RESEARCH ARTICLE

New Azo Ligand Synthesis, Characterization, and Bacterial Inhibition Investigation as a Derivative of 4,5-diphenylimidazole with Some Transition Metal Ions

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ABSTRACT

New (E)-4-((4, 5-diphenyl-1H-imidazole-2-yl)diazenyl)-N, N-diethylaniline (DPIED) ligand was synthesized by coupling reaction between N1, N1-diethyl benzene-1, 4-diamine, and 4, 5-diphenyl imidazole, and characterized by mass, and ^{1}HNMR. The coordination behavior of this ligand was studied with Co(II), Ni(II), Cu(II), and (IIB.) ions utilizing Fourier-transform infrared (FTIR), ultraviolet–visible (UV-Vis), community health nursing (CHN), Atomic Absorption, Magnetic susceptibility, and molar conductivity, as well as the optimal pH and the effect of time on the stability of the complexes, were studied. Also, the values of stability constants were calculated depending on the mole ration (M:L), which was equal to (1:2). The previous results referred to suggested the octahedral shape for all of the complexes in which (DPIED) behaved as bidentate give a general formula [M (DPIED)$_2$Cl$_2$]. Finally, the ligand and its complexes were shown good inhibition ability towards *Escherichia coli* comparing with *Staphylococcus aureus* and *Klebsiella pneumonia*.

Keywords: Azo, Bidentate, Biological activity, Ligand, Imidazole.

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Conflict of interest: None

INTRODUCTION

The researchers have recently been interested in the fabrication and characterization of imidazole azo compounds due to their high efficiency as analytical reagents,[1] which can be used to determine trace concentrations of elements in multiple samples[2] as well as their biological importance as an anticancer,[3,4] antibacterial,[5] antioxidant and antifungal,[6] as well as an inhibiter to COVID-19.[7]

In the field of coordination chemistry, those compounds were shown to coordinate with a variety of metal ions as mono, and multidentate to produce tetradentate, square planer, and octahedral as common shapes.[8-10] Imidazole molecule contains π* orbitals, which enable backward bonding, making more stability to the coordination process with metal ions in their lower oxidation states, also it contains azo imine (-N=N-C=N-) system, which make this type of azo compounds behave as (π-acidic).[11]

The goal of this research is to synthesize a new azo ligand as a derivate of 4, 5-diphenyl imidazole, then investigate its coordinates with six divalent metal ions (Co (II), Ni (II), Cu (II), and IIB.), as well as their biological activity toward three types of multidrug-resistant pathogenic bacteria.

The Chemicals and Instruments

Merck, Thomas Baker, and Himedia chemical companies provided the chemical compounds and the solvents with excellent purity.

The mass spectrum was recorded using an AB SCIEX 3200 QTRAP mass analyzer. In contrast, the electronic spectra were obtained using a Shimadzu UV-1650 UV-Vis Spectrophotometer, Japan, and the IR spectra were recorded using a Shimadzu FTIR 8400 and a KBr disk at the range of 400–4000 cm. The element analysis was performed with a Costech E.C.S. Elemental 4010, and the molar conductivity were determined with a 720 (WTW) spectrometer. ^{1}HNMR spectra in the dimethyl sulfoxide-d6 (DMSO-d6) solvent were acquired with a Bruker Avance-111 300 MHz NMR Spectrometer.

Synthesis of (DPIED) Ligand

1.64 gm of N1, N1-diethyl benzene-1, 4-diamine was dissolved in 20 mL of distilled water, then 3 mL of hydrochloric acid was added to this solution, that was then transported to an ice bath, and then 10 mL of 10% $NaNO_2$ solution was added drop by drop to the previous solution to produce a diazonium salt that stabilized between 0 to 5ºC in the ice bath for 20 to 30 minutes.

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This solution was added gradually to the ethanolic solution of 4, 5-diphenyl imidazole, which was prepared by dissolving 2.20 gm of in 20 mL of ethanol, and an orange precipitate of (DPIED) appeared at the end of the addition, which then was filtered, left to dry, and recrystallized, as shown in Scheme 1.

Synthesis of (DPIED) Solid Complexes

The complexes were created with the mole ratio of (1:2) (M: DPIED) in the optimum pH of each one of them by adding drops of 10 mmole of each metal ion salt solution, which was dissolved in the puffer solution to 20 mmole of ethanolic solution of ligand (DPIED) until the complexes were precipitated, after that filtered, dried, and purified by recrystallization with hot ethanol, as shown in Schemes 2 and 3.

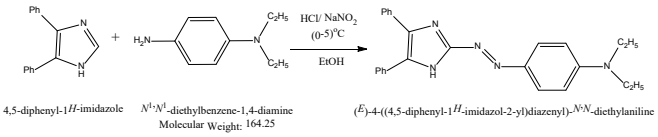
Preparation of Standard Solution of (DPIED) and Its Complexes:

The standard solution of DPIED was produced at a concentration of (10^{-3}) M by dissolving (0.395) gram of the solid ligand in 100 mL of ethanol, as well as the other concertations used in this study, were prepared using a dilution process from this standard ligand solution. In contrast, the traditional solutions for each metal ion were created by dissolving the solid $Zn(CH_3COO)_2$ salt and the chloride salts of the other metal ions in 100 mL of optimal buffer solutions; diluted concentrations were formed by dilution from the standard solution.

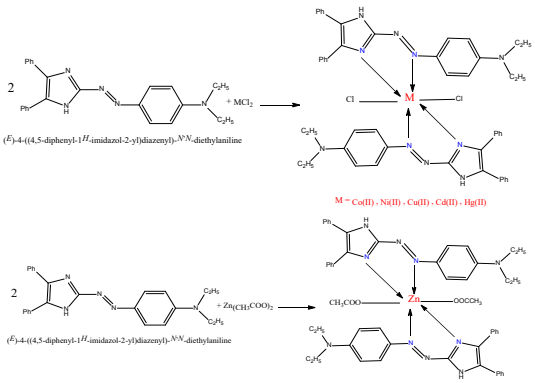
Antibacterial Activity Testing

Ramalivhana *et al*.,[12] demonstrated how to manufacture bacterial cultures; the agar well diffusion method was used to test the antibacterial activity of free ligand (DPIED) and the complexes towards three types of isolated bacteria (*Escherichia coli, Staphylococcus aureus*, and *klebsiella pneumonia*). The free ligand (DPIED) biological activity and the complexes versus bacterial isolates were evaluated using the MHA medium.

Bacterial isolate suspensions were produced to match the 0.5 McFarland standard using a micropipette, distribute 100 µL of B.H.I.B. bacterial suspension on the surfaces of the M.H.A. plate. All of the culture plates had wells perforated using a sterile cotton ball. A total of 100 µL of Gentamicin was added as a positive control; 100 µL l of DMSO was used as a negative control in the other well, and (100) µL of free ligand and complexes were added alone in the four residual wells. The cultivation plates were incubated at 37°C for 24 hours. The cleared zone of inhibition around wells has been measured in millimeters; also, the tests were carried out in triplicate



Scheme 1: (DPIED) ligand synthesis reaction



Scheme 2: (DPIED) complexes synthesis reaction

RESULTS AND DISCUSSION

^{1}HNMR spectra of the free ligand in DMSO-d6 solvent exhibited a signal (s, ^{1}H, -N.H.-) of the heterocyclic imidazole ring[13] at (12.546) ppm, while the signals between 7.947 to 6.834 ppm (m, Ar-H) for the protons of aromatic rings.[14,15]

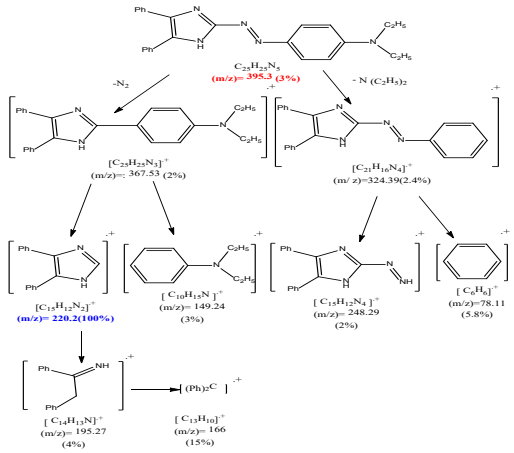
Finally, two signals have appeared at 3.364 ppm and 1.159 ppm due to (q, 2H, $-CH_2-$), and (t, 3H, $-CH_3$) respectively of ethyl groups, as shown in the Figure 1.

The mother peak of (DPIED) ligand in mass spectra was found at m/z = 595.3, which was consistent with the ligand's molecular weight., The fragmentation was based on two primary paths: the first began with the loss of (N_2) molecule at m/z = 367.3, then continued and gave the pass peak for 4, 5-diphenyl imidazole at m/z = 220,[16] and the second began with degradation of ($-N(C_2H_5)_2$) at m/z= 324.3, then $[C_{25}H_{25}N_3]$.+ fragment was dissociated into $[C_{15}H_{12}N_4]$.+, and $[C_6H_6]$.+ fragments at m/z = (248.2, 78.1), respectively as shown in ure Figure 2, and Scheme 3.

The practical values of C.H.N. were observed to agree with the calculated, and the percentage of metal ions in the complexes determined by Atomic Absorption coincided with their theoretical ones, as shown in Table 1, confirming the molecular formula of the ligand and the complexes.

The electronic spectra of (DPIED) revealed three peaks in ethanol solvent at (283) and (293) nm due to (π–π*) of aromatic ring transitions, while the third peak which appeared at (481) nm referred to Intermolecular Charge Transfer (I.M.C.T.) as seen in Figures (3–5) for the ligand and some of it, s complexes and Table 2.

The redshift in the complexes is due to (M.L.C.T.) transitions after the coordination process, whereas (d-d)



Scheme 3: Mass fragmentation of (DPIED)

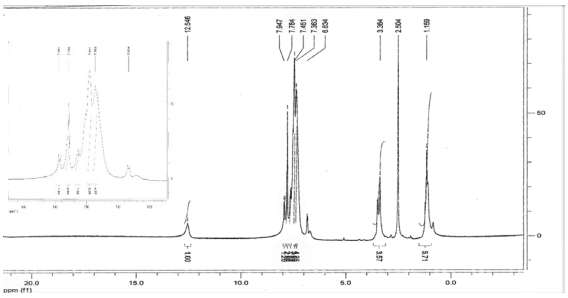


Figure 1: [1]HMNR Spectra of (DPIED) ligand in DMSO-d6 solvent

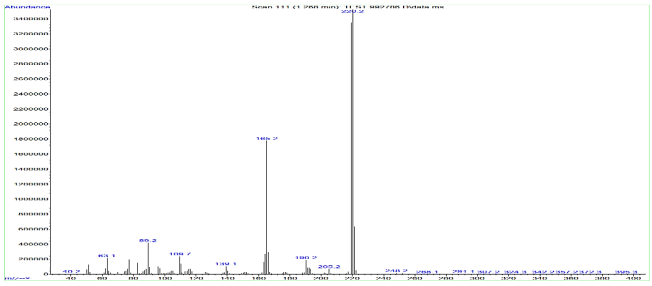


Figure 2: Mass spectra of (DPIED)

Table 1: Element analysis, and some of physicochemical properties of (DPIED) and its complexes.

Compound (Molecular Formula)	*Molecular weight*	*Color*	*Melting point (°C)*	*Found (calculated)*			
				M	*H%*	*N%*	*%C*
DPIED $C_{25}H_{25}N_5$	395.51	Orange	165–168	—	6.35 (6.37)	17.70 (17.71)	75.94 (75.92)
$[Co(DPIED)_2Cl_2]$ $C_{50}H_{52}Cl_2CoN_{10}$	922.87	Violet	150–155	6.41 (6.39)	5.70 (5.68)	15.21 (15.18)	65.05 (65.07)
$[Ni(DPIED)_2Cl_2]$ $C_{50}H_{52}C_{12}N_{10}Ni$	922.63	Dark violet	182–185	6.37 (6.36)	5.68 (5.68)	15.16 (15.18)	65.11 (65.09)
$[Cu(DPIED)_2Cl_2]$ $C_{50}H_{52}Cl_2CuN_{10}$	927.48	Dark violet	175–178	6.88 (6.85)	5.63 (5.65)	15.12 (15.10)	64.77 (64.75)
$[Zn(DPIED)_2(CH_3COO)_2]$ $C_{54}H_{58}N_{10}O_4Zn$	976.50	Red	250>	6.72 (6.70)	6.01 (5.99)	14.31 (14.34)	66.44 (66.42)
$[Cd(DPIED)_2Cl_2]$ $C_{50}H_{52}CdC_{12}N_{10}$	976.35	Red	160–163	11.49 (11.51)	5.38 (5.37)	14.37 (14.35)	61.48 (61.51)
$[Hg(DPIED)_2Cl_2]$ $C_{50}H_{52}C_{12}Hg\ N_{10}$	1064.53	Dark Red	182–185	-----	4.90 (4.92)	13.19 (13.16)	56.38 (56.41)

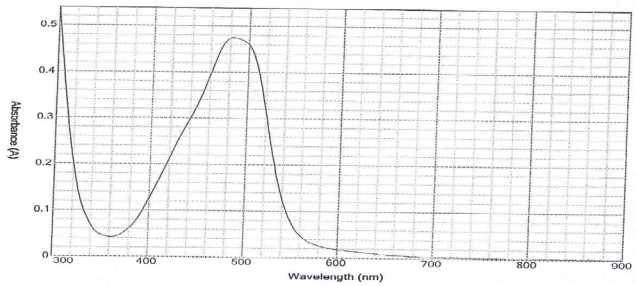


Figure 3: Uv-Vis. Spectrum of (DPIED)

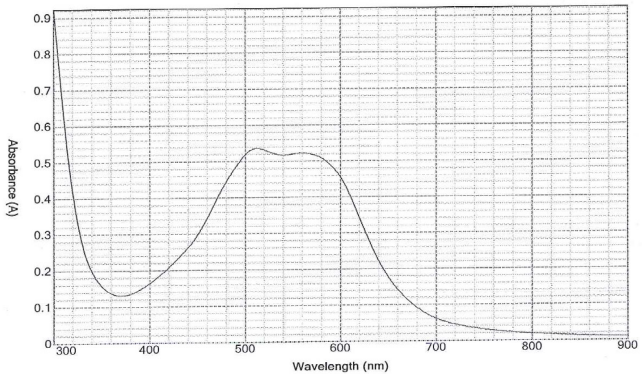


Figure 4: Uv-vis spectrum of $Co(DPIED)_2Cl_2$

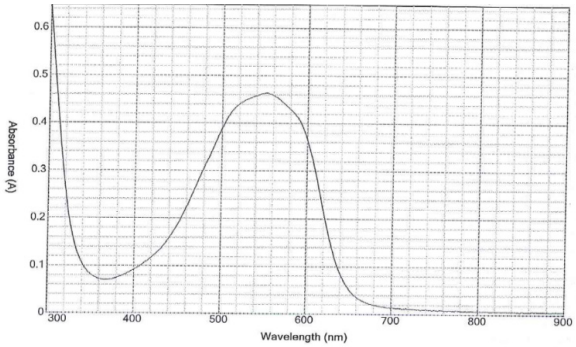


Figure 5: Uv-vis spectrum of $Ni(DPIED)2Cl_2$

Table 2: Type of electronic transitions, and values of (λ_{max}) in (nm), and (cm^{-1}) unites

Compound	*Type of electronic transition*	*λ_{max} (nm)*	*v (cm^{-1})*
DPIED	ILCT	481	20790
Co(II)	MLCT	511	19569
Ni(II)	MLCT	526	19011
Cu(II)	MLCT	534	18726
Zn(II)	MLCT	488	20491
Cd(II)	MLCT	502	19920
Hg(II)	MLCT	512	19531

transitions did not emerge due to their lower intensity compared to charge transfer.

The FTIR spectrum of (DPIED) revealed v(N-H) of the heterocyclic imidazole ring[17-19] at (3417) cm^{-1}, which had no significant change in the complexes spectra, that referred to the nihility of nitrogen number (1) in the coordination, and the same concept has been applied to the v(C-H) aromatic, and aliphatic at (3059) cm^{-}, and (2993–1818) cm^{-}, v(C=N) of imidazole[20] appeared at (1506) cm^{-1}. It was shifted to lower frequencies in the complexes, which supported the coordination process through nitrogen atom number (3), also as a result of sharing one of the nitrogen atoms in the coordination, the frequencies of v(N=N)[21-24] at 1450 cm^{-1} suffered from significant changes in position and intensity in the complexes, and new peaks appeared in the complex spectra at (408–459) cm^{-} due to the v(M-N)[25,26] as shown in Figures 6 to 8 and Table 3.

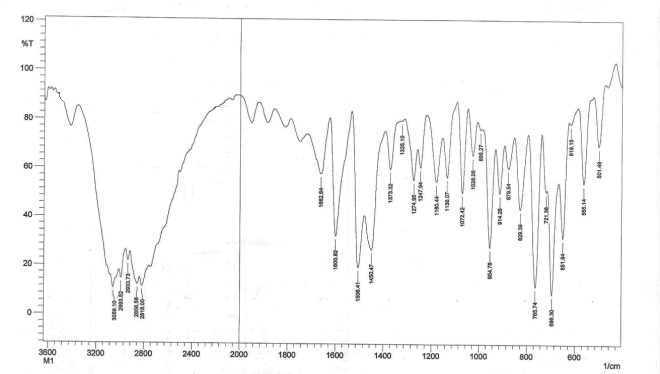


Figure 6: FT-IR spectrum of (DPIED)

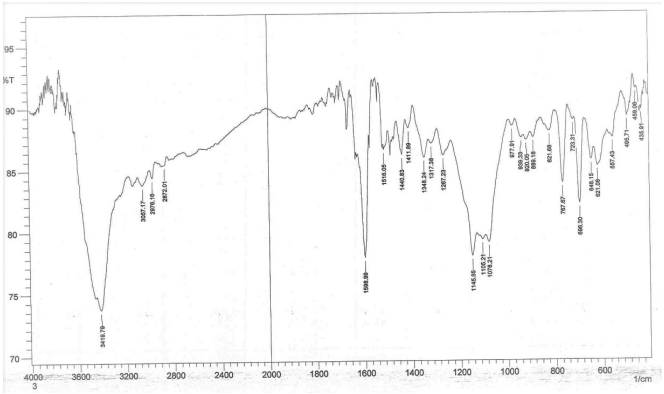


Figure 7: FT-IR of $Zn(DPIED)_2Cl_2$

The values of optimum pH for the complexation medium were measured between (pH= 5–10), the results are obvious that Co(II) and Ni(II) complexes formed at pH=8, while Cu(II) and (IIB.) complexes formed at pH=7 as shown in the Figures 9 and 10, these values attest to the basicity of imidazole ring in the ligand molecule.

Calibration curves representing the relationship between absorbance and concentration were drawn for the complexes, and the concentration that obeyed Lambert-Law Beer's for the complexes were found between (0.1×10^{-4}–2×10^{-4}) M, with values of R2 =(0.9964, 0.9964, 0.9985, 0.9986, 0.9984, 0.9985) for Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes respectively, as shown in the Figures 11 and 12.

The Mole Ratio method was used to estimate the number of (DPIED) molecules that coordinated with each central metal ion in the complex; the cross point of lines contacts in the mole ratio curve alluded to a ratio (M: (DPIED)) of (1:2) in all of the complexes, (i.e., two (DPIED) molecules were coordinated to the metal ion inside the coordination sphere as seen in Figures 13 and 14.

The effect of stability time of the complexes was studied by measuring the absorbance of all complexes from the moment of mixing the solution of each metal ion with the solution of the ligand to (145) minutes. Then the values of absorbance were also measured after 24 hour, The results refer to the high stability of the complexes, as shown in the Figure 15.

Stability constants of the complexes were calculated according to the following equations:

$$M + nL \leftrightarrow MLn \ldots\ldots (1)$$

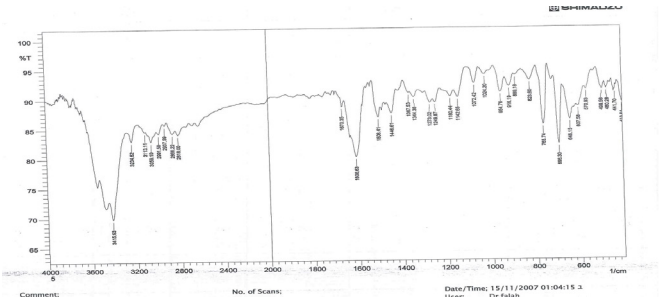


Figure 8: FT-IR of $Cd(DPIED)_2Cl_2$

Table 3: IR frequencies values of functional groups of (DPIED) and its complexes (cm-)

Compound	*v (C=N) Imidazole ring*	*N=N))v*	*C-N))v Imidazole ring*	*N=C-C=N))v*	*M-N))v*
DPIED	1506m	1450m	1136m	1247m, 1274m	1408 m
Co(II)Complex	1512m	1446m	1147m	1249m, 1276m	445w
Ni(II)Complex	1513m	1444m	1147m	1251w, 1269w	443w
Cu(II)Complex	1489m	1445m	1149m	1247w, 1273w	459w
Zn(II)Complex	1616m	1440m	1145m	1254w, 1267w	435w
Cd(II)Complex	1508m	1446m	1142m	1249w, 1273w	441w
Hg(II)Complex	—	1443m	1140m	1255m, 1267m	408w

$$\alpha \; n \; \alpha C \; 1-\alpha$$

M: Metal ion n: No. of coordinated ligands
L: Ligand α: Degree of dissociation C: Concentration of ligand

$$K_{Staibilty} = \frac{[ML\,n]}{[M]\,[L]^n} \ldots\ldots\ldots\ldots (2)$$

$$K = \frac{1-\alpha}{4\alpha^2 C^3} \ldots\ldots\ldots\ldots (3)$$

For the complexes which have Mole Ratio (M: L) (1:2)

$$\alpha = \frac{Am - As}{Am} \ldots\ldots\ldots\ldots (4)$$

When Am: Value of the complex absorption in the Mole Ratio.
An s: Value of the complex absorption with increasing ligand concentration.

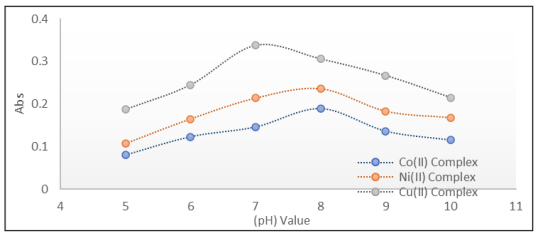


Figure 9: Optimum (pH) of Co(II), Ni(II), and Cu(II) complexes

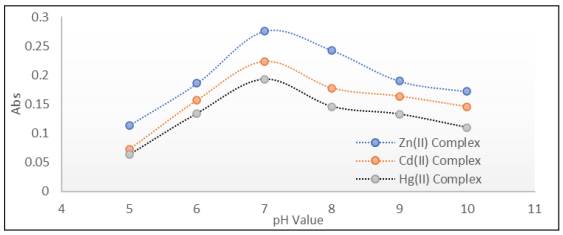


Figure 10: Optimum (pH) of Zn(II), Cd(II), and Hg(II) complexes

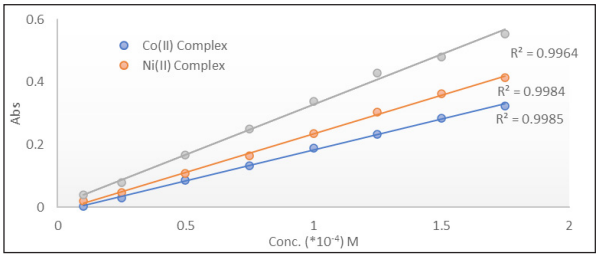


Figure 11: Calibration curve of Co(II), Ni(II), and Cu(II) complexes

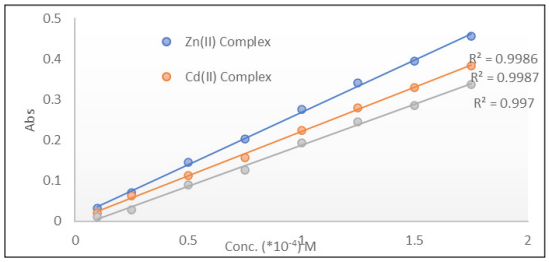


Figure 12: Calibration curve of Zn(II), Cd(II), and Hg(II) complexes

The values of stability constants established that all of the complexes have a high amount of stability; also, the values of the first serious of metal ion complexes agreed with Irving -Williams, as shown in the Table 4.

The molar conductivity values for the complexes with a concentration of 10^{-3} M in both ethanol and DMSO solvents indicate that they were non-ionic,[27-30] supported by the absence of $AgCl_2$ precipitation when a drop of $AgNO_3$ solution was added to the complex's solutions., according to these observations, chloride ions are connected with a central metal ion inside the coordination sphere. The magnetic susceptibility measurements of the complexes demonstrated a diamagnetic character for Zn(II), Cd(II), and Hg(II) complexes, revealing an electronic configuration n-1(d10) ($t_2g^6eg^2$) of these ions' outer shells. In contrast, the value (4.62) B.M of Co(II) complex owing to three unpaired electrons supported the electronic configuration ($t2g5eg^2$) of the distorted octahedral shape of this complex, while the value (2.82) B.M of Ni(II) complex due to the two unpaired electrons in the outer shell which have a ($t2g^6eg^2$) for an octahedral geometry. Finally, the value 1.74 B.M four Cu(II) complex indicated the distorted octahedral geometry with one electron in the outer shell of cupper divalent ion,[31] as shown in the Table 5 (Tables 16 and 17).

The complexes offered structures are an octahedral (DPIED) ligand behaved as bidentate through nitrogen atom (3) of the heterocyclic imidazole ring. One nitrogen atom

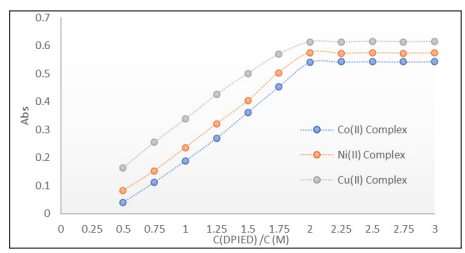


Figure 13: Mole Ratio curve of Co(II), Ni(II), and Cu(II) complexes with (DPIED)

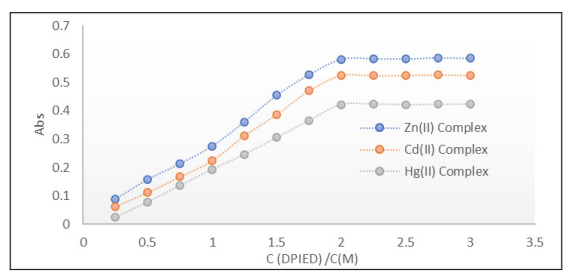


Figure 14: Mole Ratio curve of Zn(II), Cd(II), and Hg(II) complexes with (DPIED)

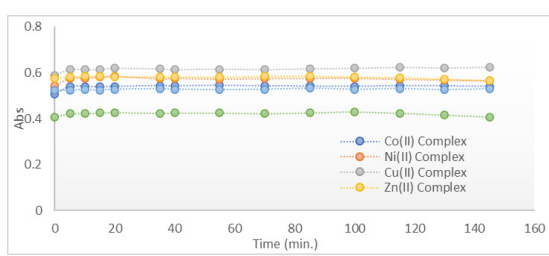


Figure 15: Effect of time on the absorbance of the complexes

Table 4: Values of (Am), (As), α, K (stability), and log (K) of the Complexes

Compound (M:L)(1:2)	*Am*	*As*	*α*	*K(mole-.L^2)*	*Log K*
$[Co(DPIED)_2Cl_2]$	0.544	0.541	0.005	1.990×1014	14.298
$[Ni(DPIED)_2Cl_2]$	0.578	0.576	0.003	9.231×1014	14.965
$[Cu(DPIED)_2Cl_2]$	0.615	0.614	0.001	5.805×1015	15.763
$[Zn(DPIED)_2(CH_3COO)_2]$	0.588	0.584	0.006	7.887×1013	13.896
$[Cd(DPIED)_2Cl_2]$	0.530	0.525	0.009	2.949×1013	13.469
$[Hg(DPIED)_2Cl_2]$	0.428	0.422	0.014	8.983×1012	12.953

Table 5: Molar Conductivity values and Magnetic susbtibility of (DPIED) complexes

	Molar Conductivity		
Compound	*Ethanol*	*DMSO*	*μ, eff.*
$[Co(DPIED)_2Cl_2]$	14.1	12.5	*4.62*
$[Ni(DPIED)_2Cl_2]$	13.5	12.3	2.82
$[Cu(DPIED)_2Cl_2]$	13.0	11.8	1.74
$[Zn(DPIED)_2(CH_3COO)_2]$	14.6	13.5	Diamagnetic
$[Cd(DPIED)_2Cl_2]$	13.8	12.7	Diamagnetic
$[Hg(DPIED)_2Cl_2]$	12.5	10.6	Diamagnetic

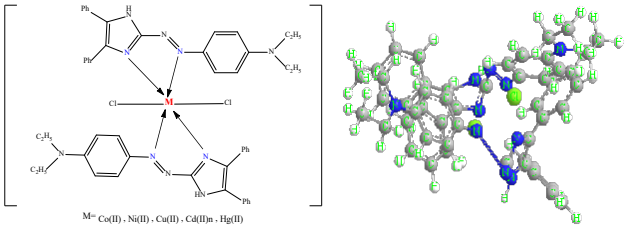


Figure 16: Offered structure of Co (II), Ni (II), Cu (II), Cd(II), and Hg(II) complexes with (DPIED)

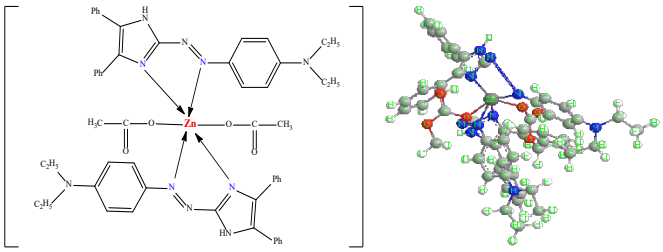


Figure 17: Offered structure of Zn (II) complex with (DPIED)

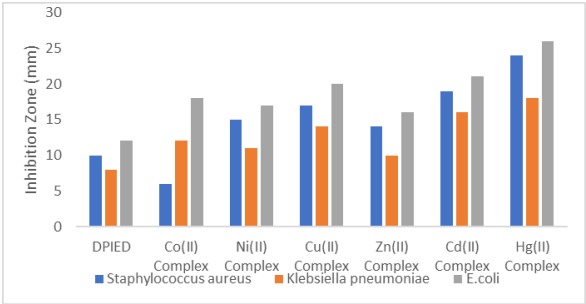


Figure 18: Microbial activity of (DPIED), and the complexes againt *E. coli, S. aureus* and *K. pneumonia* bacteria.

of the azo group formed a five-member with the central metal ion, Acetate ions in the Zn (II) complex, and chloride ions in the alkali metal complex occupied the offal two coordination

The biological activity of DPIED and its synthesized complexes were tested against three species of bacteria (*E. coli*, *S. aureus* and *K. pneumonia*) using a concentration of (100 mg/mL) in DMSO solvent for all of these compounds.

The results were summarized in Figure 18, which demonstrated all the complexes having a better ability to inhibit than the free ligand, owing to the complexes' proclivity for breaking open. DNA bands of the bacterial cells through the electrostatic connections, The following that's how the biological activity of the ligand (DPIED) and the complexes were explained:

Hg(II) Complex > Cd(II) Complex > Cu(II) Complex > Co(II) Complex > Ni(II) Complex > Zn(II) Complex > (DPIED

CONCLUSION

New heterocyclic imidazole azo ligand (DPIED) was prepared, and its coordination nature was studied with Co(II), Ni(II), Cu(II), and (IIB.) ions, which indicated the formation of octahedral geometry for all of the complexes at mole ratio (1:2) (M: DPIED). Also this ligand and the complexes have good microbial activity against *E. coli, S. aureus* and *K. pneumonia* bacteria.

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