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SYNTHESIS, SPECTRAL, DNA CLEAVAGE AND ANTIMICROBIAL STUDIES OF HOMO TRINUCLEAR Cu (II), Ni (II) AND Mn (II) COMPLEXES

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ABSTRACT

The template synthesis of benzil, p-phenylenediamine and metal salt in 1 : 2 : 1 molar ratio yielded the mononuclear Schiff base complex with N_4 donors. The mononuclear complex has been used as a ligand, for further condensation of 2-aminobenzaldehyde and metal salts as a same kind, the stable homo trinuclear Cu (II), Ni (II) and Mn (II) Schiff base complexes were obtained. The characterization and nature of bonding of the trinuclear complexes have been deduced from elemental analysis, molar conductivity, FT-IR, UV-visible, magnetic and EPR studies. The pUC18 DNA gel electrophoresis experiment was conducted at room temperature using our synthesised trinuclear complexes in the presence of H_2O_2 as an oxidant. As can be seen from the results at high concentration, all the three homo trinuclear complexes exhibit nuclease activity. The *in vitro* biological screening effects of the investigated compounds were tested against the gram negative and gram positive bacteria by disc diffusion method. A comparative study of minimum inhibitory concentration values of the complexes indicate that the all trinuclear metal complexes exhibit higher antibacterial activity.

Key words: Schiff base, Trinuclear, DNA cleavage, Antimicrobial, 2-aminobenzaldehyde.

INTRODUCTION

Trinuclear transition Schiff base metal complexes bridged by polyatomic ligands have gained much attention in the recent years towards synthesis and characterization[1,2]. In particular, transition metal complexes have been the subject for thorough investigation because of their extensive applications in wide ranging areas from material science to biological sciences[3,4]. Metal complexes are well known to accelerate drug action and the efficiency of a therapeutic agent can often be enhanced upon coordination with a metal ion[5]. The pharmacological activity has been found to be highly dependent on the nature of the metal ion and the donor sequence of the ligands, with different complexes showing widely

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dissimilar biological properties, although they may vary only slightly in their molecular structure[6].

Identifying molecules that intercalate into DNA helices have attracted considerable interest over the last few decades. Intercalation was first proposed by Lerman and is defined as insertion between base pairs[7]. The cleavage of nucleic acids may be considered as an enzymatic reaction which comprises of various biological processes as well as the biotechnological manipulation of genetic material. The application of artificial DNA cleaving agents is manifold : biotechnology, structural studies of nucleic acids, or development of new drug[8-10]. Compounds showing the property of effective binding as well as cleaving double stranded DNA under physiological conditions are of importance since these could be used as diagnostic agents in medicinal and genomic research[11]. Noting the very sensitive nature of DNA towards oxidative cleavage, the majority of the studies on artificial DNA have been centered around molecules capable of cleaving DNA with an oxidative mechanism. Several efficient cleaving agents have been developed in course of time. These involve reactive oxygen species or free radicals that are able to induce an oxidative pathway. The antitumor antibiotic leinamycin and its analogues have been shown to play the role of chemical nuclease exhibiting reduction of molecular oxygen to form reactive hydroxyl species[12]. This paper reports the synthesis and characterization of three novel homotrinuclear Cu (II), Ni (II) and Mn (II) complexes by using benzil, p-phenylenediamine and 2-aminobenzaldehyde. We have also investigated the antimicrobial and DNA cleavage ability of all the homo trinuclear complexes.

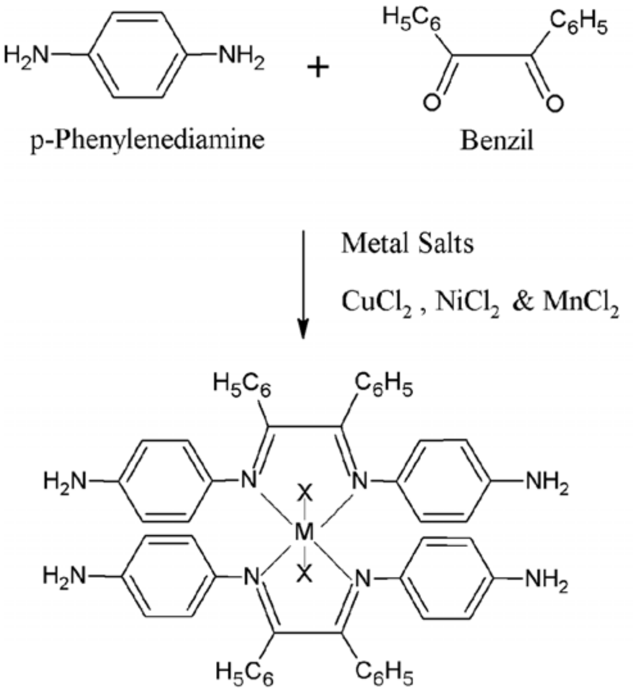
EXPERIMENTAL

Materials and physical measurements

$CuCl_2.2H_2O$, $NiCl_2.6H_2O$, $MnCl_2.4H_2O$, benzil and p-phenylenediamine were purchased from Loba chemicals. 2-aminobenzaldehyde was obtained from Aldrich. Ethanol, DMSO and DMF were used as solvents. The elemental analysis was performed using Carlo-Eraba 1106 instrument. Molar conductances of the complexes in DMF solution were measured with ELICO CM 185 conductivity bridge. The infrared spectra were recorded on the Perkin-Elmer FT-IR-8300 model spectrometer using KBr disc. Electronic absorption spectra in the UV-Visible range was recorded on Perkin-Elmer Lambda-25 between 200-800 nm by using DMF as the solvent. EPR spectra were recorded on a Varian JEOL-JES-TE100 ESR spectrophotometer at X-band microwave frequencies for powdered samples at room temperature. Magnetic susceptibility data were collected on powdered sample of the compounds at room temperature with PAR155 vibrating sample magnetometer.

Synthesis of mononuclear Cu (II) Schiff base metal complexes

An equimolar amount of the ethanolic (20 mL) solution of benzil and p-phenylenediamine was refluxed at 90°C for 2 hours. $CuCl_2$ (1 mmol) in ethanol (20 mL) were then added to the resulting solution and again refluxed for one hour (Fig. 1). The reaction mixture was cooled to room temperature, filtered and filtrate on slow evaporation yielded greenish brown coloured solid. The same procedure was adopted for the synthesis of mononuclear Ni (II) and Mn (II) complexes.

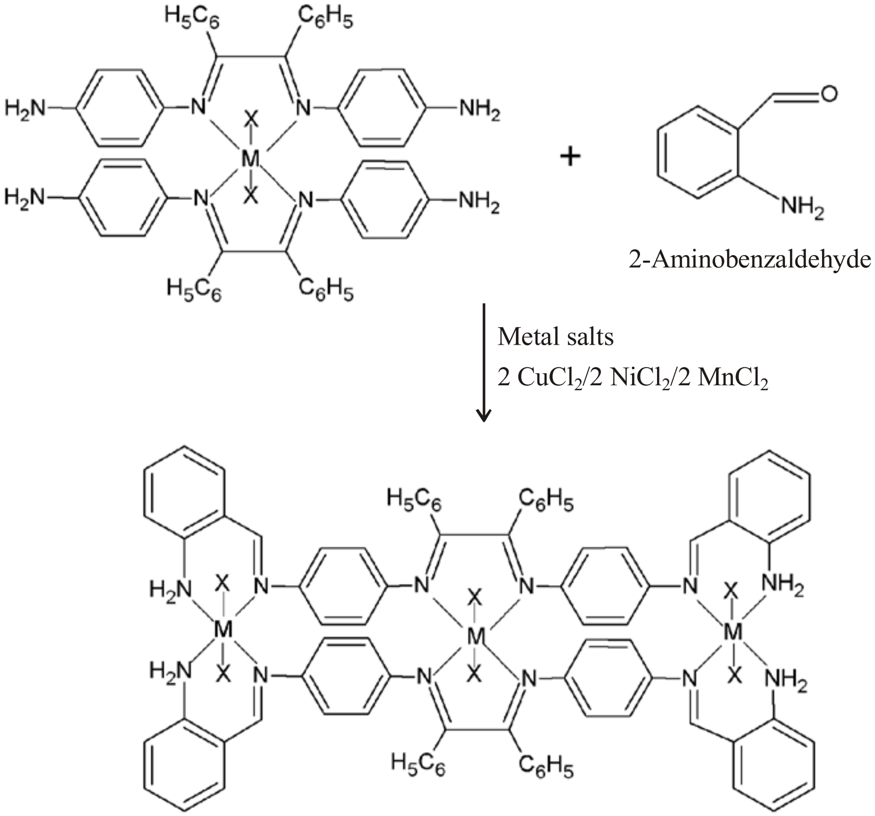


$M = Cu^{2+}, Ni^{2+}, Mn^{2+}$
$X = Cl^{-}$

Fig. 1: Synthesis of mononuclear Schiff base metal complexes

Synthesis of trinuclear Cu (II) Schiff base metal complexes

An hot ethanolic solution (20 mL) of bis-(p-phenylenediamine, benzil) metal (II) complexes (1 mmol) and 2-aminobenzaldehyde (4 mmol) in 1 : 4 molar ratio were refluxed for 2 hours and $CuCl_2$ (2 mmol) in ethanol (20 mL) were then added dropwise to the resulting solution. The contents were again refluxed for one hour. It was cooled to room temperature. The precipitate was obtained. It was filtered and dried over fused $CaCl_2$. The same procedure was adopted for the synthesis of another two trinuclear Ni (II) and Mn (II) complexes. The synthesis pathway is shown in Fig. 2.



M = Cu^{2+}, X = Cl^{-}
M = Ni^{2+}, X = Cl^{-}
M = Mn^{2+}, X = Cl^{-}

Fig. 2: Synthesis of trinuclear Schiff base metal complexes

Antimicrobial activity

The antibacterial activity of the complexes of Cu (II), Ni (II) and Mn (II) were checked by the disc diffusion technique. This was done on Gram negative bacteria like *Klebsiella pneumoniae, Escherichia coli and* Gram positive bacteria *Staphylococcus aureus* at 37°C. The disc of Whatmann No. 4 filter paper having the diameter 8.00 mm were soaked in the solution of compounds in DMSO (1.0 mg cm^{-3}). After drying, it was placed on nutrient agar plates. The inhibition areas were observed after 36 hours. DMSO was used as a control and streptomycin as a standard.

Gel electrophoresis

The cleavage of pUC18 DNA was determined by agarose gel electrophoresis. The gel electrophoresis experiments were performed by incubation of the samples containing 40 μM pUC18 DNA, 50 μM metal complexes and 50 μM H_2O_2 in tris-HCl buffer (pH 7.2) at 37°C for 2 h. After incubation, the samples were electrophoresed for 2 h at 50 V on 1% agarose gel using tris-acetic acid-EDTA buffer (pH 7.2). The gel was then stained using 1 μg cm^{-3} ethidium bromide (EB) and photographed under ultraviolet light at 360 nm. All the experiments were performed at room temperature.

RESULTS AND DISCUSSION

All the synthesised homotrinuclear Schiff base complexes are soluble in DMF and DMSO and slightly soluble in ethanol and dichloromethane. All the complexes are intensely coloured and stable at room temperature. Attempts to isolate crystals suitable for X-ray diffraction were unsuccessful. Therefore, elemental analysis, conductivity, spectroscopic techniques and magnetic susceptibility measurements were employed in order to determine the structural characteristics of the complexes.

Elemental composition

The results of elemental analyses were in good agreement with those required by the proposed formulae. These are given in Table 1.

Table 1: Analytical and physical data of the trinuclear Schiff base metal complexes.

Complexes	Calculated (Found) (%)				μ_{eff} (B.M)	ΛM (Ohm^{-1} cm^2 mol^{-1})
	C	H	N	Metal		
$[Cu_3(C_{80}H_{64}N_{12}Cl_6)]$	60.17 (60.24)	4.01 (4.07)	10.53 (10.50)	11.94 (11.92)	1.58	13.87
$[Ni_3(C_{80}H_{64}N_{12}Cl_6)]$	60.72 (60.76)	4.04 (4.08)	10.62 (10.65)	11.13 (11.16)	2.54	14.56
$[Mn_3(C_{80}H_{64}N_{12}Cl_6)]$	61.16 (61.10)	4.07 (4.02)	10.70 (10.74)	10.49 (10.42)	5.52	15.12

Conductivity studies

The molar conductance of the complexes was an aid for proposing their formula. Conductivity measurements were carried out in 10^{-3} mol dm^{-3}, DMF at 30°C. The molar conductance values of the Cu (II), Ni (II) and Mn (II) complexes in the range of 13.87 – 15.12 Ohm^{-1} cm^2 mol^{-1} (Table 1), which indicates the non-ionic nature of these complexes. They are considered as non-electrolytes, and also indicating that the chloride ions are present inside the coordination sphere[13,14].

Infrared spectra

In the absence of a powerful technique such as X-ray crystallography, IR spectra have proved to be suitable technique to elucidate the method of the bonding mononuclear complex behaves as ligand to the metal ion. The important IR spectral bands are listed in Table 2. The appearance of strong band in 1608-1617 cm^{-1} region may be assigned to azomethine ν(C=N) vibrations[15]. Further, no strong absorption band was observed near 1680 cm^{-1} indicating the absence of C=O group of benzil moiety. The disappearance of these bands and appearance of a new strong absorption band near 1608-1617 cm^{-1} confirms the condensation of carbonyl group of benzil and amine group of p-phenylenediamine and also other end of the amine group of p-phenylenediamine and aldehydic carbonyl group of 2-aminobenzaldehyde[16]. The various absorption bands in the regon 1460-1580 cm^{-1} may be assigned due to ν(C=C) aromatic stretching vibrations of the benzil, p-phenylenediamine and 2-aminobenzaldehyde ring.

Table 2: Infrared spectral data for trinuclear Schiff base metal complexes

Complexes	(C=N) (cm^{-1})	NH_2 (cm^{-1})	(M−N) (cm^{-1})	(M−Cl) (cm^{-1})
$[Cu_3(C_{80}H_{64}N_{12}Cl_6)]$	1617	3334	445	314
$[Ni_3(C_{80}H_{64}N_{12}Cl_6)]$	1608	3330	448	318
$[Mn_3(C_{80}H_{64}N_{12}Cl_6)]$	1614	3328	434	312

In the IR spectra of Cu (II), Ni (II) and Mn (II) mononuclear complexes, the intense band in the ~3400 cm^{-1} region may be assigned to ν(N-H) of the free primary amine group. In trinuclear complexes, the band appears in the region 3328-3334 cm^{-1}, which is due to primary amine nitrogen of the 2-aminobenzaldehyde coordinated to the metal ion.

The far infrared spectra show bands in the region 434-448 cm^{-1} corresponds to ν(M-N) vibrations[17]. The presence of bands in all the complexes in the region 420-450 cm^{-1} orginates from the (M-N) azomethine vibration modes and identifies coordination of azomethine nitrogen. The band present in the region 312-318 cm^{-1} may be assigned due to ν(M-Cl) vibration[18].

Electronic spectra

The geometry of the metal complexes has been deduced from the electronic spectra of the complexes. Electronic spectra of all the complexes were recorded in DMF medium in Table 3. The peaks obtained in the range of 39215-37879 cm^{-1} was assigned to the intra ligand charge transfer transition ($\pi \rightarrow \pi^*$). An intense peak in the range of 24390-23696 cm^{-1} was due to ligand-to-metal charge transfer transitions. The bands are indicative of benzene and other chromophore moieties present in the complexes.

The mononuclear copper (II) complex shows a broad absorption peak at 18348 cm^{-1} and arises due to the d-d transition $^2E_g \rightarrow ^2T_{2g}$ of Cu (II) ion suggest that the copper ion exhibits a distorted octahedral geometry[19]. The homotrinuclear copper (II) complex shows an additional band in the region 16666-14285 cm^{-1}, which may be expected to arise from the terminal Cu (II) ions indicate that all three metal centres have distorted octahedral geometry.

Table 3: UV–Visible data of trinuclear Schiff base metal complexes

Complexes	Absorption nm (cm^{-1})			
	$\pi \rightarrow \pi^*$	**$n \rightarrow \pi^*$**	**L→ M CT**	**d-d**
$[Cu_3(C_{80}H_{64}N_{12}Cl_6)]$	256 (39062)	337 (29673)	410 (24390)	539, 618 (18552, 16181)
$[Ni_3(C_{80}H_{64}N_{12}Cl_6)]$	264 (37879)	328 (30487)	417 (23981)	526, 632, 714 (19011, 15823, 14006)
$[Mn_3(C_{80}H_{64}N_{12}Cl_6)]$	255 (39215)	330 (30303)	422 (23696)	515, 616, 684, 745 (19417, 16234, 14620, 13423)

According to the literature data, the principal feature of octahedral nickel (II) complexes is the presence of three well-defined bands[20]. The universally accepted ground term for octahedral Ni (II) ions is $^3A_{2g}(F)$. We have also observed three weak intensity bands of the mononuclear Ni (II) complex at 14005 cm^{-1}, 18552 cm^{-1} and 19011 cm^{-1} corresponding to $^3A_{2g} \rightarrow ^3T_{2g}(F)$, $^3A_{2g} \rightarrow ^3T_{1g}(F)$, $^3A_{2g} \rightarrow ^3T_{1g}(P)$ transitions, respectively. In homotrinuclear Ni (II) complex shows an additional band in the region 18181-14285 cm^{-1}. It is due to terminal Ni (II) ions, which indicates that the all metal centres are distorted octahedral geometry.

The electronic spectra of mononuclear Mn (II) complexes exhibit four weak intensity absorption bands at 13422, 14619, 16233 and 19417 cm^{-1}. These bands may be assigned to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}$ (4G), $^6A_{1g} \rightarrow {}^4E_g$ (4G), $^6A_{1g} \rightarrow {}^4E_g$ (4D) and $^6A_{1g} \rightarrow {}^4E_g$ (4P). The homotrinuclear Mn (II) complex shows an additional band in the region 19607-14285 cm^{-1}, which may be expected to arise from the terminal Mn (II) ions[21] in distorted octahedral geometry.

Magnetic moment studies

The magnetic susceptibility measurements provide information regarding the structure of the trinuclear metal complexes. Magnetic susceptibility was determined using a magnetic susceptibility balance. The magnetic moment data of the solid-state complexes at room temperature are reported in Table 1. The magnetic susceptibility measurements show that the complexes are paramagnetic at ambient temperature. The magnetic moment values of the mononuclear copper (II) complexes are in the region of 1.72 B.M. while those of the homotrinuclear copper (II) complexes are in the region of 1.58 B.M. The magnetic moment values found for the mono and trinuclear copper (II) complexes are not consistent with the expected spin-only magnetic moment of an $S = 1/2$, Cu (II) d^9 system. These low values are due to magnetic interaction between copper metal centers[22]. The homotrinuclear copper (II) complexes have subnormal magnetic moment values. The strong antiferromagnetic coupling that was found for the homo polynuclear copper (II) complexes are explained by the good superexchange properties of the imine groups. Similarly, the magnetic moment of mononuclear Ni (II) complex has 2.64 B.M. indicating a octahedral geometry[23], but in homotrinuclear Ni (II) complex has 2.54. The magnetic moment of mononuclear Mn (II) complex 5.64 B.M. indicating a octahedral geometry[24] and in trinuclear complex 5.52 B.M. The subnormal magnetic moment values indicate that all the complexes are trinuclear in nature[25].

EPR spectra

The EPR spectra of complexes provide information of importance in studying the metal ion environment. The EPR spectra of the trinuclear [$Cu_3(C_{80}H_{64}N_{12}Cl_6)$] and [$Mn_3(C_{80}H_{64}N_{12}Cl_6)$] Schiff base complexes recorded on powder samples with room temperature, on X-band at frequency 9.3 GHz under the magnetic field strength 4000G. The EPR spectrum of the trinuclear copper complex shows a broad signal with G average at 2.1274, which is consistent with an distorted octahedral geometry. The broadening of this signal might be due to dipolar interactions, indicating lowered site symmetry suggesting that the unpaired electron resides mainly in the dx^2-dy^2 orbital. This indicates a considerable exchange interaction in the complex[26]. Keivelson and Neiman[27] have shown that $g_{\|}$ is a moderatively sensitive function for indicating covalency. For an ionic environment, $g_{\|}$ is normally greater than 2.3 and for a covalent environment, it is less than 2.3. In the copper complex, the $g_{\|}$ (2.145) value was less than 2.3, indicating appreciable metal ligand covalent character. In a similar fashion, a single unresolved signal observed in the trinuclear Mn (II) complex suggests an exchange interaction between the Mn (II) centres. In the present case, the average G value is found to be 2.0144, which can be corroborated with a distorted octahedral environment. Thus, the EPR spectrum supports the binding of the ligand with four potential nitrogen donor atoms to the metal ion in a distorted octahedral environment.

In addition, there is exchange coupling interaction between the copper centres explained by Hathaway expression $G = (g_{\|} - 2.0023)/ (g_{\perp} - 2.0023)$. According to Hathaway[28], if the value of G is greater than four, the exchange interaction is negligible, whereas when the value of G is less than four, a considerable interaction is indicated in solid complex. The observed values of the exchange interaction parameter, for the homotrinuclear copper complex exhibit 1.043, which suggests that considerable exchange interactions were present in the homotrinuclear copper complex.

Cleavage of Plasmid pUC18 DNA

The ability of Cu (II), Ni (II) and Mn (II) complexes to perform DNA cleavage in the presence of H_2O_2 has been studied by agarose gel electrophoresis using supercoiled pUC18DNA in a medium of 50 mM tris–HCl/NaCl buffer. All the complexes show considerable DNA cleavage ability at high concentrations. When circular plasmid DNA is subjected to electrophoresis, relatively fast migration will be observed for the intact supercoil form (Form I). If scission occurs on one strand (nicking), the supercoil will relax to generate a slower moving open circular form (Form II). If both strands are cleaved, a linear form (Form III) that migrates between Forms I and II will be generated[29]. Fig. 3 shows the gel electrophoretic results of trinuclear complexes interaction with plasmid pUC18 DNA. The control experiments did not show any apparent cleavage of DNA (lane 1 & 2). Copper trinuclear complex in the presence of H_2O_2 (lane 3) at higher concentration (50 μM) shows more cleavage activity compared to trinuclear nickel and manganese complexes. The supercoiled plasmid DNA was completely degraded. This shows that a slight increase in the concentration over the optimal value led to extensive degradations, resulting in the disappearance of bands on agarose gel. Nickel trinuclear complex in the presence of H_2O_2 resulting the conversion of supercoiled form (Form I) into linear form (Form III) (lane 4). Manganese trinuclear complex in the presence of H_2O_2 (lane 5) at higher concentration (50 μM) shows cleavage activity in which supercoiled DNA (Form I) cleaved and supercoiled form converted to open circular form (Form II). These highly reactive hydroxyl radical species can cleave the DNA by abstraction of the hydrogen atom from the deoxyribose sugar.

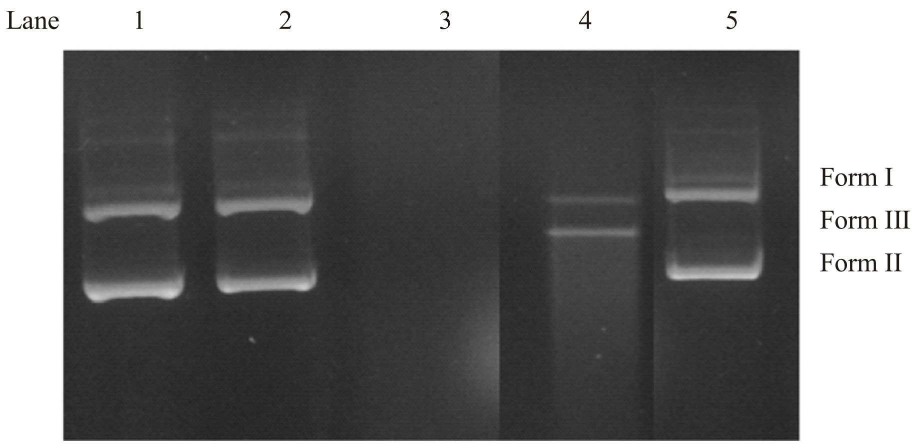


Fig. 3: DNA Cleavage studies for trinuclear Schiff base metal complexes

(1) DNA alone, (2) DNA + H_2O_2, (3) DNA + $[Cu_3 (C_{80}H_{64}N_{12}Cl_6)]$ + H_2O_2, (4) DNA + $[Ni_3(C_{80}H_{64}N_{12}Cl_6)]$ + H_2O_2 , (5) DNA + $[Mn_3(C_{80}H_{64}N_{12}Cl_6)]$ + H_2O_2.

Antimicrobial assay

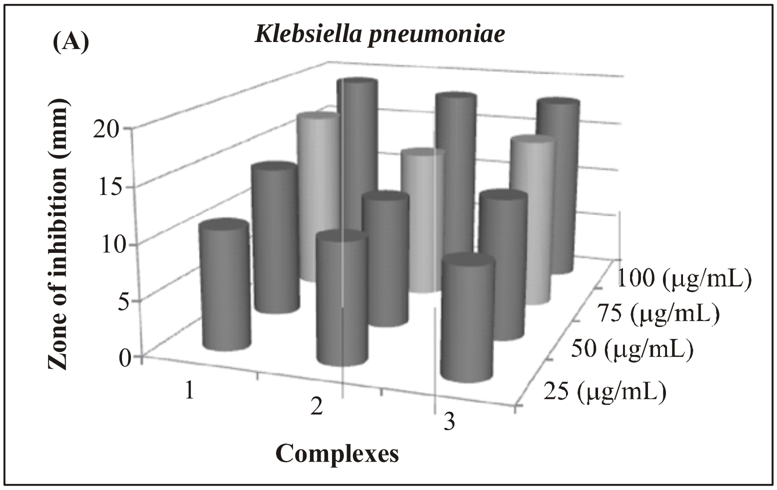
The main aim of the production and synthesis of any antimicrobial compound is to inhibit the causal microbe without any side effects on the patients. In addition, it is worthy to stress here on the basic idea of applying any chemotherapeutic agent which depends essentially on the specific control of only one biological function and not multiple ones. The chemotherapeutic agent affecting only one function has a highly sounding application used in the present time affect both; cancerous diseased cells and healthy ones which in turn affect the general health of the patients, Therefore, there is a real need for having a chemotherapeutic agent which controls only one function[30].

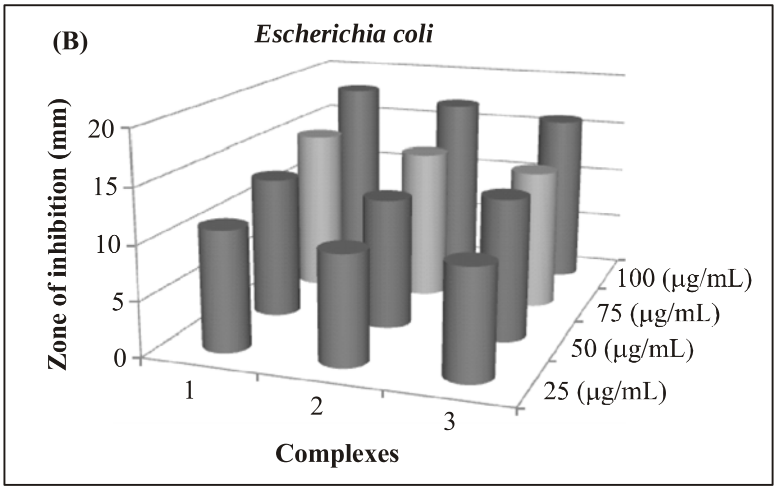
In testing the antibacterial activity of these entire complexes more than one test organism was used to increase the chance of detecting antibiotic principles in tested materials. All of the tested compounds show a remarkable biological activity against different types of Gram positive and Gram negative bacteria. The data are listed in Table 4 and Fig. 4. The biological activity of Cu (II), Ni (II) and Mn (II) trinuclear complexes are higher than that of the standard streptomycin. In addition, the biological activity of the Cu (II) and Mn (II) complexes are higher than the Ni (II) complex.

The Cu (II), Ni (II) and Mn (II) complexes inhibited Gram positive and Gram negative bacterial strains. The importance of this unique property of the investigated Schiff base complexes lies in the fact that, it can be applied safely in the treatment of infections

Table 4: Antibacterial activity of the trinuclear Schiff base metal complexes

Complexes	*Klebsiella pneumoniae* (mm)				*Escherichia coli* (mm)				*Staphylococcus aureus* (mm)			
	Concentrations (μg/mL)											
	25	50	75	100	25	50	75	100	25	50	75	100
$[Cu_3(C_{80}H_{64}N_{12}Cl_6)]$	11	14	17	19	11	13	15	18	12	14	17	19
$[Ni_3(C_{80}H_{64}N_{12}Cl_6)]$	10	12	14	18	10	12	14	15	11	13	15	16
$[Mn_3(C_{80}H_{64}N_{12}Cl_6)]$	10	13	16	18	10	13	14	15	11	14	16	17





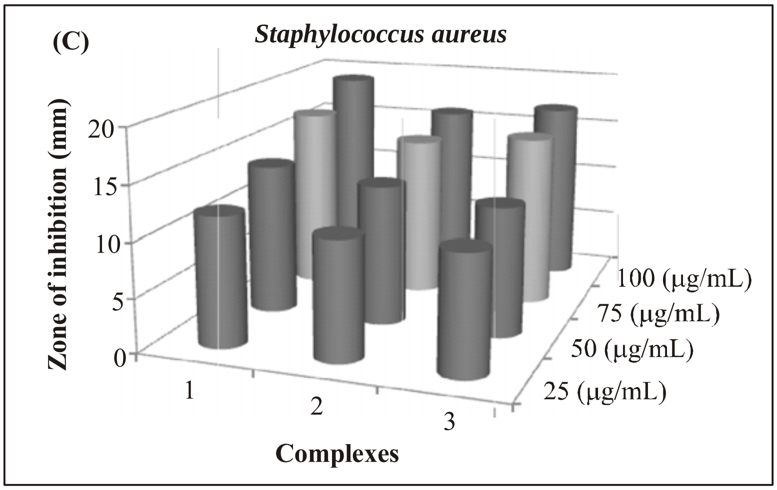


Fig. 4: Difference between the antimicrobial activities of the trinuclear Schiff base metal complexes. (A) [$Cu_3(C_{80}H_{64}N_{12}Cl_6)$], (B) [$Ni_3(C_{80}H_{64}N_{12}Cl_6)$] and (C) [$Mn_3(C_{80}H_{64}N_{12}Cl_6)$]

caused by any of these particular strains. Since almost all scientists working in the field of search for new antitumour depend basically on the line of antibiotics affecting Gram negative bacteria, and since there are certain organisms which have proved difficult to treat and most of them are Gram negative rods. It is, therefore, believed that all the complexes which are biologically active against both the Gram negative strains may has something to do with the barrier function of the envelop of these Gram negative strains activity.

CONCLUSION

The design and synthesis of three trinuclear Cu (II), Ni (II) and Mn (II) Schiff base complexes have been demonstrated in this report. All the three complexes were synthesized from p-phenylenediamine, benzil and 2-aminobenzaldehyde containing N_4 donors set in different environments. They were characterized by spectral and analytical data. The molar conductance values indicate that the complexes were non-electrolytic in nature and also indicate that the chloride ion present inside the coordination sphere. FT-IR spectra reveal that the azomethine stretching frequency observed for all the complexes suggests the complex formation and far IR spectra indicate that the chloride ion is bonded to the metal ion. The UV-Vis, magnetic susceptibility and EPR spectral data of the complexes suggest a distorted octahedral geometry around the central metal ion and terminal metal ions. The DNA cleavage studies reveals that the copper complex cleaves DNA more effectively as compared to nickel and manganese complexes. The antibacterial activity of the Cu (II) and Mn (II) trinuclear complexes are higher than the Ni (II) trinuclear complex.

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