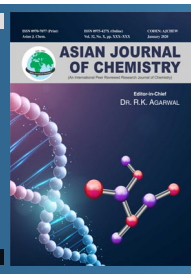
Asian Journal of Chemistry; Vol. 32, No. 4 (2020), 759-764

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2020.22391



# Synthesis, Structural Investigations and Antimicrobial Activities of Homo Binuclear Complexes Derived from 2-Amino-4-chlorophenol

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*Received*: 10 August 2019; *Accepted*: 28 October 2019; *Published online*: 25 February 2020; AJC-19788

Co(II), Ni(II) and Cu(II) homo binuclear Schiff base metal complexes were synthesized from terephthalaldehyde and 2-amino-4-chlorophenol in methanol using template method. The structure of the ligand and its metal complexes were established by elemental, molar conductance, UV, magnetic moment, IR, $^{1}H$ & $^{13}C$ NMR, EPR, mass, thermal and PXRD. Molar conductance values showed that all complexes were non-electrolytic in nature. The IR spectral data provides the coordination of azomethine nitrogen and oxygen with central metal ion. UV, ESR and magnetic moment values suggest square planar geometry for Co(II), Ni(II) and Cu(II) complexes. TGA and DSC analysis data show the thermal stability of the ligand and its metal complexes. The crystalline nature of ligand and its metal complexes were investigated by powder-XRD. The DNA cleavage activities of all the complexes assayed on PUC18 DNA shows nuclease ability.

**Keywords: Homo binuclear complexes, Terephthalaldehyde, 2-Amino-4-chlorophenol, Antimicrobial activity, DNA cleavage.**

## INTRODUCTION

Schiff bases are useful chelating ligands in organometallic chemistry and first described by Hugo Schiff during 19th century [1,2]. Schiff base consists of azomethine and azo groups, metal complexation alters the therapeutic efficiency of azo-linked ligands, the treatment of infections is challenged by multidrug resistance in pathogenic organisms and oxidative stress, so the development of newer Schiff base compounds for the management of infections and oxidative stress is warranted [3]. A large number of Schiff base and their metal complexes have been discovered to possess useful pharmaceutical activity due to their great flexibility and diverse geometrical aspects [4]. The metal complexes are used to cleavage agent for DNA and they can cleave the DNA through three types of mechanisms *i.e.*, hydrolytic, oxidative and photolytic cleavage [5]. The condensation reaction between one mole of an aldehyde with two mole of primary amines to give the yield of symmetrical diazomethine (~N=HC-Ar-CH=N~), symmetric diimine of tetradentate Schiff bease was prepared to directly condensation of amines and aldehyde, but asymmetric diimine groups are cannot be synthesized directly [6]. Tetra- and polydentate Schiff bases having electron donor atoms of nitrogen and oxygen in their structure act as chelating agents for the non-transition and transition metal ions and it forms a stable complexes with transition metal(II) ions [7]. Several reports have showed that Schiff bases with low (or) no biological ability became more activity upon binding with Co(II), Ni(II) and Cu(II) metal ions [8]. Recently, hydroxyl substituted Schiff base have received considerable attention due to good anti-cancer ability [9]. The symmetric diimines and their metal complexes have high biological applications for antimicrobial and antitumour activity [10]. In published review reports, 2-aminophenol and its derivative compounds give the tetradentate Schiff base product with carbonyl group and it has more biological activities of medicinal fields [11]. Schiff base compounds have shown a wide range of medicinal activities of antimalarial, antiviral, antioxidant, antipyretic and antiproliferative [12-16]. Macrocyclic complexes are very good effort for enzyme catalysis and organic synthesis [17,18]. Binuclear metal complexes have various applications in biological systems, clinical, dyes and pigments for analytical, polymers, medicines such as antibiotics, anti-inflammatory agents and in pharmaceutical fields [19-26]. The symmetric azomethine compounds and its transition metal(II)

complexes play important roles in protein synthesis, nitrogen fixation, inhibition of DNA & RNA and photodynamic therapy of cancer [27-29].

The present work deals with the synthesis, characterization and biological investigations of homo binuclear Co(II), Ni(II) and Cu(II) complexes with the synthesized Schiff base having $N_2O_2$ donor atoms derived from terephthalaldehyde with 2-amino-4-chlorophenol. The antimicrobial and DNA cleavage activity for ligand and all the homo binuclear complexes were also studied.

## EXPERIMENTAL

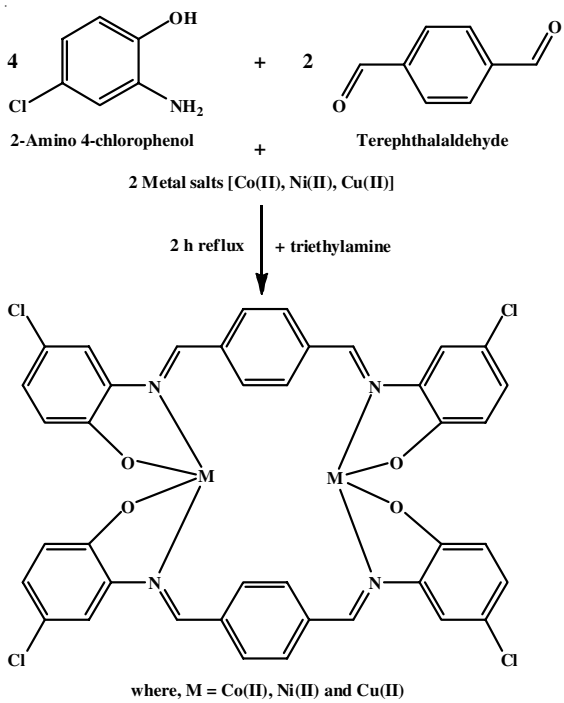
Terephthalaldehyde, 2-amino-4-chlorophenol and metal(II) salts of AR grade were received from Sigma-Aldrich. Ethanol, methanol, DMSO, DMF and diethyl ether were purchased from Merck, Loba chemicals and were purified by standard procedure [30].

Elemental analysis was determined on a Thermo-Finningan Flash EA 1112 series elemental analyzer. The molar conductance of the complexes in DMF solution was measured by Elico CM 180 conductivity bridge. Magnetic moment studies were recorded using Gouy balance calibrated with $Hg[Co(SCN)_4]$ method. The UV-visible spectra was measured using Perkin Elmer Lambda -25 spectrophotometer. IR spectra was obtained on a Shimadzu FT-IR-8300 spectrometer using KBr pellet technique. $^1H$ and $^{13}C$ NMR was recorded on a Bruker Advanced III 400 MHz spectrometer with TMS as an internal standard. EPR spectra was recorded on JES-FA200 ESR spectrometer with X-band microwave frequencies. Powder X-ray diffraction was obtained on Perkin Elmer TA/SDT-2960 and Philips 3701 instrument.TGA/DSC studies were carried out in 0-1000 ºC range using an SDT Q600 V20.9 Build 20 thermal analyzer. ESI-Mass spectra were measured on a Perkin-Elmer R MU-6E instrument.

**Synthesis of Schiff base (2,2′((1*E*,1′E)(1,4-phenylene-*bis*(methanylidene))*bis*(azanylidine))*bis*(4-chlorophenol)):** Tetradentate Schiff base ligand was synthesized from the mixture of terephthalaldehyde (1 mmol) with 2-amino-4-chlorophenol dissolved in methanol. The mixture was kept under stirring for 2 h. The resulting yellow solid obtained was separated by filtration, washed and purified by methanol. The ligand was recrystallized from ethanol.

**Synthesis of binuclear metal complexes:** The binuclear metal complexes were synthesized using template method. A methanolic solution of terephthalaldehyde (2 mmol) with 2-amino-4-chlorophenol (4 mmol) were added to the corresponding metal(II) salts (2 mmol) dissolved in methanol [31]. The mixture was stirred, followed by the addition of few drops of triethylamine. After complete addition, the mixture was stirred for 1 h and under reflux for 3 h. The resultant hot solution was partly evaporated and cooled to room temperature. The complexes obtained was separated, washed with methanol, diethyl ether and dried in vacuum (**Scheme-I**).

**Antimicrobial activity:** The *in vitro* antibacterial and antifungal assay were performed by agar-well diffusion method. The Schiff base ligand and their metal complexes were tested against bacteria *S. aureus*, *B. subtilis* (Gram-positive), *S. typhi*, *E. coli* (Gram-negative) and fungi *Candida albicans*, *Fusarium*




**Scheme-I:** Structure of metal complexes

spp. tetracycline, kanamycin were used as standard drugs for antibacterial and antifungal studies. The ligand and its metal complexes were dissolved in DMSO. All the microbial cultures were maintained at 4 ºC nutrient agar-well plates. A 100 µL concentration of culture supernatant was placed on well plate and then it was incubated at 37 ºC for 24 h.

**Gel electrophoresis:** DNA cleavage activity of complexes was studied using pUC18DNA in the presence of $H_2O_2$ by agarose electrophoresis method, in a medium of 40 µM pUC18-DNA, 50 µM metal complexes and $H_2O_2$ in tris-HCl buffer (pH 7.2) for 2 h. A mixture of plasmid pUC18DNA and the synthesized complexes were incubated at 37 ºC for 2 h. After incubation, electrophoresis was carried out at 50 V for 2 h in tris-acetic acid-EDTA buffer (pH 7.2). Agarose gel was stained using 1 µg $cm^{-3}$ ethidium bromide and cleaved DNA bands were visualized by UV light at 360 nm.

## RESULTS AND DISCUSSION

The synthesized Schiff base ligand and its binuclear metal complexes were characterized by various physico-chemical techniques. The Schiff base ligand and its binuclear metal complexes are soluble in DMF and DMSO and partially soluble in methanol and ethanol. The composition of C, H and N are analyzed by using elemental analyzer. The results of elemental analysis data (Table-1) agreed well with the proposed formula $[M_2L_2]$.

**Molar conductivity measurements:** The molar conductance of all the metal complexes in DMF solution ($10^{-3}$ M) measured at room temperature shows low conductance values (10.3 Ω to 13.7 Ω), which indicates that all the complexes are non-electrolytic in nature [32,33].

**Electronic spectra and magnetic moment:** The electronic absorption spectrum ranges between 200-800 nm and absorption bands were measured in DMSO at room temperature.

TABLE-1
PHYSICO-CHEMICAL DATA OF SCHIFF BASE LIGAND AND ITS BINUCLEAR METAL(II) COMPLEXES

| Compd. | m.f. | Colour | m.w. | Yield (%) | m.p. (°C) | Elemental analysis (%): Found (calcd.) | | | | Molar cond. ($\Omega^{-1}$ $cm^2$ $mol^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N | M | |
| $H_2L$ | $C_{20}H_{14}N_2O_2Cl_2$ | Yellow | 385.24 | 80 | 220 | 61.34 (62.35) | 3.22 (3.66) | 7.10 (7.27) | – | – |
| $Co_2L_2$ | $C_{44}H_{36}N_4O_4Cl_4Co_2$ | Black red | 944.02 | 76 | >300 | 55.63 (55.95) | 3.73 (3.84) | 5.91 (5.93) | 12.44 (12.48) | 10.3 |
| $Ni_2L_2$ | $C_{44}H_{36}N_4O_4Cl_4Ni_2$ | Brown | 943.98 | 70 | >300 | 55.70 (55.98) | 3.40 (3.83) | 5.89 (5.94) | 12.42 (12.44) | 11.6 |
| $Cu_2L_2$ | $C_{44}H_{36}N_4O_4Cl_4Cu_2$ | Black | 953.69 | 75 | >300 | 55.01 (55.41) | 3.33 (3.80) | 5.83 (5.87) | 13.32 (13.33) | 13.7 |

The spectrum of free tetradentate ligand shows two bands at 299 and 388 nm assigned to $\pi\rightarrow\pi^*$ transition of the aromatic benzene ring and $n\rightarrow\pi^*$ transition of the azomethine groups (C=N) [34].

The spectrum of binuclear $[Co_2L_2]$ complex displays two new bands at 476 and 566 nm are attributed to the L→M charge transfer and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions for each Co(II) in square planar geometry. The magnetic moment for Co(II) is 1.80 B.M. [35]. The electronic spectrum of $[Ni_2L_2]$ complex shows peaks at 479 and 614 nm, which may be referred to ligand to metal charge transfer and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions. This transition supports square planar geometry around each Ni(II) ions. The Ni(II) complex have $\mu_{eff}$ value zero, because Ni(II) complex is diamagnetic in nature [36].

The electronic absorption spectrum of homobinuclear Cu(II) complex exhibits broad bands at 439 and 584 nm, which are due to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, respectively in the square planar geometry. The observed magnetic moment value is 1.76 B.M. The magnetic moment and *d-d* band strongly favours the square planar environment around the Cu(II) ion [37].

**Infrared analysis:** An intense band in the region 1557-1554 $cm^{-1}$ is attributed to the coordinated (-C=N), which is shifted to lower energy region from the free Schiff base ligand at 1621 $cm^{-1}$ to the metal complexes [38]. The sharp band around 3351 $cm^{-1}$ in the free Schiff base [39] is due to the phenolic -OH is absent in the metal complexes, which indicates the deproto-nation of the ligand. The absence of ν(C=O) signal at about 1700 $cm^{-1}$ confirms the ligand formation of azomethine (C=N). The key IR data values are summarized in Table-2.

TABLE-2
FT-IR DATA OF SCHIFF BASE LIGAND AND ITS BINUCLEAR METAL COMPLEXES

| Compd. | ν(OH) | ν(C=N) | ν(C–O) | ν(M–O) | ν(M–N) |
|---|---|---|---|---|---|
| L | 3351 | 1621 | 1281 | – | – |
| $Co_2L_2$ | – | 1557 | 1310 | 540 | 470 |
| $Ni_2L_2$ | – | 1554 | 1306 | 597 | 519 |
| $Cu_2L_2$ | – | 1567 | 1313 | 586 | 492 |

A new broad bands obtained at 597-540 and 519-470 $cm^{-1}$ in the vibration spectrum of complexes corresponds to the ν(M-O) and ν(M-N) vibrations, respectively. These bands indicates the coordination of the azomethine nitrogen and phenolic oxygens to the metal atom in the complex [40-42].

**$^1$H and $^{13}$C-NMR analysis:** $^1$H NMR spectrum results of 2,2′((1*E*,1′E)(1,4-phenylene*bis*(methanylidene))*bis*(azanylidine))*bis*(4-chlorophenol) were recorded at room temperature using DMSO-$d_6$ solvent. The peak at δ 8.8 ppm represents the presence of azomethine proton (CH=N), which confirms the formation of Schiff base ligand [43,44]. The signals observed at δ 9.4 ppm and δ 6.7-8.7 ppm are assigned to the phenolic -OH group and aromatic protons [45,46]. In $^{13}$C NMR spectra, the signal at δ 160 ppm is due to azomethine carbon (CH=N) group [47]. The peaks exhibited at δ 150, δ 143 and δ 143-113 ppm represents phenolic -OH carbon, substituted -Cl atoms by amino-phenol and aromatic carbon groups [48].

**ESR analysis:** At room temperature, ESR spectra of Cu(II) complex was obtained at X-band frequencies in the solid state. The complex exhibits an axial symmetry and the obtained spectra totally without resolved in their hyperfine components, because of the strong spin-spin interaction due to the more copper density [49]. The observed g values are $g_{\parallel} = 2.3408$ and $g_{\perp} = 2.0723$. The g values are related by $G = (g_{\parallel} - 2)/(g_{\perp} - 2) = 4.0$. If $G > 4$, there is no exchange interaction between the copper centers, whereas if $G < 4$, a considerable interaction occurs in the solid complex. The G value of Cu(II) complex is found to be 4.71, where $g_{\parallel} > g_{\perp} > 2.0023$, showing $d_{x^2-y^2}$ ground state for square planar geometry of Cu(II) complexes [50,51]. The EPR spectra of the ligand and its Cu(II) complex are shown in Fig. 1.

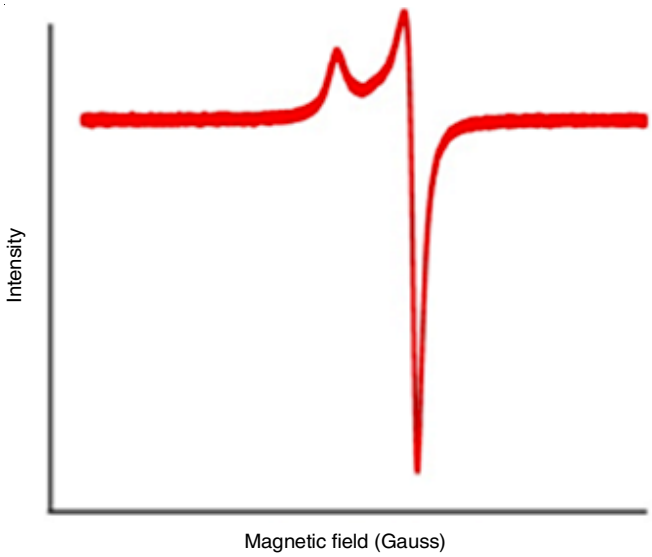



Fig. 1. ESR spectrum of Cu(II) complex

**Mass analysis:** The mass spectra of Schiff base and its Cu(II) complex were recorded using Electro spray technique. The ESI spectrum of ligand and its copper(II) complex were observed and is in good agreement with their suggested stoichiometric structure [52,53]. The resulting spectra displayed the molecular ion ($M^+$) peaks at *m/z* 385 and *m/z* 953 confirming their formula weights for ligand $[C_{20}H_{14}Cl_2N_2O_2]$ and its Cu(II) complex $[C_{44}H_{36}Cl_4Cu_2N_4O_4]$, respectively. Furthermore, frag-

mentation peaks of ligand and its copper complex exhibited at *m/z* (313, 295, 277, 129) and *m/z* (811, 742, 592, 529, 315, 222, 129), respectively.

**Thermal analysis:** The DSC/TGA analysis of ligand and its complexes were studied in the temperature range between 0 to 1000 ºC under air atmosphere. Thermal analysis of ligand and its metal(II) complexes showed that the decomposition is occured in a three steps elimination process and the formation of metal oxide residue in final stage for the complexes (Fig. 2) [54-56].

Thermal decomposition of the ligand occured at 50-270 ºC, 270-416 ºC and 416-850 ºC for TGA and exo (60-280 ºC), endo (280-425 ºC) and in DSC, exo (425-800 ºC) peaks are due to the elimination of two chlorine atoms attached in aminophenol, loss of amino phenolic group and loss of terephthalaldehyde group, respectively.

The TG curve of cobalt(II) complex indicates that decomposition at 20-104 ºC, 104-432 ºC and above 750 ºC for TG analysis and in DSC, exo (25-110 ºC), endo (110-450 ºC) and exo (450-800 ºC) peaks were assigned to the loss of four Cl atoms by aminophenol, partial decomposition and complete decomposition of the complex leading to the formation of cobalt oxide residue.

Similarly, thermogram for Ni(II) complex showed that the decomposition temperature ranges are 97-217 ºC, 217-666 ºC and above 750 ºC for TGA and in DSC, exo (100-230 ºC), endo (230-670 ºC) and endo (670-800 ºC) peaks are attributed to the elimination of four chlorine atoms of aminophenol moiety, complex was decomposed partially and the NiO formed after complete decomposition of the complex.

Thermogram of Cu(II) complex showed the peaks in the range 86-262 ºC, 262-592 ºC and above 750 ºC for TG analysis and in DSC analysis, exo (90-270 ºC), exo (270-590 ºC) and endo (590-850 ºC) peaks are referred to the removal of four molecule of substituted chlorine atoms by aminophenol, partly decomposition of copper(II) complex and the formation of CuO.

**X-ray diffraction analysis:** The structure of ligand and its binuclear Co(II), Ni(II) and Cu(II) complexes were evaluated using powder XRD method showed the amorphous nature of the compounds. Powder XRD patterns of metal complexes were investigated in the range 5-80º (2θ) at the X-ray wavelength of 1.5406 Å. The obtained peaks showed the crystalline nature of the synthesized metal(II) complexes. The PXRD patterns of metal complexes are shown in Fig. 3.

**Antimicrobial activity:** The ligand and its Cu(II), Ni(II), Co(II) complexes were evaluated against Gram-positive (*S. aureus*, *B. subtillis*), Gram-negative (*S. typhi*, *E. coli*) bacteria and tetracycline was used as standard. The antibacterial results indicate that the ligand do not have zone of inhibition while its metal(II) complexes has inhibition activity. Furthermore, macrocyclic Cu(II) complex shows the higher antibacterial activity than other Co(II)and Ni(II) complexes (Fig. 4).

Similarly, synthesized compounds were also tested against different types of fungi (*Candida albicans*, *Fusarium* spp.) and standard drug kanamycin was used. The results showed that the Schiff base ligand has no inhibition zone for fungi, while its transition metal(II) complexes exhibited the antifungal activity. The copper(II) complex revealed better antifungal assay against the tested microorganisms compared to other metal complexes (Fig. 4).

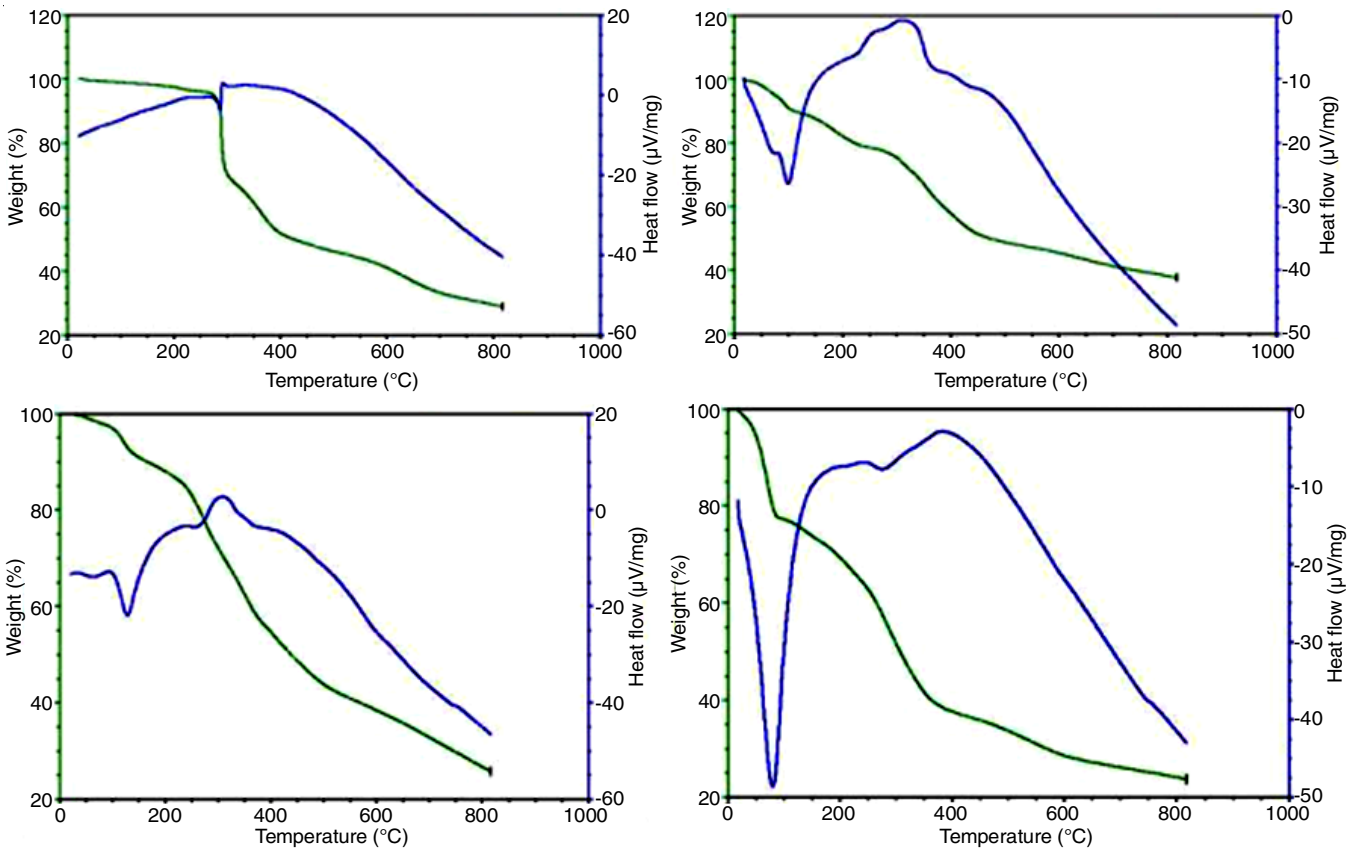



Fig. 2. TGA and DSC analysis curves of ligand and its metal complexes

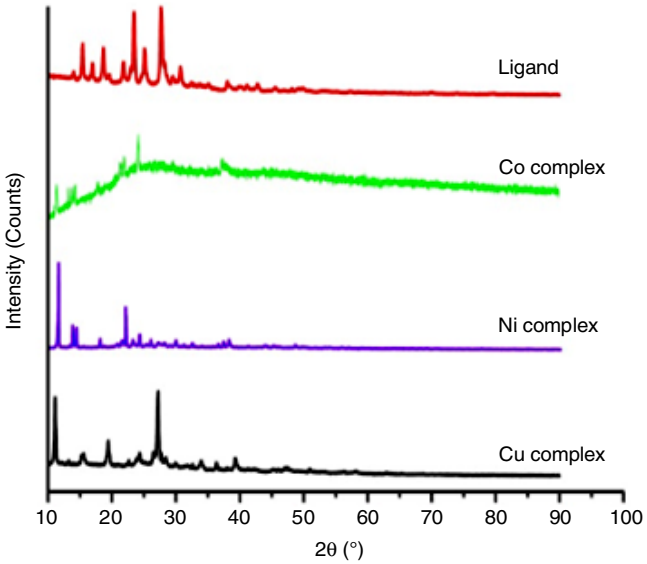



Fig. 3. Powder-XRD spectrum of ligand and their metal complexes

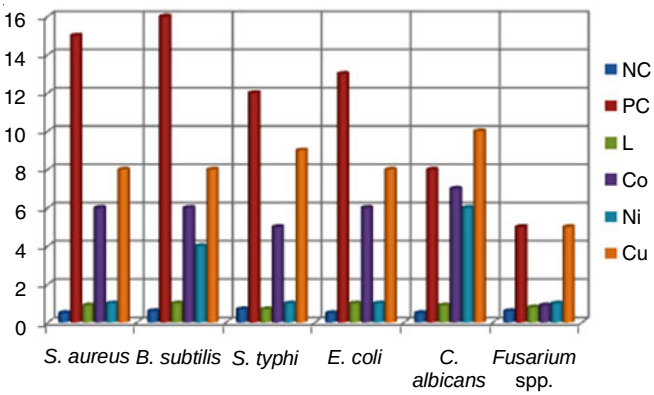
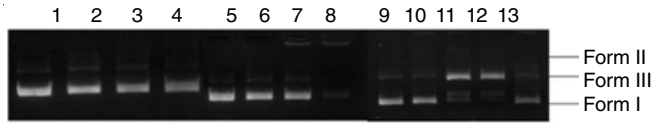



Fig. 4. Antimicrobial activity test for ligand and its metal complexes

**Chemical nuclease activity studies:** The activity of ligand and its Co(II), Ni(II) and Cu(II) binuclear complexes were tested to perform DNA cleavage in the presence of $H_2O_2$ by agarose gel-electrophoresis method using super coiled PUC18DNA in a medium of 50 µm tris-HCl/NaCl buffer solution (pH 7.2). The ligand and its metal(II) complexes exhibited substantiate DNA cleavage ability at higher concentrations.The DNA cleavage activity of ligand and its metal complexes were evaluated by their ability to convert super coiled circular form (I) of PUC18-DNA into nicked form (II) and linear form (III).

When PUC18DNA is conducted by electrophoresis, relatively the fastest migration will be observed for the super coiled circular form (form I). If cleavage occurs on one strand, the super coils relax to generate the slow moving open circular form (form II). If both form I and form II strands are cleaved, the linear form (form III) will be produced that migrates between form I and form II [57]. Fig. 5 shows the results of gel electrophoretic separations of complexes interaction with plasmid PUC18DNA in the presence of $H_2O_2$. All super coiled circular plasmid DNA form I was cleaved to mixture of form II and form III along with the addition of complex. This results revealed that the Co(II), Ni(II) and Cu(II) complexes induced intensively the cleavage of DNA in the presence of $H_2O_2$. This observation showed that all the synthesized metal(II) complexes effectively cleave plasmid DNA [58,59].




Lane 1,5,9 — PUC18 DNA — Control, Lane 2,6,10 — DNA + $H_2O_2$ (1 mM), Lane 3 — DNA + $H_2O_2$ (1 mM) + $Co_2LX_2$ complex (40 µM), Lane 4 — DNA + $H_2O_2$ (1 mM) + $Co_2LX_2$ (50 µM), Lane 7 — DNA + $H_2O_2$ (1 mM) + $Ni_2LX_2$ (40 µM), Lane 8 — DNA + $H_2O_2$ (1 mM) + $Ni_2LX_2$ (50 µM), Lane 11 — DNA + $H_2O_2$ (1 mM) + $Cu_2LX_2$ (40 µM), Lane 12 — DNA + $H_2O_2$ (1 mM) + $Cu_2LX_2$ (50 µM), Lane 13 — DNA + $H_2O_2$ (1 mM) + Ligand (50 µM)

Fig. 5. DNA cleavage activity of ligand and its metal complexes

## Conclusion

Homobinuclear complexes of Co(II), Ni(II) and Cu(II) of terephthalaldehyde and 2-amino-4-chlorophenol Schiff base were synthesized and characterized by spectroscopic methods. The structure of all the synthesized complexes assumes a square planar geometry in nature, which is confirmed by electronic spectra and magnetic moment values. The antimicrobial results showed that the metal(II) complexes have higher activity compared to the free Schiff base. DNA cleavage studies revealed that the complexes has good efficiency that cleaves the DNA molecules and has more potent scavenging activity than ligand.

## CONFLICT OF INTEREST

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

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