Preparation and Identification of Some New Mixed ligand Complexes Containing Imidazole and 1,10-phenanthroline Compounds

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Abstract

New mixed ligand complexes of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) were prepared and identified. We prepared new azo imidazole compound and investigated the ternary complexes of (4- SuMBAI) and (1,10-Phenanthroline) with different transition metal ions by available analytical and spectral tools. Based on data obtained, the octahedral geometry was suggested for all mixed ligand complexes.

Keywords: Preparation, mixed ligand complexes, identification.

الخلاصة

تضمن هذا البحث تحضير مركب آزو جديد مشتق من الإميدازول وهو (4- SuMBAI=L) وذلك بإزواج ملح الديازونيوم لملح السلفانيل أمايد مع المركب 5,4- ثنائي (4-ميثوكسي فنيل) بصفته إميدازول قاعدة إزواج في محيط قاعدي كحولي. شخص الليكاند بعد ترسيبه وتنقيته بالوسائل التحليلية والطيفية المتاحة منها التحليل الدقيق للعناصر والأشعة فوق البنفسجية – المرئية وتحت الحمراء كما حضرت بعض معقدات مزيج الليكاند لمركب الآزو إميدازول المذكور مع الليكاند (10,1- فينانثرولين) لأيونات كل من الكوبلت والنيكل والنحاس والخارصين والكادميوم ثنائية الشحنة الموجبة وذلك من مفاعلة المحاليل المائية للأيونات المذكورة مع محلول كحولي لمزيج الليكاندين وبنسبة (1 :1: 1). وقد تم التعرف على هوية الليكاند ومعقداته عن طريق وسائل التحليل المتاحة منها طيف الكتلة وطيف الرنين المغناطيسي و الاشعة تحت الحمراء و والاشعة فوق البنفسجية- المرئية والتحليل الدقيق للعناصر وحساب نسبة الفلز في معقده فضلا عن الحساسية المغناطيسية والتوصيل الكهربائي المولاري. ومن خلال نتائج هذه التحاليل تم اقتراح الشكل ثماني السطوح لجميع معقدات مزيج الليكاند المحضرة.

1. Introduction

Imidazole is a commonly named of 1,3-diaza-2,4-cyclopentadiene[1]. This compound and their derivatives play an important role in many areas such as medicinal chemistry [2], material sciences for nonlinear optical application [3], in addition of some imidazole derivatives are used as a catalyst in industrial uses [4]. Azo imidazole molecules bears the azoimine (–N=N–C=N–) functional group, and it is an efficient π– acid system, therefor these organic molecules used as ligand to forming stable complexes with 3d-transition metal ions and non-transition (Group 12 elements) metal ions [5-9]. On the other hand, 1,10- phenanthroline (1.10- phen) classified as chelating nitrogen donor ligand which it form stable complexes with transition and non-transition metal ions, since their coordination may affect the properties of the photosensitive group giving rise to an optical response [10- 12]. It is well known been also reported that some ternary complexes of (phen) have an antitumor activity where it inhibited DNA or RNA polymerase activities [12, 13]. In this paper, we report the preparation of new azo imidazole ligand and the attempt to prepare and identify some of mixed ligand complexes derived from this ligand and 1,10-phenanthroline (1,10- phen).

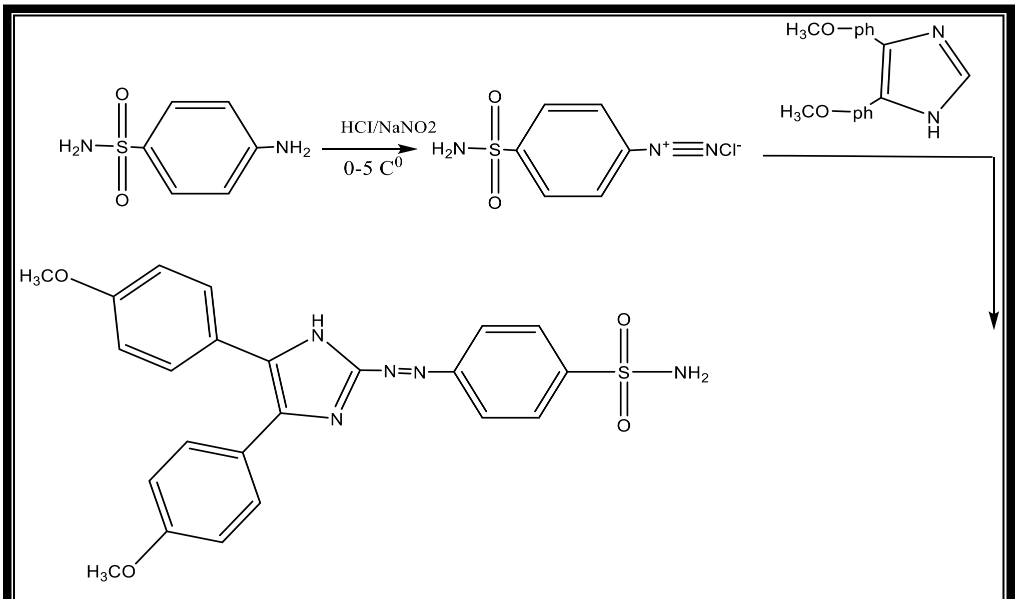
2. Experimental

2.1. Reagents and physical measurements

All chemicals were of highest purity and used as supplied by the manufactures, except of 4,5-Bis(*p*-methoxy phenyl)- imidazole which was prepared as described before [14]. Melting points were determined in an open glass capillary tube using a Stuart melting point SMP10 and are uncorrected. The mass spectrum analysis of ligand was done on a Shimadzu Agilent (HP) 5973 mass spectrometer. ^{1}HNMR spectrum was conducted using a Bruker Biospin Gmph instrument (500 MHz) in DMSO-d_6 as a solvent consisting TMS as the internal reference compound. Microanalytical data (Carbon, Hydrogen and Nitrogen) was carried out on Euroverctor, EA300A elemental analyzer. FTIR spectra studies were carried out using KBr discs on FTIR Testscan Shimadzu 8400 Spectrophotometer in the range of 4000 – 400 cm^{-1}**.** Electronic spectra were recorded in ethanol on Shimadzu model 1700 UV–Vis Spectrophotometer. The metal content of the complexes was measured using atomic absorption technique by Flam Atomic Absorption (q AA 680). Magnetic susceptibilities were measured as powder samples using Faraday method, Balance Magnetic (Sherwood Scientific) was employed for this purpose. Molar conductance measurements were determine in DMSO by using a Digital Conductivity Series Ion. Lab.(720).

2.2. Preparation of the azo ligand (4-SuMBAI)

This heterocyclic azo ligand was prepared as described before [14] (Scheme.1). A solution of sulfanilamide (1.72 g, 10 mmol) in (100 mL) water and (3 mL) concentrated HCl (37%) was stirred until a clear solution was obtained. This solution was cooled to (0–5 ^{O}C) and while maintaining the temperature below (5 ^{O}C) a solution of sodium nitrite (0.75 g, 11 mmol) in 10 mL water was then added drop by drop. The resulting mixture was stirred for (30 min) in an ice bath and excess nitrite was destroyed by addition of urea [15]. The resulting diazonium chloride solution was mixed with coupling component 4,5-Bis-(*p*-.Methoxy phenyl) imidazole (2.80 g, 10 mmol) dissolved in (150 mL) alkaline ethanol cooled below (5 ^{O}C). After leaving in the refrigerator for 24 hour, the mixture was acidified with dilute hydrochloric acid until (pH ~6). The red-violet crude precipitate was filtered and washed several times with distilled water, air dried and twice recrystallized from hot ethanol, and then dried in oven at (80 ^{O}C). Some analytical and physical data for this azo dye was tabulated in Table (1) .



4-((5-(4-((λ^{1}-oxidaneyl)-λ^{5}-methyl)phenyl)-4-(4-methoxyphenyl)-1*H*-imidazol-2-yl)diazenyl)benzenesulfonamide

Scheme. 1: Preparation of the ligand (4-SuMBAI)

2.3. Preparation of the mixed ligand complexes

General procedure for preparation chelate complexes, the aqueous solution of respective salts [$CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$ and $CdCl_2$], was slowly mixed with hot mixture ethanolic solution of (4-SuMBAI) and (1,10-phen) ligand, in (1:1:1) (L: M: L) molar ratio. After the addition was complete, the reaction mixture was refluxed for (90 min) then cooled. The solids that precipitate were filtered off, washed with (5 mL) hot (50%) (ethanol : water) to remove any traces of the unreacted starting materials air dried and recrystallized from ethanol and heated in the oven at (90 ^{O}C). all data for these compounds tabulated in Table (1).

3. Results and Discussion

3.1. Identification of azo imidazole and mixed ligand complexes

The azo ligand was violet semi crystal, but all ternary metal complexes are fine powder, vary in color depended of metal ions, stable, non-hygroscopic solids and are soluble in most organic solvents such as methanol, ethanol, dimethylformamide, dimethyl sulfoxied, chloroform, acetone, and pyridine giving stable solutions at room temperature. The analytical data of prepared compounds presented in Table (1), are in good agreement with the calculated values which suggest that the metal and the two ligands (4-SuMBAI=L_1) and (phen=L_2) were coordinated in the ratio (1:1:1) (L_1:M:L_2). Based on the analytical data, [Co (L_1) (L_2) Cl_2]. H_2O, [Ni(L_1) (L_2) Cl_2]. H_2O, [Cu(L_1) (L_2) Cl_2]. H_2O, [Zn(L_1) (L_2) Cl_2]. H_2O and [Cd(L_1) (L_2) Cl_2]. H_2O. are the empirical formulae suggested for these chelate complexes. The molar conductance at room temperature was determined using (10^{-3}M) solutions of the chelate complexes in the solvent dimethyl sulfoxied. These values support the non-electrolytic nature of all the complexes. The conductance values along with the magnetic moments are also shown in Table (3).

Table(1): Some physical and analytical data of the ligand (4-SuMBAI) and metal chelate complexes

Compound	Formula	m.p. °C	Yield%	Color	Found (Caled) %)			
					C	H	N	M
(SuMBAI) = L_1	$C_{23}H_{21}N_5SO_4$	257-259	80	Violet	59.61 (59.69)	4.56 (460)	15.12 (15.21)	....
[Co(L_1)(L_2) Cl_2].H_2O	$C_{35}H_{31}N_7SO_5Cl_2Co$	203-205	75	Red	53.13 (53.23)	3.69 (3.74)	12.39 (12.44)	7.44 (7.59)
[Ni(L_1)(L_2) Cl_2].H_2O	$C_{35}H_{31}N_7SO_5Cl_2Ni$	216-218	76	Reddish violet	53.13 (53.34)	3.69 (3.72)	12.40 (12.47)	7.45 (7.58)
[Cu(L_1)(L_2) Cl_2].H_2O	$C_{35}H_{31}N_7SO_5Cl_2Cu$	209-211	78	Deep-red	53. 50 (53.65)	3.71 (3.76)	12.47 (12.49)	6.81 (6.96)
[Zn(L_1)(L_2) Cl_2].H_2O	$C_{35}H_{31}N_7SO_5Cl_2Zn$	93-95	75	Deep-red	52.71 (52.78)	3.66 (3.68)	12.29 (12.32)	8.20 (8.26)
[Cd(L_1)(L_2) Cl_2].H_2O	$C_{35}H_{31}N_7SO_5Cl_2Cd$	153-155	72	Red	49.77 (49.81)	3.45 (3.49)	11.06 (11.14)	13.31 (13.43)

L_1= (4-SuMBAI) and L_2= (1,10-phen)

3.2. Mass spectrum of azo ligand (4-SuMBAI)

Mass spectrum of azo compound is given in Fig(1). The mass spectrum pattern give the expected molecular ion peak at (*m*/*z* 463). The base peak was observed at (*m*/*z* 309) corresponding to the 4,5-Bis-(*p*-.Methoxy phenyl) imidazole connected with (azo-group)

[16]. Another fragments at (*m/z* =279 and 219) due to 4,5-Bis-(*p*-.Methoxy phenyl) imidazole and 4,5-(di phenyl) imidazole respectively.

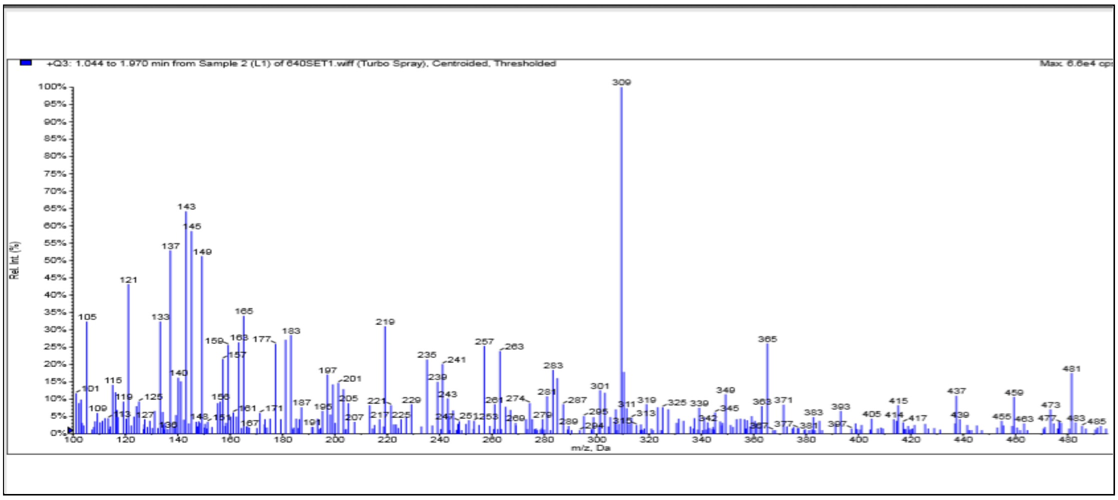


Fig.1 :The mass spectrum of azo ligand (4-SuMBAI)

3.3. ^{1}HNMR Spectrum of azo ligand (4-SuMBAI)

^{1}HNMR spectrum of this compound was recorded in DMSO-d6. The singlet signal at δ 3.79 ppm was due to the methoxy protons. The aromatic protons were seen in the range of δ 7.04 –8.02 ppm as multiple signals. Another weak signal at δ 13.52 ppm attributed to imidazole (-NH-) proton.

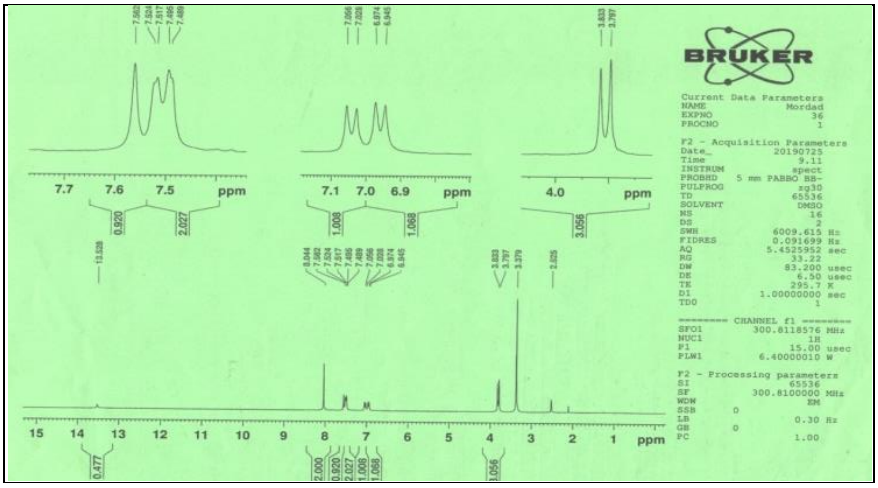


Fig.(2): The ^{1}HNMR spectrum of ligand (4-SuMBAI)

3.4. Infrared spectra

The Infrared spectroscopy can be used as a good analytical tool to follow the complexation of the transition metal ions by the organic ligands [17, 18]. The mode of bonding between the azo ligand and the titled metal ions was elucidated by examining the

IR spectra of the metal complexes in comparison to those of the free ligand (Table.2). The IR spectrum of the free ligand (4-SuMBAI) showed a medium and broad band around 3277 cm^{-1}, which can be attributed to (N─H) stretching vibration of the imidazole moiety[19]. This band disappeared at all mixed ligand complexes and anew bands exhibited in the region 3253-3496 cm^{-1} due to the existence of lattice water molecules [20]. The spectrum of the azo ligand shows band at 1662 cm^{-1} due to ν($S-NH_2$) stretching vibration [21]. The position of this band remained at nearly the same frequency in spectra of the metal chelate complexes, suggesting the uncoordination of this group to the metal ions. Another absorption band at 1612 cm^{-1} due to ν(C═N) of the N3 imidazole nitrogen. It is observed with a little change in shape and shifted to lower frequencies 1608 – 1604 cm^{-1} in the prepared complexes spectra. These differences suggest the linkage of metal ion with nitrogen imidazole ring[22,23]. The ν (N═N) stretching vibration appears at 1427 cm^{-1} in the free ligand spectra. This band appearing at 1425 – 1422 cm^{-1} with different in shape and reduced in intensity in the spectra of prepared complexes. Both band shifted and reduced intensity due to chelate complex formation[24-26]. The far infrared spectra of the mixed ligand complexes exhibited new bands that are not present in the free ligand. These band are located at 501 – 437 cm^{-1}, assigned to ν(M─N) [27]. Thus the above IR spectral data lead to suggest that the ligand behaves as a bidentate chelating agent. The mixed (1,10-phen) complexes show new characteristic band at(1608-1610)cm^{-1} assigned to the coordinated azo methane group of the (1,10-phen) ring.

Figs.3 and 4, shows the spectra of ligand and [Co(L) phenCl_2].H_2O complex.

Table (2): Characteristic IR frequencies (in cm^{-1}) of the ligand (4-SuMBAI) and metal chelate complexes

Compound	**ν (O─H) H_2O**	**ν (N─H)**	**ν ($S-NH_2$)**	**ν (SO_2N)**	**ν (C═N)Im**	**ν(C═N) *(1,10phen)***	**ν (N═N)**	**ν (M─N)**
(4-SUMBAI =L)	…………	3277 m.	1662 s	1330-1178	1612 m	…….	1427 w	…….
[Co(L)phenCl_2]. H_2O	3496 m.br	………	1661 s	1340-1176	1604 m	1608	1425 w	501 w
[Ni(L)phenCl_2]. H_2O	3390 m.br	………	1662 s	1336-1174	1608 m	1608	1423 w	466 w
[Cu(L)phenCl_2]. H_2O	3253 m.br.	………	1664 s	1346-1174	1606 m	1608	1425 w	464 w
[Zn(L) phenCl_2],H_2O	3430m.br	………	1664 s	1332-1172	1604 m	1608	1427 w	439 w
[Cd(L)phenCl_2] H_2O	3496 m.br	………	1663 s	1334-1176	1604 m	1610	1423 w	439 w

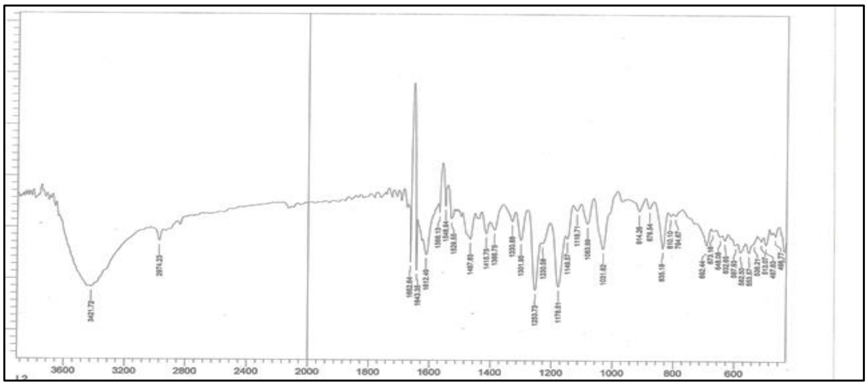


Fig.(3): IR- spectrum of ligand (SuMBAI)

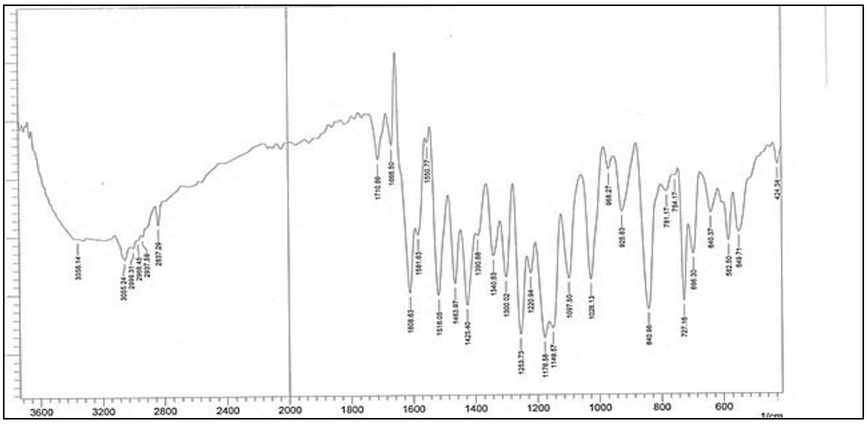


Fig.(4): IR- spectrum of [Co(L) phenCl_2]H_2O

3.5. Absorption spectra

The electronic absorption spectra of all the compounds were recorded using **ethanol** solution in the range 200-1100 nm at room temperature Table (3). The spectral data of organic ligand (4-SuMBAI) exhibited two recognizable absorption bands. The first band which appeared at (292 nm) can be ascribed to the ($\pi \rightarrow \pi^*$) transition of the phenyl rings while, the second band appeared at (466 nm) can be assigned to ($n \rightarrow \pi^*$) electronic transition due to the azo group [28]. Further, it is recognized that the absorptions bands were shifted to longer wavelength in all the metal complexes, which may be assigned to $d(M^{2+}) \rightarrow \pi^*$ (ligand) charge transfer transitions suggesting metallization with the azo dye ligand [29].

3.6. Magnetic moment and conductivity measurements

The magnetic susceptibility and molar conductance values are listed in Table (3). The magnetic moment values are found to be 4.97, 3.43 and 1.78 (B.M) for Co(II), Ni(II) and Cu(II) mixed ligand complexes, respectively, suggesting an octahedral geometry [30,31]. While Zn(II) and Cd(II) chelate complexes was diamagnetic and according to its empirical formula, an octahedral geometry was proposed for these complexes. Molar conductance data of the complexes were measured in DMF and the complexes were found to be non-electrolytic in nature [32].

4. Conclusions

This work described the preparation and identification of a new series of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) mixed ligand complexes derived from new arylazo imidazole ligand (4-SuMBAI) as primary ligand and (1,10-phen) as secondary ligand. These chelate complexes with azo dye were characterized by using different physiochemical techniques. The IR spectra revealed that (4-SuMBAI)behaves as neutral bidentate ligand coordinated to the metal ions through imidazole-N, azo-N donor atoms. The spectral and magnetic studies of the prepared metal complexes of azo ligand reveals that all mixed ligand chelate complexes are having octahedral geometry and the (M : L : (1,10-phen)) ratio is (1:1: 1). The ligand can be good analytical reagent for some metal ions.

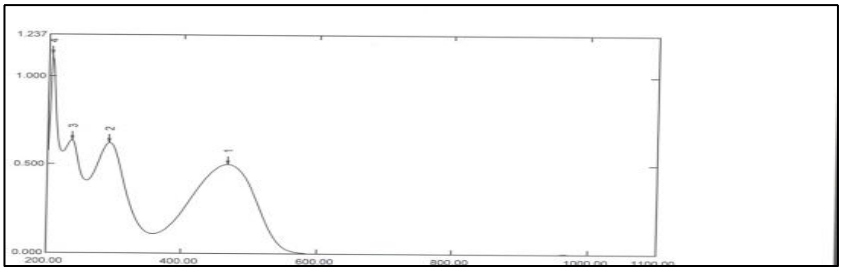


Fig.(9): UV-Vis spectra of (SUMBAI)

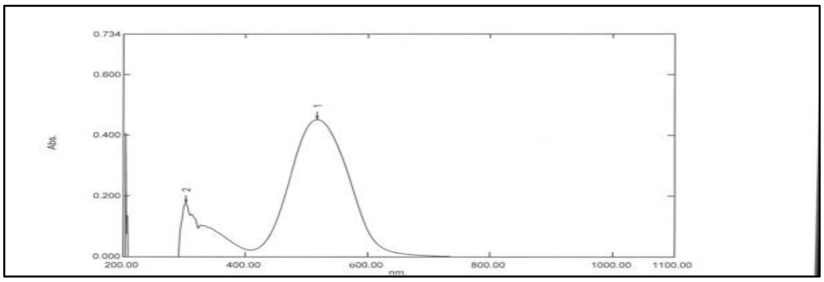
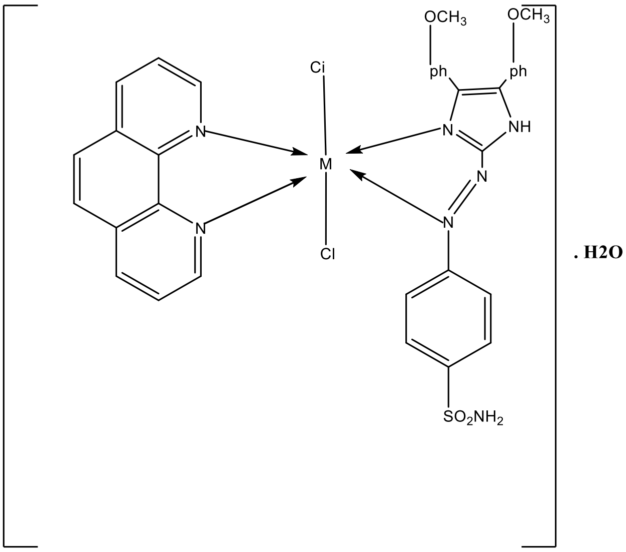


Fig.(11): UV-Vis spectra of [Ni(L) phenCl$_2$]H$_2$O

Table (3) : Electronic spectra, conductivity and magnetic moment of the ligand (4-SuMBAI) and metal chelate complexes

Compounds	Assignment	Absorption Band (nm)	μeff (B.M)	Proposed Structure
(4-SuMBAI =L$_1$)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	292 466	……	…….
[Co (L)(1,10-phen)Cl$_2$]. H$_2$O	C. T.	503	4.97	Oh
[Ni (L)(1,10-phen)Cl$_2$]. H$_2$O	C. T.	517	3.43	Oh
[Cu (L)(1,10-phen)Cl$_2$]. H$_2$O	C. T.	505	1.79	Oh
[Zn (L)(1,10-phen)Cl$_2$]. H$_2$O	C. T.	505	Dia	Oh
[Cd (L)(1,10-phen)Cl$_2$]. H$_2$O	C. T.	507	Dia	Oh



M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)
Fig. (5): structural formula of transition metal complexes

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