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RESEARCH ARTICLE

PREPARATION, CHARACTERIZATION AND BIOLOGICAL STUDY OF HETEROCYCLIC AZO-SCHIFF BASE COMPOUND AND SOME OF ITS METAL COMPLEXES

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ABSTRACT

A new series of transition metal complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), have been prepared from the azo-schiff base ligand (L) formed by coupling reaction of 1-(4-Aminophenyl)ethlidene-3-nitroaniline diazonium chloride with 4,5-diphenyl imidazole. The structural features have been arrived from their elemental analyses, magnetic susceptibility, molar conductivity, IR and UV-Vis spectral studies. The data show that the complexes have composition of [M(L)$_2$Cl$_2$] type M= Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The magnetic susceptibility and UV-Vis spectral data of the complexes suggest octahedral geometry around all the central metal ions. The invitro antibacterial activities of the synthesized compounds have been tested against the gram positive and gram negative bacteria's. The activity data show that the metal complexes higher antibacterial activity than the free ligand.

INTRODUCTION

The imidazoles are common components of a large number of natural products and pharmacologically active molecules (El-Subbagh *et al.*, 2000; Gupta, *et al.*, 2000). The biological importance of the imidazole ring system has made it a common structure in numerous synthetic compounds, such as fungicides (Ho, *et al.*, 2003), herbicides (Maier, *et al.*, 1989), plant growth regulators (Schmierer, *et al.*, 1987), and therapeutic agents (Adams *et al.*, 2001). A considerable number of Schiff-base complexes were used as more or less successful models of biological compounds (Prakash, *et al.*, 2010; Mourya and Rajput, 2006). Azo refers to a chemical compound that contains double nitrogen atoms with a double bond between them (-N=N-) (Bruce and Goodall, 1975). Azo imidazole compounds were found to be a valuable dyes (Komatsu, *et al.*, 1970), as well as they were applied for analytical separation and determination of some metal cations (Ali, *et al.*, 2010; Ali *et al.*, 2010; Ali *et al.*, 2008; Shibata *et al.*, 1976). This class of azo compounds possess active (π-acidic) azo imine (–N═N–C═N–), function, for this reason a number of these azo imidazoles were prepared and their abilities as chelating ligands (Abdul Hussein *et al.*, 2013; Ali *et al.*, 2012; Bawa and Kumar, 2009; Ali *et al.*, 2005) was investigated. A search through literature reveals that, no work has been done on the transition metal(II) complexes of azo schiff base derived from 1-(4-aminophenyl) ethlidene-3-nitroaniline and 4,5-diphenyl imidazole. The aim of this work is to preparation and characterization of transition metal-azo schiff base complexes derived from 1-[4-{(4,5-diphenyl-1H-imidazol-2-yl)diazenyl}phenyl ethylidene]-3-nitroaniline (DPDPI) along with their biological activity against some bacteria.

MATERIALS AND MEASUREMENTS

All the chemicals used in the preparation of the azo-schiff base ligand and metal complexes were A. R. products from BDH and Merck., except of 1-(4-aminophenyl)- ethlidene-3-nitroaniline was prepared as reported procedure (Jasim and Ali 2012), and 4,5-diphenyl imidazole was prepared as described earlier (Hofmann, 1953). Melting points was determined by open capillary tube method and are uncorrected by using a Stuart melting point SMP10. Elemental analyses (C, H, N) were carried out using a C.H.N.S EA-99. mth instrument. The metal contents of the complexes was measured using atomic absorption technique by Shimadzu AA-6300. IR spectra were recorded on a Shimadzu 8400S FTIR spectrophotometer in the (4000-400) cm^{-1} range using KBr discs. Electronic spectra were obtained on a Shimadzu 1700 UV spectrometer using ethanol as solvent in the (1100-200) nm range. Magnetic susceptibilities were determined by faraday method at room temperature using Balance Magnetic (MSB-MKI) apparatus, and diamagnetic corrections for the ligand were calculated using Pascal's constant (Hatfield, 1976). Molar conductance of the transition metal complexes were determined in (DMSO) using Digital conductivity Series Ino. Lab- 720 at 25°C, the concentration of the solutions was (10^{-3} mol L^{-1}). Antibacterial screening was done at Department of Biology, Faculty of Education for Girls, University of Kufa.

Preparation of the azo-azoimine ligand (DPDPI)

The azo-schiff base ligand (DPDPI) Fig.1, was prepared as in the procedure described for arylazo-imidazole dyes (Ali, *et al.*, 2008). The details are given as follows:

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1-(4-aminophenyl) ethlidene-3-nitroaniline (2.55 g, 10 mmol) was dissolved in 3.5 mL of concentrated hydrochloric acid and 20 mL distilled water. This solution was diazotized below 5°C with 11 mL of aqueous (1.0 mol L^{-1}) sodium nitrite. A drop of the reaction mixture is tested from time to time with starch-iodide paper until nitrous acid persists in the solution during a 15 min interval. The resulting diazonium chloride solution was added drop wise with vigorous stirring to 4,5-diphenyl imidazole (2.2 g, 10 mmol) dissolved in 150 mL alkaline ethanol cooled below 5°C. After leaving in the refrigerator for 24 hour, the mixture was acidified with diluted (0.1 mol L^{-1}) hydrochloric acid until (pH = 6). The precipitate was filtered off, and twice recrystallized from hot ethanol, then dried in the oven at 70°C for several hrs.

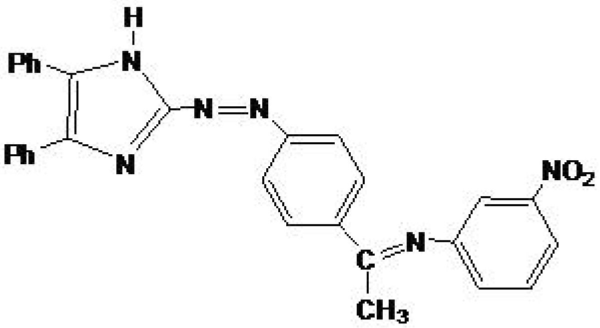


Fig.1. Structure of the ligand (DPDPI)

Preparation of complexes

Addition of ethanolic solution of the Co(II), Ni(II) and Cu(II) hydrated metal chloride and anhydrous Zn(II) and Cd(II) chloride to the azo ligand (DPDPI) dissolved in the solvent in 1:2 (metal : ligand) molar ratios. After reflexing with stirring at least for 30 min, colored precipitates formed at room temperature, the rustling solids were filtered off, washed with 5 mL hot 50 vol. % ethanol to remove any traces of the unreacted starting materials air dried, and recrystallized from ethanol and dried in the oven at 90°C for several hrs.

Antibacterial activity assays

The invitro antibacterial activity of the synthesized ligand and all complexes was investigated against several pathogenic representative Gram- positive bacteria:- *Staphylococcus aureus and Streptococcus pyogenes*, Gram-negative bacteria : *Escherichia coli*, *Enterobacter spp*, *Pseudomonas aeruginosa* and *Klebsiella pneumonia*. All bacteria used was obtained from the microbiology laboratory, Department of biology. One ml of the spore suspension of each bacteria was spread all over the surface of the cold solid media placed in the petri-dish. The test compounds was dissolved in ethanol to give (8.92 mg/ml) solutions. An amount of 0.1 ml of test solutions was added carefully in spots on the surface of the inoculated solid media. The petri dishes was incubated at 37 ^{0}C for 24 h. The inhibition zone formed by the compounds against the particular tested bacterial strain determined the antibacterial activities of the synthetic compounds. The mean value obtained for three individual replicates was used to calculate the zone of growth inhibition of each sample.

RESULTS AND DISCUSSION

Characterization of ligand and its metal complexes

The azo ligand was orange semi-crystal, but the chelates complexes of this ligand vary in color depended of metal ions. The experimental results of the elemental analyses of the prepared ligand and its metal chelates are in good agreement with theoretical expectations. The elemental analyses of the complexes indicate that the metal-ligand ratios were 1:2 in the $[M(DPDPI)_2Cl_2]$, [M = Co(II), Ni(II), Cu(II) Zn(II), or Cd(II)], metal complexes. The ligand and its complexes were quiet air stable, insoluble in water but soluble in common organic solvents such as methanol, ethanol, acetone, chloroform, and pyridine giving stable solutions at room temperature. However, some physical and analytical data are given in Table 1.

Infrared Spectral Studies

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. In order to study the binding mode of the ligand to metal ion in the complexes, the IR spectrum of the free ligand (DPDPI) was compared with the corresponding metal ion complexes. Selected vibrational bands of the ligand and its metal complexes are listed in Table 2, and the IR spectra of the ligand and Ni(II) complex are given in Figures 2 and 3. The IR spectrum of the ligand showed a medium and broad band around 3200 cm^{-1}, which can be attributed to ν(N–H) stretching vibration of the imidazole moiety (Mahmoud, *et al.*, 1986). The position of this band remained at nearly the same frequency in spectra of the metal complexes, which may be

Table 1. Some physical and analytical data of the ligand and its complexes

No.	Cheimiecal formul	m.p. °C	Yield %	Color	C % (cal.)	H % (cal.)	N % (cal.)	M % (cal.)
1	$(C_{29}H_{22}N_6O_2)$ =L_2	227-228	79	Orange	71.39 (71.60)	4.41 (4.52)	17.16 (17.28)	------
2	$[Co\ (C_{29}H_{22}N_6O_2)_2Cl_2]$	124-127	82	Deep red	62.89 (63.16)	3.83 (3.99)	15.11 (15.24)	**5.13** **(5.34)**
3	$[Ni\ (C_{29}H_{22}N_6O_2)_2Cl_2]$	142-145	78	Deep brawn	62.97 (63.18)	3.86 (3.99)	15.17 (15.25)	**5.21** **(5.32)**
4	$[Cu\ (C_{29}H_{22}N_6O_2)_2Cl_2]$	149-152	80	Deep red	62.63 (62.90)	3.82 (3.97)	15.03 (15.18)	**5.58** **(5.74)**
5	$[Zn(C_{29}H_{22}N_6O_2)_2Cl_2]$	>300	77	Redish-brawn	62.51 (62.79)	3.87 (3.96)	14.97 (15.15)	**5.78** **(5.90)**
6	$[Cd(C_{29}H_{22}N_6O_2)_2Cl_2]$	202-207	80	Redish-orange	60.12 (60.24)	3.68 (3.80)	14.41 (14.54)	**(9.72)**

Table 2. Infrared spectral data (cm^{-1}) of the ligand and its complexes

Compounds	ν(N-H)	ν(C-H)$_{or.}$	ν(C-H)al.	ν(C=N)$_{Schiff}$	ν(C=N)$_{Im.}$	ν(N=N)	ν (N=O)	ν (M-N)
DPDPI	3200	3059	2900	1681	1625	1480	1525 (1352)	----
[Co(DPDPI)$_2$Cl$_2$]	3220	3097	2902	1681	1599	1456	1525 (1348)	418
[Ni(DPDPI)$_2$Cl$_2$]	3200	3059	2890	1680	1597	1467	1525 (1350)	430
[Cu(DPDPI)$_2$Cl$_2$]	3180	3090	2933	1681	1620	1440	1525 (1346)	425
[Zn(DPDPI)$_2$Cl$_2$]	3200	3080	2900	1683	1575	1456	1525 (1350)	426
[Cd(DPDPI)$_2$Cl$_2$]	3200	3057	2900	1683	1616	1440	1525 (1350)	428

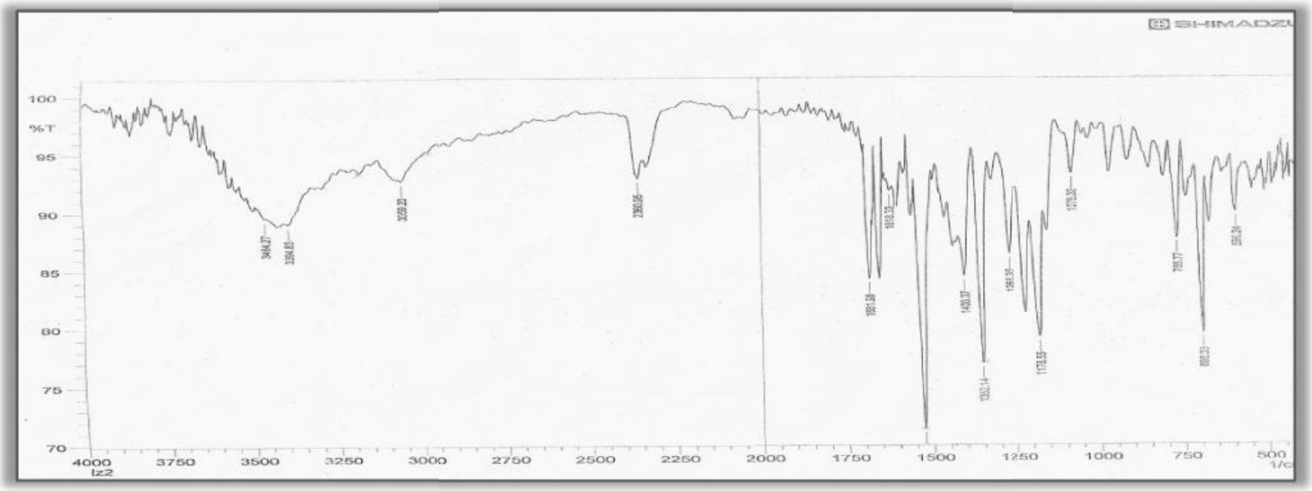


Fig. 2. The IR spectrum of the ligand (DPDPI)

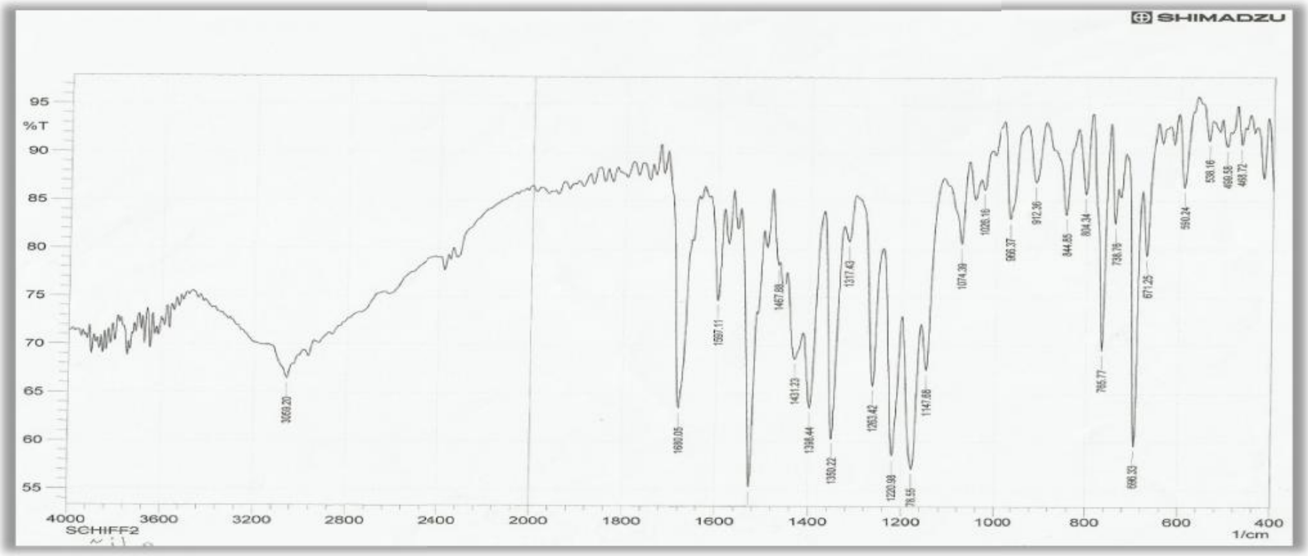


Fig. 3. The IR spectrum of the [Ni(DPDPI)$_2$Cl$_2$] Chelate complex

explained by nonparticipation in complex (Witwit and Radhi 2005). The sharp band at 1681 cm^{-1} is assigned to the stretching vibration of the azomethine group of the ligand and the infrared spectra of the complexes did not show any frequency shift of this band, which may be explained by nonparticipation in complex formation (Sahep, *et al.*, 2012). The spectrum of the ligand shows absorption band at 1625 cm^{-1} due to ν(C=N) of the N3 imidazole ring. It is observed with a little change in shape and shifted to lower frequencies 1616-1575 cm^{-1} in the prepared complexes spectra. These differences suggest the linkage of metal ion with N3 imidazole molecule (Raut and Shirote, 2012). The band at 1480 cm^{-1} is characteristic of the diazo group in the free ligand. The lowering in this frequency to 1440–1467 cm^{-1} in all the complexes indicates involvement of the (–N=N–) nitrogen in coordination with metal ion (Yildiz *et al.*, 2013). The ligand shows ν(–N=O) at 1352 cm^{-1}, and the appearance of this band at the same position in spectra of all complexes indicates that this group was nonparticipation in complex formation (Montazerozohor *et al.*, 2013). The far infrared spectra of the metal complexes exhibited new bands that are not present in the free ligand. These band are located at 430 - 418 cm^{-1}, assigned to ν(M–N) (Ibrahim *et al.*, 2012). Thus the above IR spectral data lead to suggest that the ligand behaves as a neutral bidentate chelating agent, and the coordination sites are, the nitrogen atom of azo group nearest to a phenyl ring, and N3 atom of the hetero cyclic imidazole ring, to give five-membered chelate ring (Ali *et al.*, 2007).

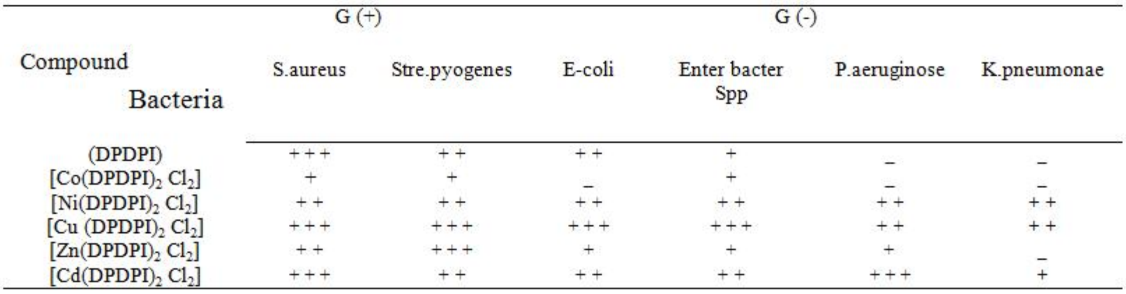
Electronic Spectral Studies

Solution electronic spectra of the complexes were recorded in ethanol solution in the UV-Vis region (200-1100 nm). The spectral data and the magnetic moment of prepared complexes are listed in Table.3. UV-Vis spectral studies of the complexes exhibit transition at lower than 400 nm corresponding to intramolecular $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ charge transfer transitions (Valarmathy and Subbalakshmi, 2013). Intense absorption bands (ε ~ 10^4) appear in the range 458-542 for the complexes which may be assigned to d M → π* (ligand) charge transfer transitions (Pal and Sinha, 2001).

Table 3. Spectral data, magnetic moment, conductivities, and proposed Structure of prepared complexes

Compound	Assigument	Absorption band(nm)	μ_{eff} (B.M)	Λ_M ($S.cm^2.mol^{-1}$)	Proposed Structure
DPDPI	$(\pi \rightarrow \pi^*)$ $(\pi \rightarrow \pi^*)$ $(n \rightarrow \pi^*)$	232 282 442	-----	-----	-----
$[Co(DPDPI)_2Cl_2]$	C. T.	542	4.81	10.57	Oh
$[Ni(DPDPI)_2Cl_2]$	C. T.	506	3.91	12.82	Oh
$[Cu(DPDPI)_2Cl_2]$	C. T.	516	1.79	11.76	Oh
$[Zn(DPDPI)_2Cl_2]$	C. T.	536	Dia	13.15	Oh
$[Cd(DPDPI)_2Cl_2]$	C. T.	458	Dia	10.86	Oh

Table 4. Antibacterial activity data (zone of inhibition in mm) of ligand (DPDPI) and its metal complexes



Compound / Bacteria	G (+)		G (-)			
	S.aureus	Stre.pyogenes	E-coli	Enter bacter Spp	P.aeruginose	K.pneumonae
(DPDPI)	+ + +	+ +	+ +	+	–	–
$[Co(DPDPI)_2 Cl_2]$	+	+	–	+	–	–
$[Ni(DPDPI)_2 Cl_2]$	+ +	+ +	+ +	+ +	+ +	+ +
$[Cu (DPDPI)_2 Cl_2]$	+ + +	+ + +	+ + +	+ + +	+ +	+ +
$[Zn(DPDPI)_2 Cl_2]$	+ +	+ + +	+	+	+	–
$[Cd(DPDPI)_2 Cl_2]$	+ + +	+ +	+ +	+ +	+ + +	+

Note: Highlyactive = + ++ Inhibition zone > 12mm, Moderately = ++ Inhibition zone = 9-12mm, Silightly = + Inhibition zone = 6-8mm Inactive = ⁻ Inhibition zone < 6mm

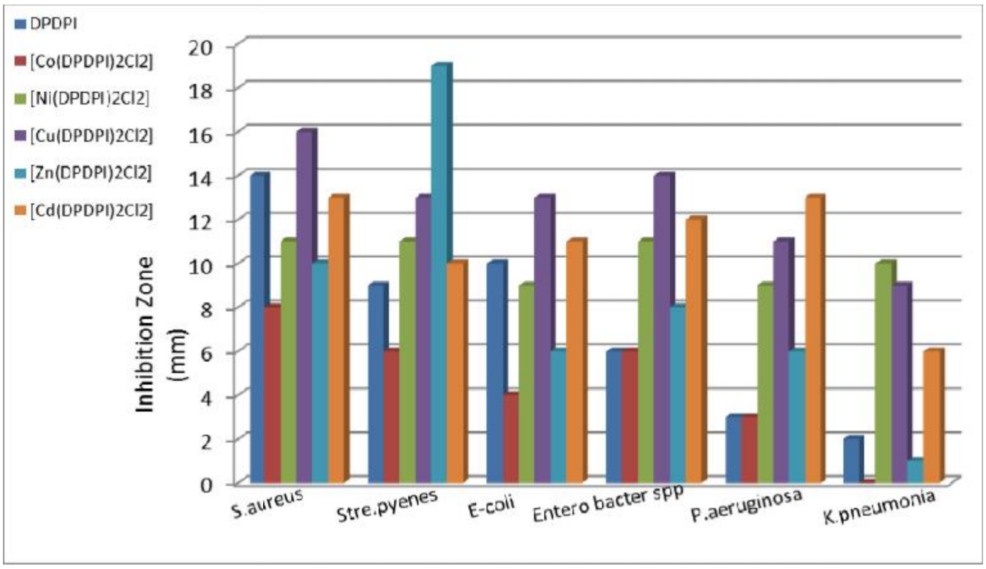


Fig. 4. Statistical representation for antibacterial activity of ligand (DPDPI) and its metal complexes

Magnetic measurements

The magnetic moment values for the Co(II) complexes have been used as criterion to determine the type of coordination around the metal ion. Due to the intrinsic orbital angular momentum in the ground state, there is consistently a considerable orbital contribution and the effective magnetic moment lies between 4.7 and 5.2 B.M. at room temperature. In the present complex the magnetic moment value (4.81 B.M.) suggests an octahedral geometry for the Co(II) complex in the high-spin state (Parameswari, *et al.,* 2013). The larger variation in the magnetic moment values (2.9-3.4 B.M.) for a high-spin Ni(II) complex (2.83 B.M.) depends on the magnitude of the orbital contribution. The magnetic moment value (3.19 B.M.) in the present work is within the range expected for similar octahedral Ni(II) ions (Makode and Aswar, 2004). The magnetic moment value of Cu(II) complex (1.79 B.M.) is very close to the spin value (1.73 B.M.) expected for one unpaired electron which offers the possibility of an octahedral geometry (Singh *et al.,* 2010). The magnetic moment value of Zn(II), and Cd(II) metal complexes are diamagnetic consistent with the (d^{10}) configuration (Oatto, *et al.,* 1993).

Estimation of chloride

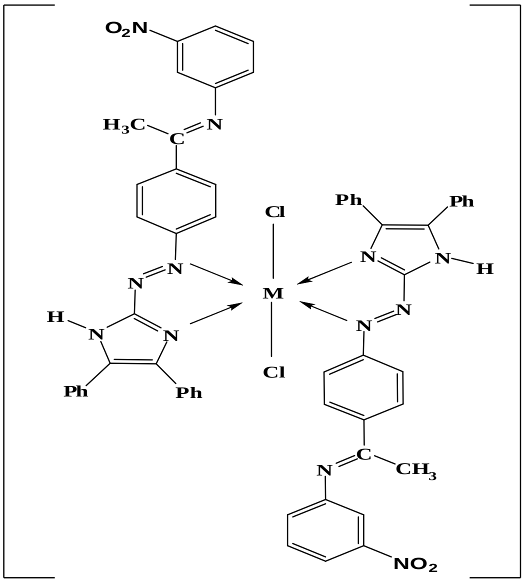
Chloride was determined gravimetrically as silver chloride (Vogel, 1985). The sample was acidified with 5N HNO_3 and 1% silver nitrate solution was added, till the precipitation was complete. The precipitate was filtered through a G-4 sintered glass crucible, dried at 110°C and weighed as silver chloride

Conductivity measurement

Molar conductance data of the complexes were measured in the solvent DMSO and the complexes were found to be non-electrolytic (Geary, 1971) in nature. Conductivity value of the chelate complexes are lie in the range (10.57-13.15) S. cm^2. mol^{-1}.

Antibacterial activity

The effect of the ligand (DPDPI) and their complexes have been tested for invitro growth inhibitory activity against gram-positive bacteria: *Staphylococcus aureus* and *Streptococcus pyogenes*, Gram-negative bacteria: *Escherichia coli, Enterobacter spp, Pseudomonas aeruginosa* and *Klebsiella pneumonia* by using spots diffusion method. All of tested compounds show a remarkable antibacterial activity against tested bacteria. The results are listed in Table 4, and its statistical presentation is shown in Fig. 4. The ligand and its complexes revealed that *S. aureus, Stre. pyogenes* and *Enterobacter Spp* was sensitive to ligand and its complexes while E. coli showed a reverse activity which resistance Co(II) complex but to ligand and Ni(II), Cu(II), Zn(II), and Cd(II) complexes. The *P. aeruginosa* was sensitive to all complexes except the ligand and Co(II) complex was resistance. Where *K. pneumonia* was resistance to ligand, Co(II) and Zn(II) complexes but sensitive to rest complexes. The ligand and Ni(II), Cu(II), Cd(II) and Zn(II) complexes showed an activity to most bacteria. Cu(II) complex showed highly activity and sensitivity against all bacteria while Co(II) complex which inactive towards all bacteria except the *S. aureus, Stre. pyogenes* and *Enter. Spp* Slightly activity. The mechanism of action of antibacterial drug can be discussed under four headings, (1): inhibition of cell wall, (2): inhibition of cell membrane function, (3): inhibition of protein synthesis and (4): inhibition of nucleic acid (Jawetz, *et al.,* 2007) thensis. Finally, the toxicity of Ni(II), Cu(II), Zn(II) and Cd(II), complexes was found to be better than the ligand.



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

Fig.5. The proposed structural formula of chelate complexes

Conclusion

In the present study, the preparation and characterization of Co(II), Ni(II) Cu(II), Zn(II) and Cd(II) complexes of arylazo-4,5-diphenylimidazole ligand (DPDPI) have been carried out by elemental analyses, IR, and UV-Vis spectral studies. Electronic spectral data and magnetic susceptibility measurements support octahedral geometry of the complexes. Fig.5. The complexes are found to have higher biological activities as compared to the respective ligand.

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