Fluorescence spectra*

The emission spectra of the Schiff base (BPQT) and its Ni(II), Cu(II), and Zn(II) complexes (figure 2 and Supplemental material) have been investigated in different solvents. The Co(II) complexes do not show promising effects. In DMF the Schiff base

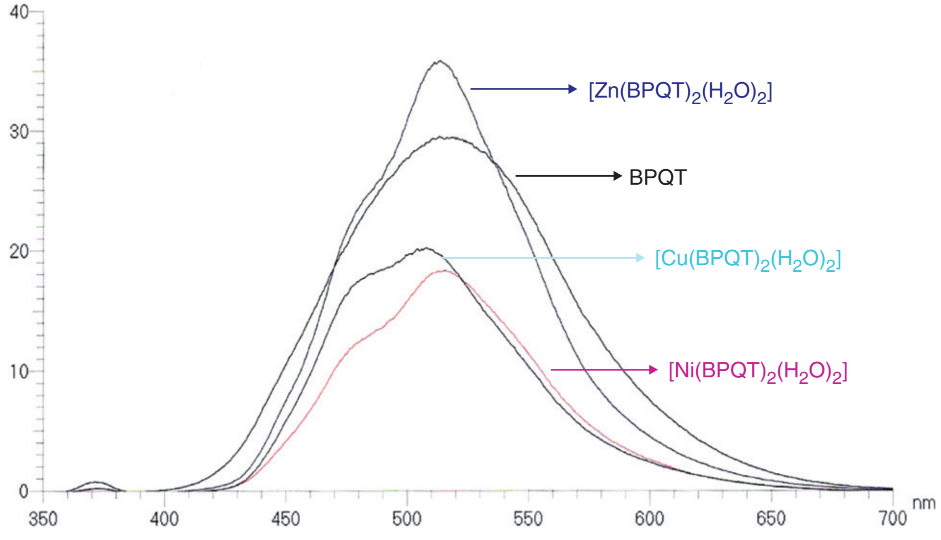

Figure 2. Fluorescence spectrum of the ligand (BPQT) and its Cu(II), Ni(II), and Zn(II) complexes.

was characterized by a broad emission band *ca* 516 nm (EX-370 nm) and the Cu(II) and Ni(II) complexes *ca* 508 and 513 nm [35]. The ligand has emission at 516 nm showing a Stoke shift of 146 nm. Quenching has been found in Ni(II) and Cu(II) complexes. The Zn(II) complex shows enhanced emission at 519 nm with a Stoke shift of 149 nm, indicating that the Zn(II) complexes may be employed as sensors [36].

3.8. *Thermogravimetric study*

In the present investigation TGA and DTG studies of Co(II), Ni(II), Cu(II), and Zn(II) complexes have been carried out in static air at a limiting temperature of 1000°C using the heating rate of $10^\circ\mathrm{C\,min^{-1}}$ (table 4). The spectrum of one representative Ni(II) complex (**2**) is presented in Supplemental material with the proposed chemical change with temperature range and percentage of metal for the Co(II), Ni(II), Cu(II), and Zn(II) complexes. The results are in good agreement with the proposed chemical formula. The decomposition of the complex proceeds with an endothermic peak at 115°C indicating loss of $2H_2O$. In the second temperature range *ca* 303°C the phenyl decomposes. In the third stage at the temperature range *ca* 357°C the 2-mercaptoquinoline decomposes. The final material is metal oxide.

3.9. *Cyclic voltammetry*

Cyclic voltammetry studies of Schiff base and its Cu(II) complex (**3**) were studied at room temperature in DMF solution. Complexes of Co(II), Ni(II), and Zn(II) were redox inactive. In the Cyclic voltammetry (CV) spectrum of Schiff base a sharp irreversible peak (single electron transfer) at −1.24 was observed. Thus, the Schiff base shows reduction and there was no response for oxidation [37].

Complex **3** was studied from the negative to positive scale exhibiting a redox process corresponding to the Cu(II) → Cu(I) at cathodic peak $E_{\mathrm{pe}} = -0.5\,\mathrm{V}$ and an associated cathodic peak corresponding to the Cu(I) → Cu(0) at $E_{\mathrm{pe}} = +1.24\,\mathrm{V}$. As Cu was present in elemental state it had no reversible peak. Further, there was an oxidation peak corresponding to the Cu(I) → Cu(II) at $E_{\mathrm{pa}} = -1.4\,\mathrm{V}$. This couple of −0.5 and −1.4 V was quasi-reversible as the peak separation between the anodic and cathodic potential was high [38, 39], but the ratio between the anodic and cathodic currents indicated a simple one-electron transfer, quasi-reversible process [40]. The cyclic voltammetry is provided in Supplemental material.

Table 4. Thermal data of complexes.

Complex	Temp. (°C)	% Weight loss	Proposed chemical change	Metal %
3	105	5.84 (5.61)	Water molecules	
	239	18.61 (18.84)	Phenyl moiety	25.04 (25.21)
	317	50.11 (50.34)	Quinoline moiety	
5	105	4.42 (4.63)	Water molecules	
	239	19.87 (20.18)	Phenyl moiety	24.09 (24.27)
	317	52.74 (50.92)	Quinoline moiety	
10	105	5.32 (5.48)	Water molecules	
	239	23.47 (23.63)	Phenyl moiety	24.58 (24.79)
	317	45.73 (46.06)	Quinoline moiety	

3.10. *Biological studies*

3.10.1. Antibacterial and antifungal activities. The antibacterial activity of the ligands and their Co(II), Ni(II), Cu(II), and Zn(II) metal complexes were assayed against *Escherichia coli* and *Bacillus cirroglagellous* by Minimum Inhibitory Concentration (MIC) [41, 42] method with three different concentrations of 100, 50, and 25 µg. Similar procedure was followed for the antifungal activity of the above said ligands and metal complexes against two fungi, namely *Aspergillus niger* and *Candida albicans*. The activity was also assayed for the pure solvent DMF and the standard Gentamycine for each of antibacterial and Flucanazole for antifungal cultures. Final adjustments were made using optical density measurement for bacteria (absorbance 0.05 at 580 nm).

The zone of inhibition in millimeter for the ligands and their Co(II), Ni(II), Cu(II), and Zn(II) complexes are presented in table 5. From the data of metal complexes it is clear that the metal chelates exhibit higher antimicrobial activity than that of the free ligand molecules. Cu(II) complexes were good antibacterial agents.

The ligands and metal complexes are more susceptible toward bacterial cells than fungicidal cells. Thus, it can be concluded that although these compounds are not good fungicides yet may serve as bactericides.

3.10.2. Cytotoxicity bioassay (*in-vitro* studies). In the present study brine shrimp (*Artemia salina* L.) eggs were hatched in a shallow rectangular plastic dish (22 × 32 cm), filled with artificial seawater, which was prepared [43] with commercial salt mixture and double distilled water. An unequal partition was made in the plastic dish with the help of a perforated device. About 50 mg of eggs were sprinkled approximately into the large compartment, which was darkened while the smaller compartment was opened to ordinary light. After 2 days, nauplii were collected by a pipette from the lighted side. By dissolving 20 mg of each compound in 2 mL DMF the samples were prepared. From the stock solutions, 500, 50, and 5 $\mu g\,mL^{-1}$ were transferred to vials [three for each dilution were used for each test sample and Lethal Dose (LD_{50}) was the mean of the three values]; one vial was used to as a control with only 2 mL DMF and another with the above concentrations of *Bleomycin* as a standard. The solvent was allowed to evaporate overnight. After 2 days, when shrimp larvae were ready, 1 mL of seawater and 10 shrimps were added to each vial (25 shrimps per dilution) and the volume was adjusted with seawater to 5 mL per vial. After 24 h, the numbers of survivors were counted. Data were analyzed by Finney computer program to determine the Lethal Dose for 50% killing of organisms (LD_{50}) values [44].

The data recorded (Supplemental material) show that only four compounds (**3**, **4**, **8**, and **12**) have cytotoxic activity as $LD = 6.134 \times 10^{-4}$, 7.089×10^{-4}, 6.109×10^{-4}, and $7.848 \times 10^{-4}\,\mu\,mL^{-1}$, respectively, against *A. salina* while the other compounds were almost inactive for this assay.

4. Conclusions

Due to insolubility in water and common organic solvents, all the complexes are thought to be polymeric in nature. The tentative structures of all the complexes are

Table 5. Antibacterial and antifungal activity of quinoline derivatives and their metal complexes (zone of inhibition in mm).

		Antifungal		Antibacterial	
Complex	Conc. ($\mu g\,L^{-1}$)	*Aspergillus niger*	*Candida albicans*	*Escherichia coli*	*Bacillus cirroglagellous*
PQT	100	17	16	19	18
	50	8	9	12	11
	25	3	2	7	6
1	100	20	19	22	23
	50	12	11	16	15
	25	5	4	9	10
2	100	19	18	22	21
	50	8	9	15	14
	25	–	1	8	7
3	100	21	22	26	25
	50	11	12	18	19
	25	5	6	11	12
4	100	18	17	20	19
	50	8	9	15	14
	25	–	1	8	7
CPQT	100	18	17	20	21
	50	10	9	13	15
	25	3	4	7	8
5	100	21	20	24	25
	50	14	12	15	17
	25	7	6	9	10
6	100	19	18	22	21
	50	8	9	15	14
	25	–	1	8	7
7	100	23	24	27	28
	50	14	13	19	20
	25	7	8	10	11
8	100	20	18	22	23
	50	11	8	14	15
	25	2	2	8	9
BPQT	100	14	15	17	16
	50	8	6	9	10
	25	–	–	2	1
9	100	20	19	22	24
	50	12	10	10	14
	25	4	2	3	6
10	100	17	16	20	19
	50	6	7	11	10
	25	–	–	1	–
11	100	20	21	24	26
	50	10	12	16	18
	25	4	5	7	8
12	100	16	15	19	20
	50	7	6	8	10
	25	–	–	2	–
Gentamycine	100	–	–	28	28
	50	–	–	21	21
	25	–	–	13	13
Flucanazole	100	22	22	–	–
	50	14	14	–	–
	25	7	7	–	–
DMF	100	12	12	12	12
	50	6	6	6	6
	25	2	2	2	2

Key to interpretation (for $100\,\mu g\,L^{-1}$): less than 10 mm – inactive; less than 10–15 mm – weakly active; less than 15–20 mm – moderately active; more than 20 mm – highly active.

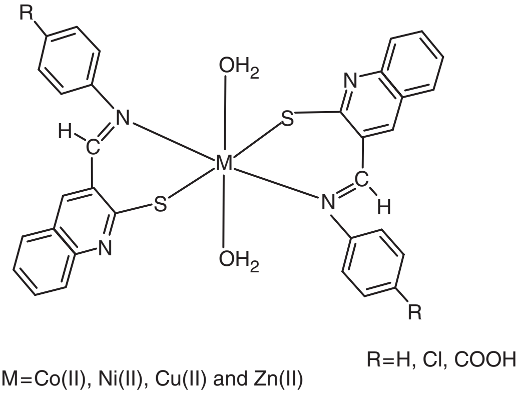

Figure 3. Proposed structure of the complexes.

based on elemental analysis, IR, ^{1}H NMR, electronic, magnetic measurements, thermal studies, and FAB-mass spectra (figure 3).

Copper compounds were most active toward the bactericidal activity at lower MIC concentrations. The cytotoxicity of **3**, **4**, **8**, and **12** indicate potent cytotoxic agents that might become potent anticancer agent in clinical trials. The lower LD_{50} values can trigger a new branch in coordination chemistry with the same compound acting as an anticancer agent and being a fluorescent probe to trace the path for cancer activity.

Excellent fluorescence properties exhibited by the Zn(II) chelates may offer wide applicability as fluorescent probes, labeling compounds, fluorescent markers with high resistance, sensor devices, binding studies, and in various fields of biochemistry and medicine.

Efforts are under continuous progress to synthesize, characterize, and evaluate the inner-transition complexes with the above ligands and find their applicability into various analytical and spectroscopical techniques.

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