

Synthesis and Characterization of New Azo 4,5-dimethyl-2-((3-((*E*)-1-(2-phenylhydrazono)ethyl)phenyl)diazenyl)-1*H*-imidazole and its Metal(II) Complexes

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In this paper, a new azo ligand, 4,5-dimethyl-2-((3-((*E*)-1-(2-phenylhydrazono)ethyl)phenyl)diazenyl)-1*H*-imidazole (DPDPIH) and its metal complexes were synthesized. The ligand (DPDPIH) and its metal complexes were characterized by elemental, IR, ¹H NMR electronic and mass spectra. The values of elemental microanalysis and metal contents were in good agreement with the calculated values. The molar conductivity indicated that all these metal complexes were non-electrolyte in nature. The magnetic susceptibility values indicated that all the metal complexes were paramagnetic except cadmium and zinc complexes.

Keywords: Imidazole derivative, Metal complexes.

INTRODUCTION

The heterogeneous azo ligands are newly bonded, compared to their previous ligands of ring homogeneous. The importance of its features is the inclusion of one of its rings association with the azo group or both [1,2] on one atom and at least in its annular structure, which can be in coordination with the metal ions.

The heterogeneous ligands of the nitrogen containing nitrogen ring are more common than other ligands containing oxygen atoms in their chemical composition [3]. The imidazole belongs to a class of compound called the azolates, which were prepared by Debus [4]. The imidazole is similar to pyrimidine in its chemical composition, both of which contain heterogeneous nitrogen atoms in their heterogeneous ring [5]. The nitrogen atom of the azole has free pair of electron and does not share to fixation of imidazole, caused the basicity of this ring and is easy to bond with the metal ions [6].

The imidazole molecule is a stronger base than pyridine and it possesses the two resonance formulas. The electron density calculations showed that the electrophilic attack must occur at the two positions of this molecule. The azo ligands derived from this molecule or its derivatives have proved this fact [7].

EXPERIMENTAL

All the chemicals used in this work were of highest purity available and were purchased from commercial sources (BDH

and Sigma) without further purification. The equipment used in the analytical spectral and physical measurements of the prepared ligand and its metal complexes are described.

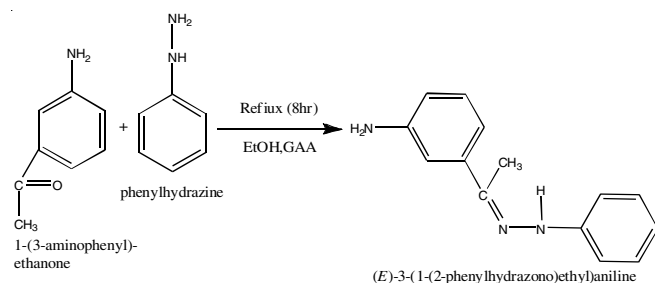
The infrared spectra of azo ligand and its complexes were recorded using infrared spectrometer (Shimadzu FTIR 8400, spectrophotometer). The melting points of ligand and its complexes were determined using a device Stuart melting point (SPM₃₀). Electrical conductivity measurements of the complexes were recorded at 25 ± 2 °C for 1 × 10⁻³ M solution of the sample in ethanol, using a Philips PW-digital conductivity meter. The electronic spectra of the ligands and its metal complexes was recorded by using Ultraviolet-Visible spectrophotometer (Shimadzu 1700) within the range (200-800 nm) using quartz made cells and ethanol as solvent.

The magnetic susceptibility of the metal complexes was performed by using Johnson Metthey and Sherwood model. The percentage of metal ion concentrations was determined using the flame atomic absorption spectrophotometer (Shimadzu 6300 AA). Carbon, hydrogen and nitrogen analysis of ligand and its metal complexes have been carried out by Euro Vector model EA3000, single V. 3.0 single. The mass spectrum of the synthesized ligand was recorded using mass spectrometer (MSD Direct Probe). The ¹H and ¹³C NMR were recorded for the ligand and its metal complexes using Bruker 400 MHz.

Synthesis of 4,5-diphenyl imidazole: The imidazole derivative was obtained from the interaction of benzil and hexamethylene tetraamine in the presence of acetic acid (condensation

α -diketo method with ammonia and aldehyde) [8]. In a round flask (250 mL), added 100 mL of acetic acid to a mixture of (4.2 g, 0.02 mol) benzyl, (0.5 g, 0.004 mol) hexamethylene tetraamine and (12 g, 0.15 mol) ammonium acetate. The mixture solution was heated under reflux for 1 h by using reflected condenser. The solution was diluted after cooling by adding 400 mL of distilled water. The imidazole derivative was precipitated by the addition of NH_4OH (0.88 N). The white precipitate was collected by filtration and then washed four times with distilled water (50 mL), dried for 3 h and then recrystallized from pyridine to obtain white crystalline product and then allowed to dry at room temperature for 2 h. Yield 86 %, m.p. (228-230 °C) [9,10].

Synthesis of (*E*)-3-(1-(2-phenyl hydrazone)ethyl)aniline: 3-Amino acetophenone (1.35 g) was dissolved in ethanol (25 mL), the phenyl hydrazine (1.4 g) was dissolved in ethanol (25 mL) and added to the solution while stirring 0.4 g NaOH was added to the mixture solution. The mixture solution was heated under reflux for 8 h and then allowed to cool at room temperature. The precipitate was collected by filtration, washed by hot water (3×10^3 mL) and then the solid was recrystallized from absolute ethanol. The brown crystals were collected by filtration and dried in vacuum for 4 h (**Scheme-I**). Yield 85 %, m.p. 94-96 °C.



Preparation of 4,5-dimethyl-2-((3-((*E*)-1-(2-phenylhydrazone)ethyl)phenyl)diazonyl)-1*H*-imidazole (DPDPIH): (*E*)-3-(1-(2-Phenyl hydrazone)ethyl)aniline (0.228 g, 0.5 mmol) was dissolved in solution of hydrochloric acid (2 mL) diluted by deionized water (20 mL). The mixture was cooled at 0 °C using ice-cooled waterbath. Sodium nitrite was dissolved in deionized water (10 mL) and added drop-wise to the mixture solution with a continuous stirring and temperature is maintained at 0-5 °C. Then the solution was added to the diazonium solution drop-wise with continuous stirring and the reaction temperature maintained at 0-5 °C. 4,5-Diphenyl imidazole (0.11 g, 0.5 mmol) was dissolved in ethanol (100 mL) and

then added to the cooling solution. Sodium hydroxide (1 g) was dissolved in ethanol and added to the mixture solution. Left the reaction mixture to overnight and then dil. HCl was slowly added until the precipitation of orange-reddish solid was obtained. The orange-reddish precipitate was collected by filtration and washed with hot deionized water (10 mL $\times$ 2) and recrystallized with absolute ethanol. The orange-reddish crystals were collected by filtration and then dried in vacuum for 5 h. Yield 80 %, m.p. (98-100 °C).

Synthesis of metal complexes: The metal salt, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 and $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ (0.237 g, 0.001 mmol, 0.2367 g, 0.001 mmol, 0.1695 g, 0.001 mmol, 0.1354 g, 0.001 mmol and 0.2184 g, 0.001 mmol respectively) were dissolved in ethanol and added to the clear solution of brown azo ligand (0.912 g, 0.002 mmol) in ethanol (30 mL). The mixture was left for 20 min, during this period precipitate colour of dark brown, puce, reddish brown, red and black respectively. The coloured solid was collected by filtration, dried in vacuum for 2 h and then purified by recrystallization from absolute ethanol. The colour powder was collected by filtration, dried in vacuum for 3 h.

RESULTS AND DISCUSSION

IR spectra: The FT-IR spectra of the prepared metal complexes were compared with that of free ligand in order to determine the coordination sites involved in complexation, that is the mean position of some guide bands in the spectrum of the free ligand were expected to change on complexation.

The DPDPIH spectrum shows the band at 3147 cm^{-1} due to stretching vibration of (N-H) of the heterogeneous imidazole ring, the weak band at 3210 cm^{-1} showed that the two groups did not experience any change in the spectra of the metal complexes, demonstrating that they did not participate in the process of symmetry. The spectrum of the ligand that showed weak frequency bands at 3066 cm^{-1} and 2895 cm^{-1} are related to the band $\nu(\text{C-H})$ aromatic and aliphatic respectively and they have not experienced changes in the intensity of the metal complexes spectra, making them far from the coordinated process. While the spectrum shows weak band of $\nu(\text{N=N})$ at 1683 cm^{-1} of the non-imidazole ring, which was shown at 1545 cm^{-1} after complexation. This group has experienced changes in the intensity of the metal complexes spectra, which proves their involvement in the process of coordination. The group (N=N) at 1431 cm^{-1} showed a shift to higher frequencies in the spectra of the metal complexes due to the participation of this group into the process of coordination. Spectra of metal complexes showed new medium and low intensity bands around $499\text{--}451\text{ cm}^{-1}$ can be assigned

TABLE-1
ELEMENTAL ANALYSIS AND KEY IR BANDS (cm^{-1}) OF AZO LIGAND (DPDIH) AND ITS METAL COMPLEXES

Compounds	$\nu(\text{N-H})$ imide	$\nu(\text{C=N})$ Schiff	$\nu(\text{C=N})$ imidazole	$\nu(\text{N=N})$	$\nu(\text{N-M})$	Elemental analysis (%): Calcd. (found)			
						C	H	N	M
DPDPIH	3417	1683	1552	1431	—	76.10 (76.06)	5.4 (5.40)	18.30 (18.20)	—
$[\text{Co}(\text{DPDPIH})_2\text{Cl}_2]$	3408	1685	1598	1438	499	33.30 (33.20)	2.3 (2.10)	8.04 (8.10)	6.5 (6.4)
$[\text{Ni}(\text{DPDPIH})_2\text{Cl}_2]$	3377	1681	1598	1438	470	33.02 (33.04)	2.3 (2.20)	7.90 (7.80)	—
$[\text{Cu}(\text{DPDPIH})_2\text{Cl}_2]$	3356	1687	1597	1440	497	33.10 (33.20)	2.3 (2.09)	8.03 (8.03)	6.0 (6.1)
$[\text{Zn}(\text{DPDPIH})_2\text{Cl}_2]$	3408	1685	1552	1438	476	33.09 (33.10)	2.3 (2.20)	7.90 (7.70)	6.2 (6.3)
$[\text{Cd}(\text{DPDPIH})_2\text{Cl}_2]$	3412	1685	1585	1438	451	31.70 (31.50)	2.2 (2.30)	7.60 (7.80)	10.0 (10.2)

to the $\nu(\text{M-N})$. Key data of ligand and its metal complexes are illustrated in Table-1.

Elemental analysis: Table-1 indicates the microanalysis results confirm that the results of the process with the theoretical calculations proved the validity of the molecular formula of the ligand and its metal complexes.

Electronic spectra: Most of the transition metal complexes are coloured and their colours are different from transition metal salts and the ligands. This is an important indication of coordination, therefore, the coloured complexes showed different characteristic absorption bands in their position and intensity [11,12].

The UV-visible spectra of the free azo ligand (DPDPIH) and its metal complexes were performed in a solution with concentration 10^{-5} mol/L, where ethanol was used as a solvent within the range 190-800 nm. The electronic spectra of the free azo ligand observed two high intensity bands, the first one showed at 295 nm (33898 cm^{-1}) and the second at 360 nm (27777 cm^{-1}) belonging to $\pi-\pi^*$ and $n-\pi^*$ electronic transition of aromatic ring, [13,14] respectively. The electronic spectrum of the cobalt complex, showed five bands, the first one strong band observed at 3000 nm (33333 cm^{-1}) assigned to $(\pi-\pi^*)$ transition, the other bands showed at 380 nm (26315 cm^{-1}), 431 nm (23201 cm^{-1}), 490 nm (20408 cm^{-1}) and 512 nm (19531 cm^{-1}) and assigned to charge transfer (C.T) transition for cobalt complex, ${}^6\text{A}_{1g(\text{F})} \rightarrow {}^4\text{T}_{1g(\text{F})}$, ${}^4\text{T}_{1g(\text{F})} \rightarrow {}^4\text{T}_{1g(\text{P})}$ and ${}^4\text{T}_{1g(\text{F})} \rightarrow {}^4\text{A}_{2g(\text{F})}$ electronic transition respectively. These transitions were characterized to octahedral geometry around the cobalt ion [15,16]. The spectrum of nickel(II) complex showed four peaks which appeared at 269 nm (33783 cm^{-1}) due to $(\pi-\pi^*)$, the second peak appeared at 372 nm (26954 cm^{-1}) can be assigned to charge transfer (C.T.) transition for nickel complex, whereas the other two peaks showed at 480 nm (20833 cm^{-1}) and 580 nm (17241 cm^{-1}) were found to be caused by $(d-d)$

electronic transition which were assigned to ${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{1g(\text{F})}$ and ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g(\text{D})}$ respectively. Suggesting the complex is octahedral geometry around the nickel ion [17-19]. The electronic spectrum of copper(II) complex has five absorption bands. The first one showed at 269 nm (33783 cm^{-1}) attributed to $(\pi-\pi^*)$ electronic transition and the second band showed at 365 nm (27397 cm^{-1}) can be attributed to charge transfer (C.T) electronic transition. The other three bands observed at 431 nm (23201 cm^{-1}), 485 nm (20618 cm^{-1}) and 590 nm (16949 cm^{-1}) can be assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$, ligand field (L.F) and ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ electronic transition respectively. These transitions indicated that complex is octahedral around the copper ion [20].

The electronic spectrum of cadmium(II) complex shows three bands at 205 nm (48780 cm^{-1}), 350 nm (28571 cm^{-1}) and 504 nm (19841 cm^{-1}) due to $\pi-\pi^*$, $n-\pi^*$ and charge transfer electronic transition, respectively [18]. The electronic spectrum of zinc(II) complex has three bands at 295 nm (33898 cm^{-1}), 431 nm (23201 cm^{-1}) and 566 nm (17667 cm^{-1}) assigned to $\pi-\pi^*$, $n-\pi^*$ and charge transfer electronic transition, respectively [21].

The absence of $(d-d)$ electronic transition in the cadmium and zinc complexes is due to the configuration (d^{10}) structure for the metal ions, suggesting octahedral for both complexes around cadmium and zinc ions respectively.

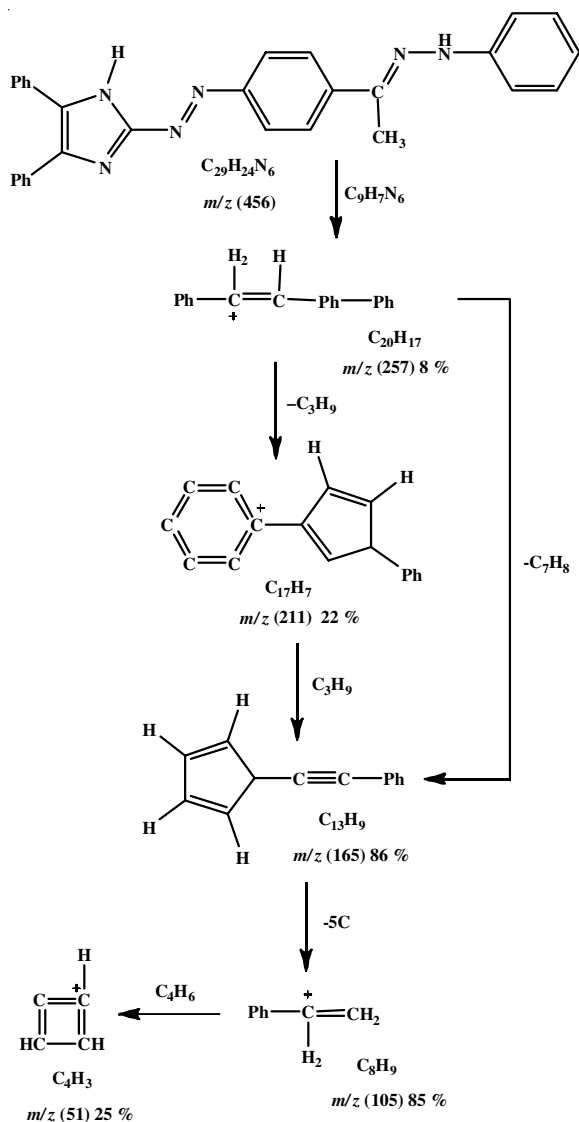
The electronic spectra of the free azo ligand and its metal complexes were demonstrated in Table-2.

${}^1\text{H}$ NMR of free ligand (DPDPIH): The proton nuclear magnetic resonance of DPDPIH was carried out in DMSO- d_6 as a solvent, the multiple signal showed at (7-8.4) ppm which belong to the protons of aromatic ring, the second signal observed at 13.69 ppm belongs to (N-H) of imidazole ring [22-25]. The multiple signals at 2.6 ppm belong to the methyl group attached at the azometine group, the signal appearing at 1.2 ppm belongs to the methyl group of the solvent [26,27]. The singlet signal showed at (11.5) ppm attributed to (N-H) of phenyl hydrazine.

TABLE-2
ELECTRONIC ABSORPTION SPECTRA DATA OF AZO LIGAND (DPDPIH) AND ITS METAL COMPLEXES

Compound	λ_{max} (nm)	Wavenumber (cm^{-1})	Absorbance	ϵ (L mol cm^{-1})	Assignments
DPDPIH	295	33898	0.75	75000	$\pi-\pi^*$
	360	27777	0.80	80000	$n-\pi^*$
[Co(DPDPIH) $_2$ Cl $_2$] Octahedral	300	33333	0.65	65000	$\pi-\pi^*$
	380	26315	0.60	60000	Charge transfer
	431	23201	0.25	25000	${}^6\text{A}_{1g(\text{F})} \rightarrow {}^4\text{T}_{1g(\text{F})}$
	490	20408	0.70	70000	${}^4\text{T}_{1g(\text{F})} \rightarrow {}^4\text{T}_{1g(\text{P})}$
	512	19531	0.80	80000	${}^4\text{T}_{1g(\text{F})} \rightarrow {}^4\text{A}_{2g(\text{F})}$
[Ni(DPDPIH) $_2$ Cl $_2$] Octahedral	296	33783	0.76	76000	$\pi-\pi^*$
	372	26954	0.80	80000	Charge transfer
	480	20833	1.25	125000	${}^3\text{A}_{2g(\text{F})} \rightarrow {}^3\text{T}_{1g(\text{F})}$
	580	17241	1.31	131000	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g(\text{D})}$
[Cu(DPDPIH) $_2$ Cl $_2$] Octahedral	296	33783	0.74	74000	$\pi-\pi^*$
	365	27397	0.76	76000	Charge transfer
	431	23201	0.25	25000	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$
	485	20618	0.80	80000	L.F
	590	16949	1.10	110000	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$
[Cd(DPDPIH) $_2$ Cl $_2$] Octahedral	205	48780	1.30	130000	$\pi-\pi^*$
	350	28571	0.92	192000	$n-\pi^*$
	504	19841	1.75	175000	Charge transfer
[Zn(DPDPIH) $_2$ Cl $_2$] Octahedral	295	33898	0.77	77000	$\pi-\pi^*$
	431	23201	0.22	22000	$n-\pi^*$
	566	17667	1.25	125000	Charge transfer

Mass spectrometer: The fragmentation pattern data for the mass spectrum of the ligand is illustrated in **Scheme-II** and Fig. 1.



Scheme-II: The fragmentation pattern of ligand (DPDPIH)

Molar conductivity: The measurements of molar conductivity of the prepared complexes were carried out using DMSO (10^{-3} M) as a solvent at room temperature. The values indicate that all the metal complexes are non-electrolyte in nature (Table-3).

Magnetic susceptibility: The measurements of the metal complexes show the values of magnetic susceptibility and they are illustrated in Table-3.

TABLE-3
MOLAR CONDUCTIVITY AND MAGNETIC SUSCEPTIBILITY DATA OF THE COMPLEXES

Compound	μ_{eff} (BM)	Molar conductivity ($\text{s cm}^2 \text{mol}^{-1}$)
[Co(DPDPIH) $_2$ Cl $_2$]	4.02	12.56
[Ni(DPDPIH) $_2$ Cl $_2$]	3.10	16.60
[Cu(DPDPIH) $_2$ Cl $_2$]	1.72	15.40
[Zn(DPDPIH) $_2$ Cl $_2$]	Diamagnetic	13.46
[Cd(DPDPIH) $_2$ Cl $_2$]	Diamagnetic	17.66

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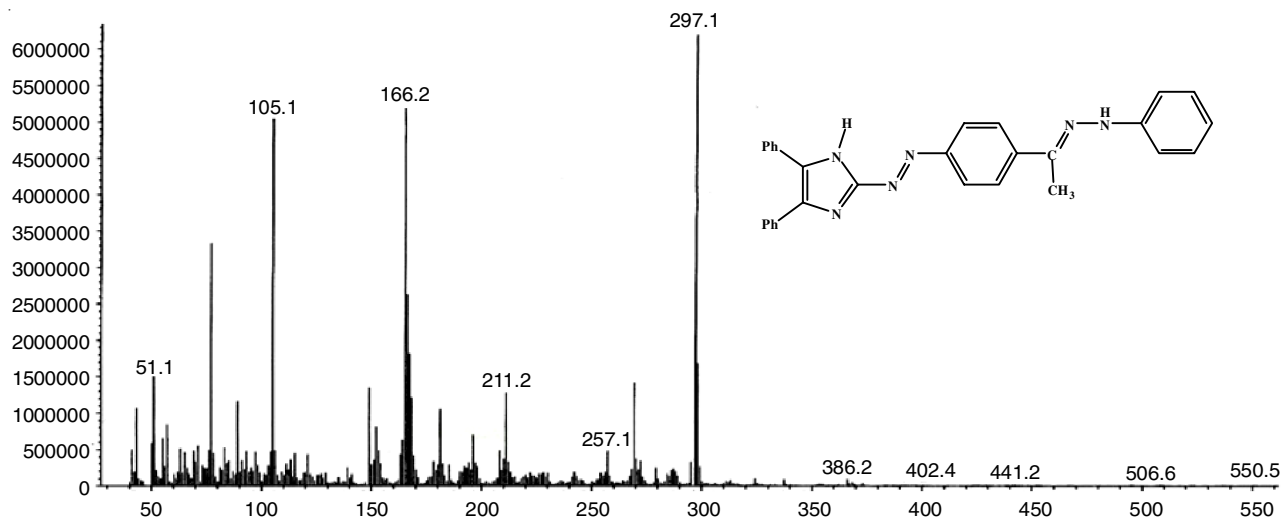


Fig. 1. Mass spectrum of azo ligand, 4,5-dimethyl-2-((3-(E)-1-(2-phenylhydrazono)ethyl)phenyl)diazanyl)-1H-imidazole (DPDPIH)

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