Acta Chimica Pharmaceutica Indica

Research | Vol 7 Iss 1

Preparation and Characterization of New Azo Ligand N-[(1-(4-(4,5-Dimethyl-1h-Imidazol-2-Yl) Diazenyl) Phenyl-3-(Trifluoromethyl)] Aniline With Some Metal Complexes Ions

Waleed A Mahmoud[1], Amir Musa[2] and Nadia H Obaid[3*]

[1]Faculty of Science, University of Baghdad, Iraq

[2]Faculty of Science, University of Kufa, Iraq

[3]Faculty of Education for Girls, University of Kufa, Iraq

[*]**Corresponding author:** Nadia H Obaid, Department of Chemistry, Faculty of Education for Girls, University of Kufa, Tel: 7265217601 (0) 00964; E-Mail: nadia.alhasnawi@uokufa.edu.iq

Abstract

A ligand which is derived from 4,5-diphenyl imidazole has been prepared, the co-ordination of this ligand with the metal ions of Co (II),Ni(II),Cu(II),Zn(II),Cd(II) under optimum circumstances of concentration and PH , the results have shown that the concentration of these complexes would be comply with Lambert- Beers law ,based on these results ,a mole ratio has been calculated for the complexes of the mentioned ligand ,so the ratio of (metal :ligand) has been found equal to (1:2) , as the ligand and its metal complexes has been distinguished using UV- Visible spectrum and IR spectrum , the H^1 NMR has shown a harmonization with chemical formulas and the results of magnetic sensitivity of metal complexes ions has confirmed that geometric figure of octahedral.

Keywords: Spectral; Characterization; Imidazole; Ligand

Received: March 15, 2017; **Accepted:** April 12, 2017; **Published:** April 19, 2017

Introduction

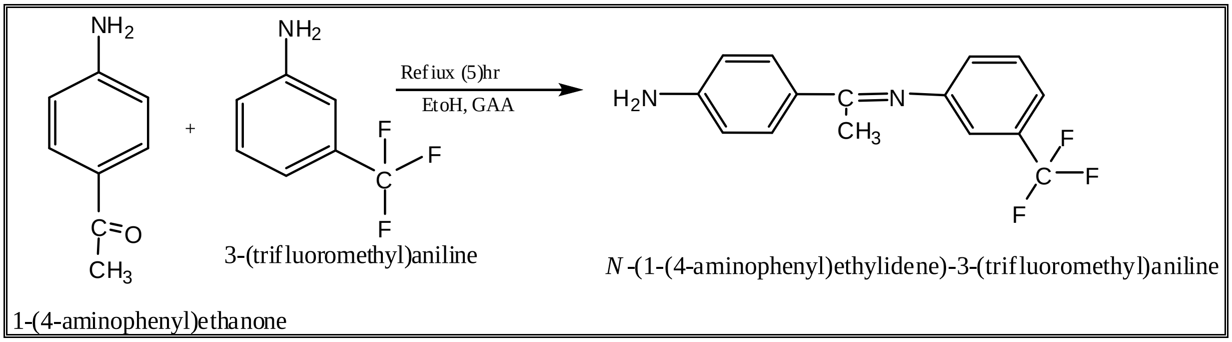
Azo compounds cover about 60 – 70 % from all azo dyes [1]. It was named with this name because it has azo group (N=N) related to SP^2 hybridization which is connected with aromatic system [2],due to the wide usage of azo dyes in organic characterization it been used as optical reagents to measure the intensity of photolithography [3]. It been used also in analytical chemistry in extraction operating such as orange methyl and red methyl and also been used in wool & wood and silk manufacturing [4]. Also it been used in medicine as germs inhibitors [5]. Prontisl from azo compounds been used as anti-cancer medicament [6]. The homo cyclic azo compounds considered as important reagents in analytical chemistry as it used as indexes or spectra- reagents [7]. These reactors specify by containing of more than one site could be used for coordination with metal ion, whereas aromatic cycles on both sides of azo group contains one or more of hybrid atoms (O, N, S), Imidazole expression is called on heterocyclic quinary which contains amino group added to secondary nitrogen atom, a series of azo- imidazole ligands prepared by added diazonium salt to imidazole ethanol solution in a weak base medium. Also many of substituted azo- imidazole ligands prepared in two position (4,5) [8].

Experimental Part

Citation: Bratty MA, Manoharan G, Hassan AA, et al. Reverse Phase - High Performance Liquid Chromatography Determination of Levocetirizine and Pseudoephedrine in Tablet Formulation. Anal Chem Ind J. 1(1):104.

The step was Preparation of Schiff base

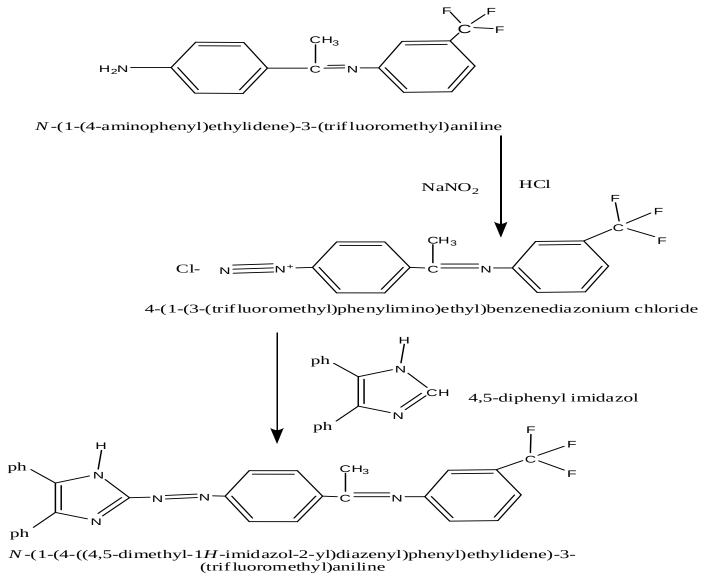
Prepared by reaction 1.35 gm of 4- amino aceto phonon with 2.5 ml of 3- (Tri flour methyl) aniline all dissolved in (25 ml) ethanol then all mixture and glacial acidic acid added in drops and the solution reflexed to term 5 hours at temperature (100 - 120) C° to the completion of the reaction the solution placed in a watch glass and left to dry (SCHEME 1).



SCHEME. 1**. Preparation of the Schiff base**

Ligand Preparation (DPEPI)

The ligand has been produced by solving an amount of (0.5 m mol) (0.253 mg) of the first Schiff base in a mixture of (HCl 2ml and a 20 ml of distilled water). The mixture has been chilled out via ice to reach a temperature of (0C°). Then an amount of (0.5 m mol) (0.035 mg) sodium nitrite which is been previously solved in (10ml) distilled water has been added to the mixture a drop by drop with continuous stirring with a maintained temperature below (5˚C). Then this mixture has been left for stabilization, a solution of dyazanium then added drop by drop with continuous stirring and fixed temperature to a (0.5m mol), (0.11mg) of (4, 5 diphenyl imidazole) which was previously solved in an amount of (100ml) of alcohol ethyl. Then an (1gm) of (NaOH) which is dissolved in alcohol was added to the mixture this will lead the mixture to be reddish. Then the mixture should be left to the next day. For the purpose of neutralization a diluted (HCl) has been added as a result orange-reddish crystals have been formed, then the settled matter has been filtered and washed with non-ionic water to remove sodium chloride then it was dried out and recrystallized using ethanol (SCHEME 2).



SCHEME. 2. **Preparation of the ligand**

Result and Discussion

Preparation of ligand complexes with metal ions

The solid complex of the ligand(DPEPI) was prepared from (1.012 g) (0.002) ml of the solid ligand in (30 ml) of ethyl alcohol, then it was added to it (0.001 ml) of the metal ion chlorides mentioned separately and dissolved in (30 ml) Where the change in the color of the mixture leaving the solutions for three hours after the deposition of the solid complexes, nominated and returned crystals with absolute ethanol and TABLE 1 shows some physical properties and the percentage of ligand and its complexities.

TABLE 1. Shows some physical properties and the percentage of ligand and its complexities

No	**Compound**	**M.wt**	**Optimal PH**	**Colour**	**m.p C°**	**Yield %**
1	L (DPEPI)	509	7	Reddish orange	117-119 decomp.	65%
2	[Co (DPEPI)$_2$ Cl$_2$]	1147.6	8.5	Dark red	186-188	82%
3	[Ni (DPEPI)$_2$ Cl$_2$]	1157.6	9	purple	159-161	77%
4	[Cu (DPEPI)$_2$ Cl$_{2]}$	1152.6	9	puce	97-99	74%
5	[Zn (DPEPI)$_2$ Cl$_2$]	1155.4	8	puce	153-155	79%
6	[Cd (DPEPI)$_2$ Cl$_2$]	1201.4	7.5	Dark red	95-97	83%

H^{1}NMR Spectrum of new ligand (DPEPI)

The H^{1}NMR spectrum express signal at (7.5- 8.2) ppm get into a rut ring aromatic proton and two single signal at (13.74) ppm get into a rut (NH) ring imidazole [9-11], as express spectrum signal at (2.6-3.4) be accustomed to group methyl proton anomaly for the solvent (DMSO) and single signal at (1.8) ppm get into a rut group methyl proton attached azo Methuen group [12] (FIG. 1).

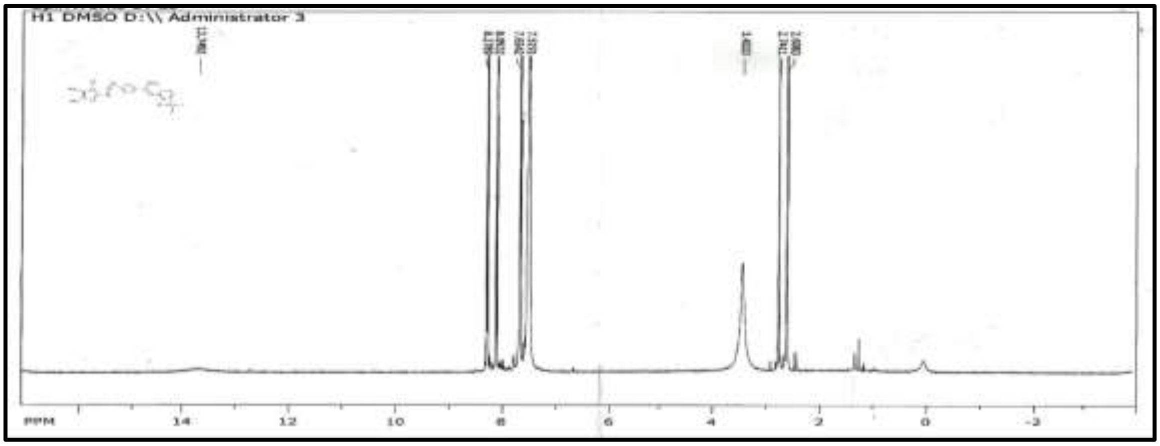


FIG 1. **H^{1}NMR spectrum of ligand (DPEPI)**

The infrared spectrum of the ligand (DPEPI) and its metallic complexes

The infrared spectra of the ligand show a continuous frequency of (NH) ν in the heterocyclic imidazole ring. This package is weak at the site (3439) [13,14] cm^{-1}. When compared with the spectra of the metal complexes, no noticeable changes Indicates their non-participation in the process of coordination. The ligand spectrum also showed a weak absorption package at the frequency of (1678) cm^{-1} which belongs to the group of azo methane (C=N) ν. This package showed no changes in the infrared spectra of the metal complexes, indicating that they did not coordination in the coordination as well, (C = N) ν due to the heterocyclic imidazole loop absorption pack at the frequencies of (1546) cm^{-1} [15]. This package showed remarkable changes in the infrared spectra of the metal complexes. This shows their coordination in the process of coordination, (C-N) ν for the imidazole ring within the range of (900-1000) cm^{-1} [16]. For frequency bands (N = N) ν for the azo bridge group is shown at (1498) cm^{-1} [17]. This package has obvious changes in the spectra of the metal complex when compared to the ligand spectrum and its displacement to lower wavelength, the group is coordination with metal ions. The infrared spectra of the metal complexes also show new absorption bundles (M-N) ν at (400-500) cm^{-1}[18]. TABLE 2 and 3 shows the packaging of the effective aggregates of the compound and its metal complexes (FIG. 1-7)

TABLE 2**. Characteristic IR absorption bands of the ligand (DPEPI) and its complexes in cm^{-1}**

Compounds	**ν(N-H)imid**	**(C=N)Schiffν**	**(C=N)Imidazoleν**	**(N=N)ν**	**(C-N)ν**	**(N-M)ν**
DPEPI	3439br	1678 w	1546 w	1498m	966w	------
Co(II)Complex	3257 br	1662 st	1595st	1436m	958m	426w
Ni(II)Complex	3423 br	1681 st	1597st	1446m	960m	449w
Cu(II)Complex	3442 br	1681 st	1595st	1444m	962m	426w
Zn(II)Complex	3431br	1680 st	1598st	1440m	962m	445w
Cd(II)Complex	3410br	1680 st	1595st	1472m	960m	432w

S: strong, w: weak, sh: shoulder, m:medium,br:broad

TABLE 3. **Types of electron spectra and locations of DPICI absorption peaks and their mineral complexes in ethanol**

Compound	**Type of transition**	**λ_{max}(nm)**	**Proposed structure**
(DPEPI)	$n\rightarrow\pi^*$ & $\pi\rightarrow\pi^*$	450	…….
$[Co(DPEPI)_2Cl_2]$	C.T	477	Oh
$[Ni(DPEPI)_2Cl_2]$	C.T	498	Oh
$[Cu(DPEPI)_2Cl_2]$	C.T	494	Oh
$[Zn(DPEPI)_2Cl_2]$	C.T	538	Oh
$[Cd(DPEPI)_2Cl_2]$	C.T	506	Oh

FIG. 2. **IR- spectrum of ligand (DPEPI)**

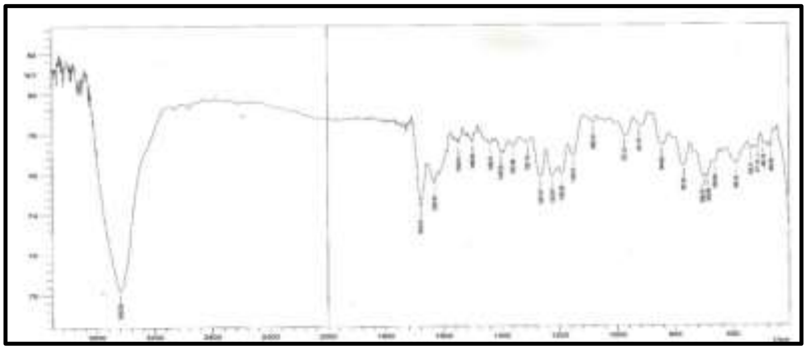


FIG. 3. **IR- spectrum of $[Co (DPEPI)_2Cl_2]$.**

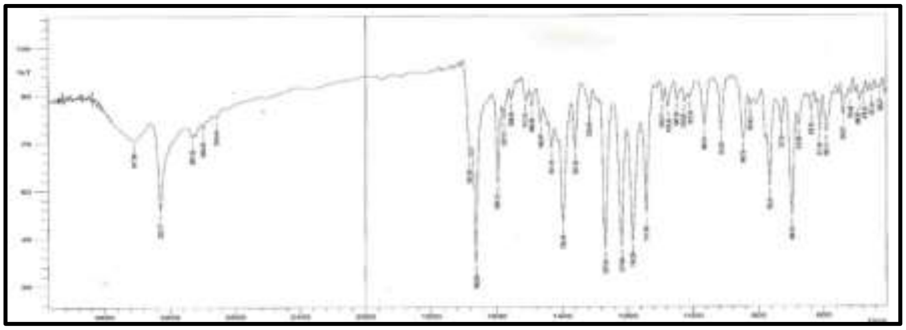


FIG. 4. **IR- spectrum of $[Ni (DPEPI)_2Cl_2]$.**

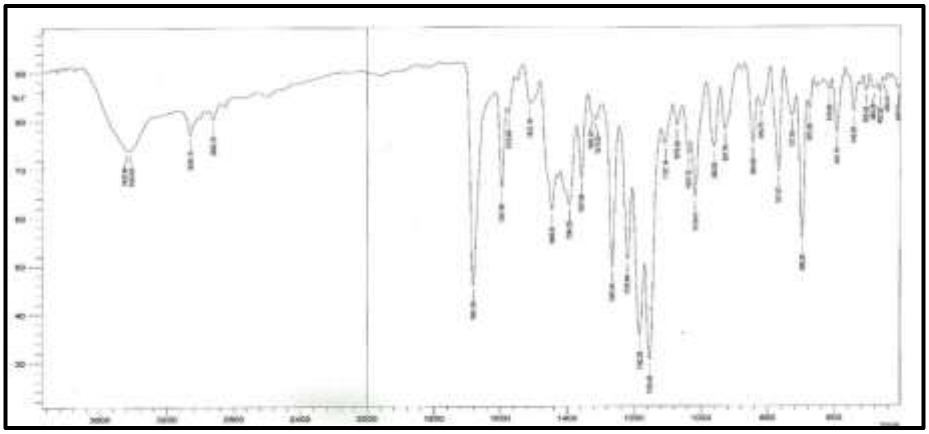


FIG. 5. **IR- spectrum of [Cu (DPEPI)$_2$Cl$_2$].**

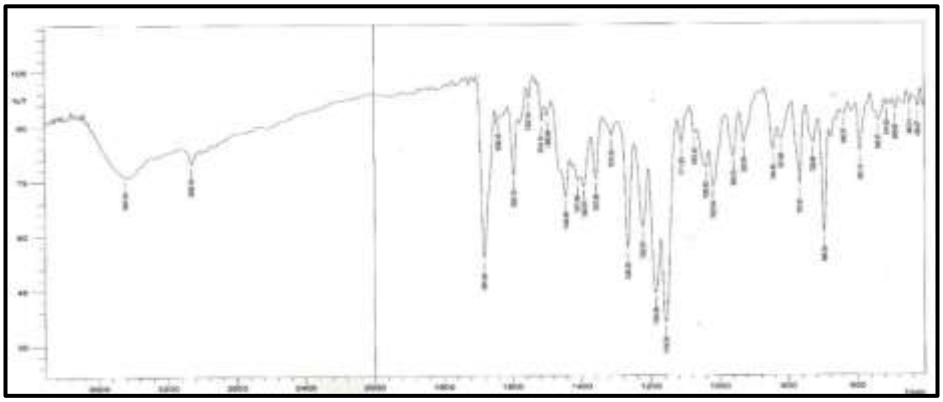


FIG. 6. **IR- spectrum of [Zn (DPEPI)$_2$Cl$_2$].**

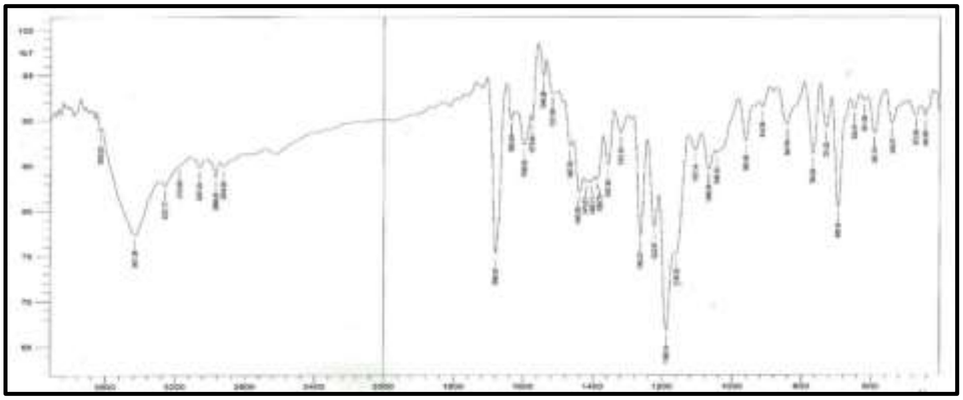
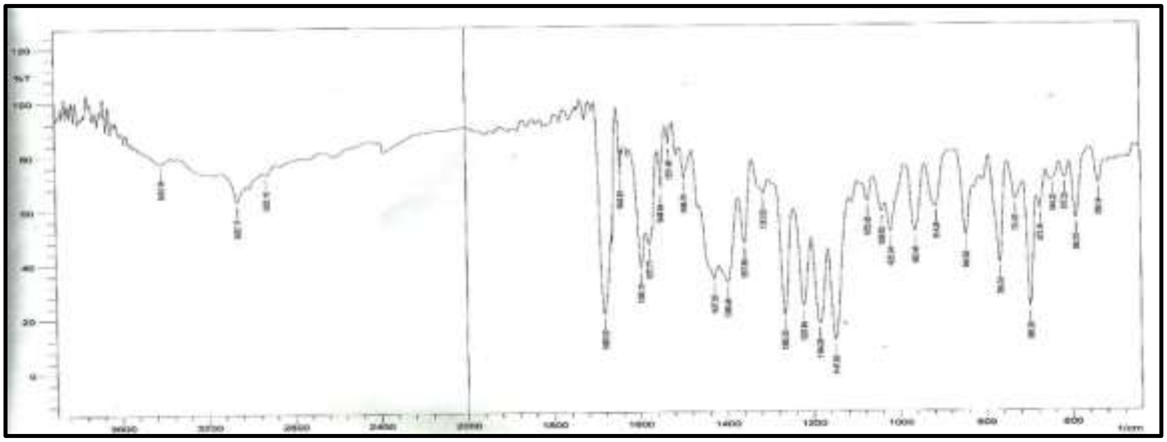


FIG. 7. **IR- spectrum of [Cd (DPEPI)$_2$Cl$_2$].**



Spectra of UV – Visible

One of the important methods used in the field of coordination chemistry is the ultraviolet-visible spectra, in which the effect of coordination on the quality of electronic transitions in the spectra of metal complexes is studied and compared with free ligand spectra. The figure returning to the ligand spectrum prepared and dissolved in ethyl alcohol shows three main bands, the first beam within the range (222-210) nm identified for electronic transmission (π→π*) of the imidazole molecule is heterocyclic while the second wavelength (296)nm for the electronic transmission of(π→π*) to the benzene ring associated with the imidazole ring via the azo bridge group, as reported in literature[19,20], and the third beam in the ligand spectra (DPEPI) at (450) nm The interior of the ligand, which is in the direction of the heterocyclic imidazole ring, was found to have suffered a red shift toward longer wavelengths in the spectra of metal complexes as reported in the literature [21-23],The spectra of the (d-d) field ligand where they are not studied in the complex because they occur under the top of the transmission of the charge formed in the metal complexes, can be included in the sites of the absorption bands of the liquefied and its metal complexes in the **TABLE 3 (FIG. 8-13)**

FIG. 8. **UV-Vis spectrum of ligand (DPEPI)**

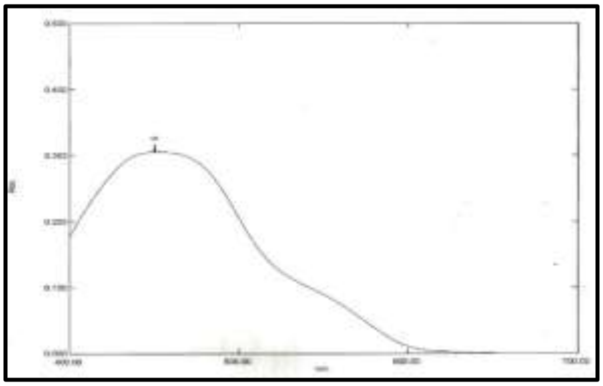


FIG. 9. **UV-Vis spectrum of $[Co (DPEPI)_2Cl_2]$**

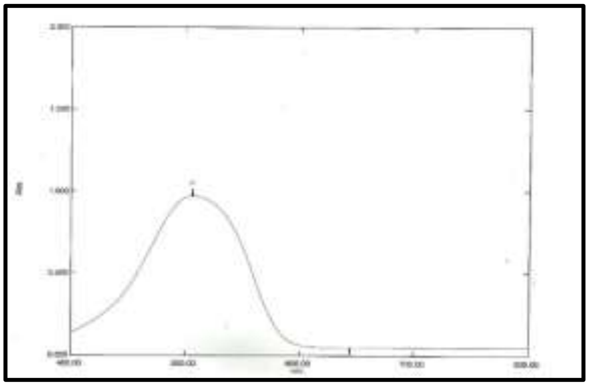


FIG. 10. **UV-Vis spectrum of $[Ni DPEPI)_2Cl_2]$**

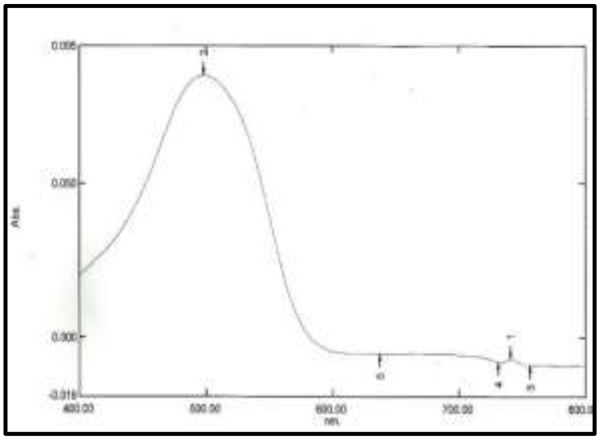


FIG. 11. **UV-Vis spectrum of $[Cu (DPEPI)_2Cl_2]$**

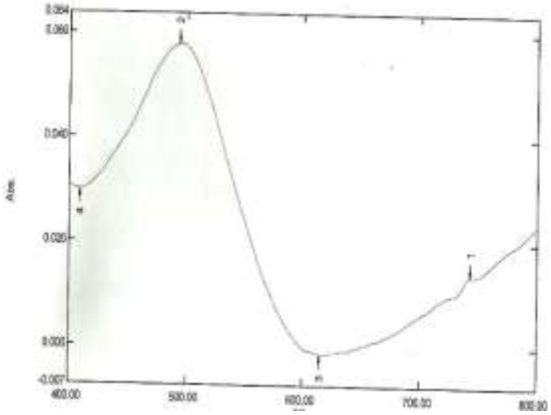


FIG. 12. **UV-Vis spectrum of $[Zn (DPEPI)_2Cl_2]$**

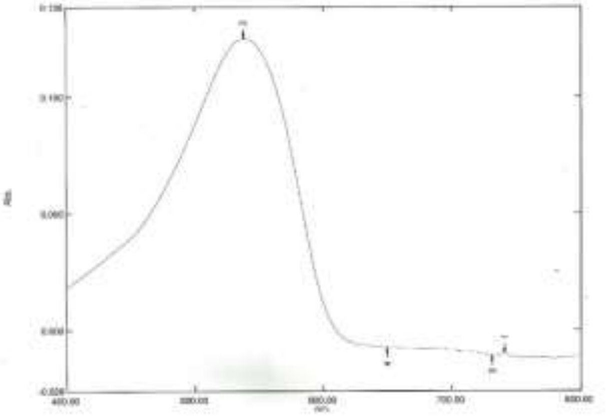
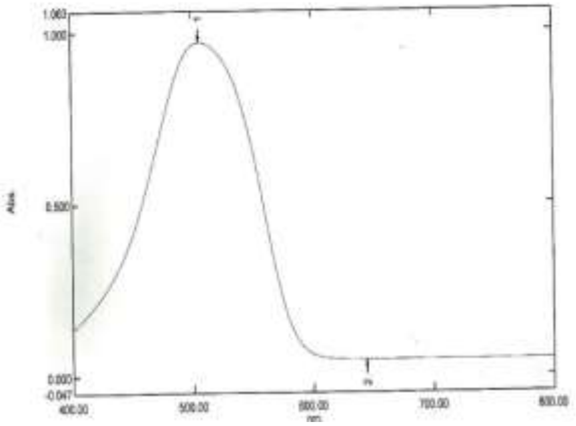


FIG. 13. **UV-Vis spectrum of [Cd (DPEPI)$_2$Cl$_2$]**.



Magnetic sensitivity measurements

Measured magnetic sensitivity complexes metallic whole prepared, and are these measurements means a successful and simple through which knowledge of the electronic arrangement and case phosphorylation of ion metalloproteinase and specifies the number of electrons individual in ion metalloproteinase and inference being high twines or low for twines, showing the magnetic properties of complexes through the movements Permic and Aloorbatallah electrons centers, metal, and when a correction dia magnetic induction through the influence of the magnetic field of ligand depending Pascal tables turned out that the values of the magnetic moments of all the complexes prepared in line with the values of octahedral high surfaces twines [24].As for bilateral and complexes of zinc and cadmium positive charge are characterized by being with the properties of magnetic dia because of the recent electronic cover is full (d^{10}) [25].

Molecular conductivity measurements

Molecular conductivity measurements of the ligand complexes recorded in the dimethyl sulfoxide (DMSO) solvent at a concentration of (1×10^{-3}) M and the laboratory temperature are determined to determine the ionic formulas of the complexes. The degree of electrical conductivity is proportional to the number of charged but low- The reason for the use of the solvent(DMSO) in the conductivity measurements is that it is an organic solvent with a high isolation and low viscosity strength, and the solubility of the complex prepared [26].When observing the results of the molar conductivity (TABLE 4). The absence of the ionic properties of all complexes prepared in the literature [27].

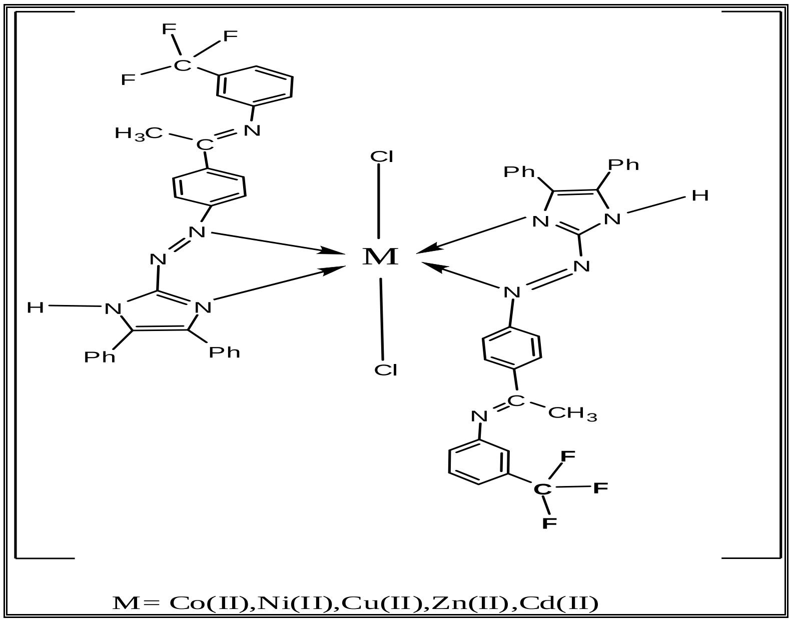
TABLE .4**. Shows the magnetic sensitivity values and the molecular conductivity of the ligand complex (DPEPI)**

Compound	μ_{eff} (B.M)	Moler Condítivity ($S.cm^2.mol^{-1}$)
$[Co(PDEPI)_2Cl_2]$	4.02	13.7
$[Ni(PDEPI)_2Cl_2]$	3.16	zero
$[Cu(PDEPI)_2Cl_2]$	1.71	11.46
$[Zn(PDEPI)_2Cl_2]$	Dia	4.26
$[Cd(PDEPI)_2Cl_2]$	Dia	16.53

Steric shapes proposed metal complexes

Based on the results obtained, the ligand used a two-stroke behavior with Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) ions. (N3) for the heterocyclic imidazole ring and the nitrogen atom of the far-off imidazole group of imidazole and the azomethin group was not involved in the coordination of the calcified ligand. The reason is that the coordination of this group with the metal ions needs high activation energy compared with Azo bridge group that ligand with metal ions at a temperature (14) The vacuum formula of metal ions (FIG .14)

FIG.14. **Proposed form of metallic complexes with ligand (DPEPI)**



REFERENCE

1. Tan GGN. Synthesis, properties and Application of organic dyes and Pigments (Ph. D. Thesis). Wageningen University; 2001
2. Zollinger H. Color chemistry; synthesis, properties and application of organic dyes and pigments. Wiley Company.
3. Hoffman VR. Organic chemistryanintermediate text. Inc America,2014.
4. Desai KC, Desai RK. Arabian Journal of science and Engineering of India, vol.29, 1A,(2004).
5. Bondock S, Gaber A. Utility of cyanoacetic acid hydrazide in heterocyclic synthesis. ARKIVOC , 2006:113-156 ,
6. Rappaport Z. The chemistry of Anilines part1. Wiley Publication,2007
7. Wada H, Nakazwa O, Nakagawa G. Evaluation of 1-(2-thiazolylazo)-2-hydroxy-3-naphthoic acid as a metallochromic indicator. Talanta, 1972; 27:94-102.
8. Hofer E, Wong W. Synthesis, Structural Characterization, Solvatochromism, and Electrochemistry of Tetra-Osmium Carbonyl Clusters Containing Azo-Ligand. Eur J Inorg Chem, 2001; 12:3163.
9. Chauveau E, Marestin C, Schiels F, et al. Osmium Carbonyl Clusters Containing Azo-Ligand Green Chemistry, 12, 1018, (2012).
10. Zamani K, Mobinikhaedi A , Forughifar N, et al. Isola.tion and Characterization of a Smectite as a Micro-Mesoporous Material from a Bentonit. Turk J Chem, 2003; 27.
11. Maru M, Shah KM. Sulfonic acid functionalized silica nanoparticles as catalysts for the esterification of linoleic acid J Chim Pur Res,2012; 4.
12. Mohamed GG, Omar MM, Ibrahim AA. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy Elec J Molec Chim, 2009; 44:4801.
13. Sahep HE. DNA Cleavage Activity of Diazonium Salts: Chemical Nucleases (M.Sc. Thesis). College of Science , University of Kufa,2012
14. M.Gomleksiz, C.Alkan , and B.Erdem. Synthesis, characterization and antibacterial activity of imidazole derivatives of 1,10-phenanthroline and their Cu(II), Co(II) and Ni(II) complexes. S Afr Chem, 2013; 66.
15. Al-Hassany MS. Synthesis and characterization of new azo dye ligand derived from 4,4'- sulfonyl dianiline and 4-methy imidazole and its binuclear complexes with Ni(II), Pd(II), Ag(I) and Au(III) (Ph.D Thesis). College of Science, University of Babylon, Iraq.
16. Ali MA. Nonanuclear lanthanide (III) nanoclusters: Structure, luminescence and magnetic properties (Ph.D. Thesis). University of Bagdad, (2001).
17. Vadher BG, Zala VR. On the estimation of manganese in spiegeleisen, and of manganese and iron in manganiferous iron ores. Inter J Chem Soc, 2011;1.
18. Karipcin F, Dede B, Ozkorucuklu PS, et al. The structure and tautomerism of azo coupled β-Enaminones Dyes and Pigments, 2010; 1:85.
19. Raut TK, Shirote PJ. Synthesis and Characterization of Novel Amide Derivatives of Nitro-Imidazole. Der Pharma Chemica, 2012; 4: 1435-1439.
20. Jana SM, Pramanik KA, Kundu S , et al. Synthesis, X-ray structure, spectroscopic and DFT study of cis-[Ru(PPh3)(L)X2] complexes (X = Cl−, Br−, I− and NCS−) (L = 1-methyl-2-{(o-thiomethyl)phenylazo}imidazole) Inorganica Chimica Acta, 2013; 394: 583-590.
21. Pratihar P, Mondal TK, Raghavaiah P, et al. Synthesis and Spectroscopic Characterization. Inorganica Chimica Acta, 2010; 363:831.

22. Datta P, Sardar D, Saha R, et al. Structure, photophysics, electrochemistry and DFT calculations of [RuH(CO)(PPh3)2(coumarinyl-azo-imidazole)]. Polyhydron,2013; 53: 193-201.
23. El-Baradie K, El-Shakwy R , El-Ghamry H, et al. Synthesis and characterization of Cu(II), Co(II) and Ni(II) complexes of a number of sulfadrug azodyes and their application for wastewater treatment. Spec Chim Acta,2014; 121:180.
24. Skooge AD. Fundamentals Analytical Chemistry. Wiley Publication. New York.
25. Mawar KN, A Joshi, Ram O, et al. Ablation of solids by Femtosecond Lasers: Potential applications; J. Chem.Bio Phys Sci, 2014; 4.
26. Shaker S, Farina Y , Mahmmod S, et al. Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Mixed Ligand Complexes of Theophylline and Cyanate: Synthesis and Spectroscopic Characterization. Mod App Sci, 2009;3.
27. Hassan AI. Cinnamic acid Derivatives and 4-Aminoantipyrine Amides – Synthesis and Evaluation of Biological Properties. Res J Chim Sci 2013;3.