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Preparation ,Characterization pand Theoretical Studies of Cobalt(II),Nickel(II) and Cupper(II) complexes of bisazo ligand derived from 4,5-diphenyl imidazole and m-Phenylenediamine

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Abstract

Transition metal complexes of Co(II), Ni(II) and Cu(II) with a new bisazo ligand 1,3-Bis (4,5-diphenyl imidazole azo) benzene (BABI) derived from m-phenylenediamine and 4,5-diphenyl imidazole were synthesized. The preparation of the complexes have been conducted after fixing the optimum conditions such as pH and concentration .UV- visible spectra of these complexes solution have been studied for a range of pH and concentration which obey Lampert-Beers Law .The structure of complexes are deduced according to mole ratio method which were obtained from the spectroscopic studies of the complexes solution .The ratios of metal: ligand obtained are (1:1) for these complexes . (UV-Vis) absorption spectra of ethanolic solution of complexes showed bathchromic shift , as compared with that of free ligand .The infrared spectra of the chelating complexes have been studied , Depending on these results the coordination between our ligand and the metal ions take place. The conductivity measurements , elemental analysis ,the percentage of metal ions was determined .Depending on these results ,we may conclude that the ligand was tetradentate . Also the proposed geometrical structure of the complexes of Co(II),Ni(II) and Cu(II) ions are octahedral.

Keywords:
Preparation, Theoretical Treatment, Bis (imidazole azo) ligand, and Elemental analysis.

Introduction

Azo compounds, with two imidazole rings separated by an azo (-N=N-) bond are versatile molecules and have received much attention in research areas both fundamental and application [(1)].Azo dyes contain one or more azo groups (-N =N-) which are linked to sp^2 hybridized carbon atoms, based on the number of such groups [(2)].

Aromatic azo compounds are widely used in the chemical industry as dyes and pigments[(3)], food additives, indicators[(4)], and therapeutic agents[(5)]. In addition, azo compounds have shown promise in electronics[(6)] and drug delivery[(7)]. Biological importance of azo compounds is well known for their use as antineoplastics, antidiabetics, antiseptics, anti-inflammatory, and other useful chemotherapeutic agents [(8-11)].

Azo compounds are also of interest for a more accurate diagnosis of Alzheimer's disease because their physiological activity

can be used as a diagnostic probe for the visualization of amyloid plaques in the brains of mentally deteriorating patients[12].Basically sulfur &Nitrogen nucleus containing heterocyclic families are very interesting due to their versatile pharmacological activities, such as anti-tumour, diuretics, fungicides, bactericides, antihelmintic, antiallergic, antiulcer and local analgesic[13-15]. Azo dyes compounds are also have a plenty of applications in industry and photodynamic therapy as well as photosensitive species in photographic or electro photographic systems and are dominant organic photoconductive In this study, the synthesis and characterization of new bis (imidazole- azo) ligand from m-materials[16]. phenylenediamine with 4,5-diphenyl imidazole as coupling component and its Co(II), Ni(II) and Cu(II) complexes are described. The structural investigation of the synthesized compounds are discussed.

Experimental

Materials and physical measurements

All chemicals used were of highest purity (BDH or Fluka) and used without further purification.

Elemental analysis was carried out by means of (Euroverctor, EA300A, Italy) C.H.N element analyzer. Absorption spectra were recorded by Shimadzu UV-Vis 1700 spectrophotometer, for solution of the complexes in aqueous ethanol at room temperature Using 1cm quartz cell. IR spectra were recorded with FT-IR-8000 Shimadzu, in the range of (4000-400) cm^{-1} using KBr disc. Electrical conductivity measured by digital conductivity meter Alpha– 800 with the prepared complexes concentration of 10^{-3}M in ethanol at room temperature. pH measurements were carried out using (pH– meter), 720, WTW 82362.

Synthesis of the ligand[17]

The ligand prepared by dissolving (1.08g/0.01 mol) of m-phenylenediamine in 5ml of distilled water and 10ml of concentrated hydrochloric acid, then the solution was cooled below 5°C. To this mixture a solution of (0.02 mol) of sodium nitrite in 10 ml of distilled water was added drop wise at (0-5)°C and the mixture was stirred for 60 min till a dark red colored solution was obtained. This diazonium solution was added drop wise to a 500 ml beaker containing (2.2g/0.02 mol) of 4,5-diphenyl imidazole dissolved in NaOH (0.02mol) was cooled and added to the tetrazo solution slowly with continuous stirring at (0-5) ^{o}C. The ligand was washed with cold water and collected by vacuum filtration .Then ligand recrystallized by Water-Ethanol(1:1). shown in scheme 1

Synthesis of complexes

The complexes were prepared by adding dissolved (0.057gm, 0.01 mol) of ligand (BABI) dissolved in 10 ml hot ethanol to a hot solution of metal chloride (0.01 mol); $CoCl_2.6H_2O$,$NiCl_2.6H_2O$ and $CuCl_2$ dissolved in 10ml buffer solution (ammonium acetate) at optimal pH for each metal ions.

The mixture was stirring and heated to 50 °C for 1 hr, then left overnight where the solid complexes precipitated. They were filtered off, washed with ethanol 10 ml to remove the remaining unreacted substances and dried in a desiccators over anhydrous $CaCl_2$ Table.1 collects some physical properties and analytical data for these complexes.

Table 1: Some Physical properties and analytical data of the ligand(BABI) and Co(II), Ni(II) and Cu(II) complexes.

No.	Compound	Color	m.p °C	Found (Calc.)% C	H	N	M
1	$C_{36}H_{26}N_8$	Red	160	75.77 (75.6)	4.59 (4.4)	19.64 (19.9)	—
2	[Co ($C_{36}H_{26}N_8$)Cl_2]	Deep brown	175	68.68 (68.28)	4.16 (3.94)	17.80 (18.21)	9.36 (9.05)
3	[Ni ($C_{36}H_{26}N_8$)Cl_2]	Reddish brown	190 d	68.70 (68.49)	4.16 (4.01)	17.80 (18.19)	9.33 (9.12)
4	[Cu $C_{36}H_{26}N_8$)Cl_2]	Blackish brown	183 d	68.18 (67.86)	4.13 (3.92)	17.67 (17.86)	10.02 (9.90)

d=decomposition temp.

Results and discussion

Effect of pH

To evaluate optimal pH values on the absorbance for the metal complexes solution were studied in the 50% (V/V) ethanolic solution in the range of (5–10) as shown in Fig.1. The ligand (BABI) formed a very stable complexes with metal ions Co(II), Ni(II) and Cu(II) wide pH range.

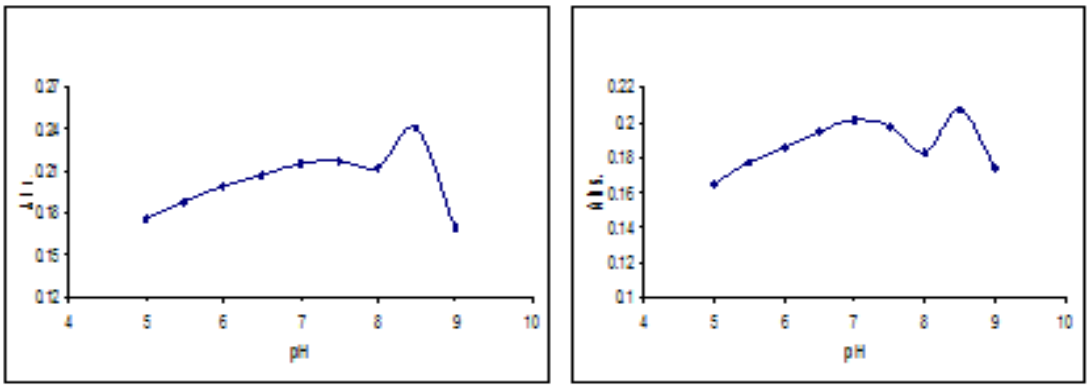


Figure 1: The effect of pH on the absorbance of Co(II),Ni(II) and Cu(II) complexes

Metal: ligand ratios

The metal: ligand ratio(M:L) of complexes was determined by the mole-ratio method at constant (λ_{max}), pH and concentration. The results are in agreement with the reported for some imidazolyazo complexes[18,19], which indicate that the ligand (BABI) was to form chelate complexes with Co(II), Ni(II) and Cu(II) ions, as shown in Fig.2.

The absorption spectra of ligand (BABI)[20,21] and its complexes were studied (figures 3-6). The wavelength for the maximum absorption (λ_{max}) of the ligand was found at 421nm. The spectra of metal complexes were recorded within wavelength range (524– 564) nm. The absorption maxima(λ_{max}) of the each complexes is shown in Table.2. Two absorption bands appeared for the ligand (BABI). The band at 313 nm referred to the $\pi \rightarrow \pi^*$ transitions of imidazole ring while the band at 421nm assigned to $n \rightarrow \pi^*$. The UV-Vis spectra of the complexes(Co(II),Ni(II) and Cu(II)) showed absorption peaks at (290, 530nm), (286, 564nm) and (300,524nm) which were assign to ligand field and charge transfer transition respectively The spectrum of the complexes shows relative change in the bands position compared to that of the ligand, as showed in figures(4-6).

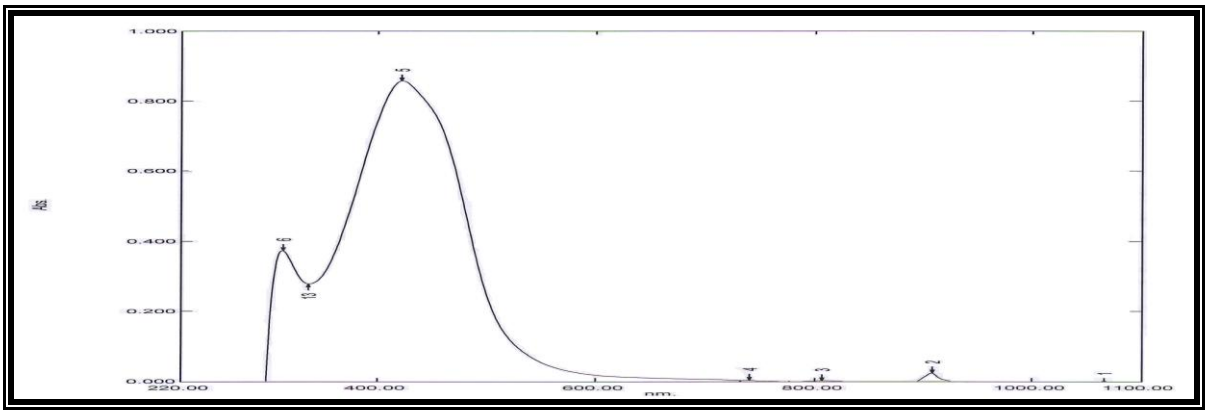


Figure 3: Absorbance spectrum of ligand (BABI)

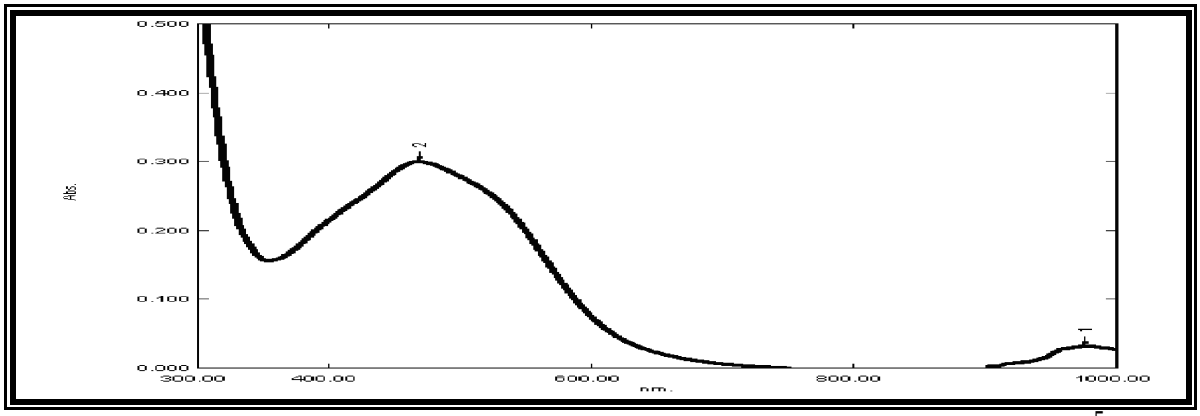


Figure 4: Absorbance spectrum of ligand (BABI) with Co(II) In Conc.9x 10^{-5} M

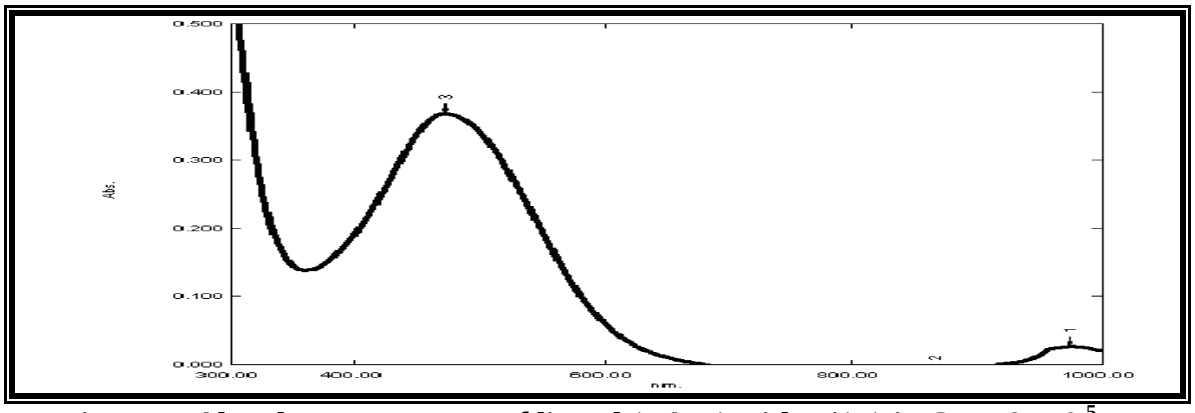


Figure 5: Absorbance spectrum of ligand (BABI) with Ni(II) in Conc.9x 10^{-5} M

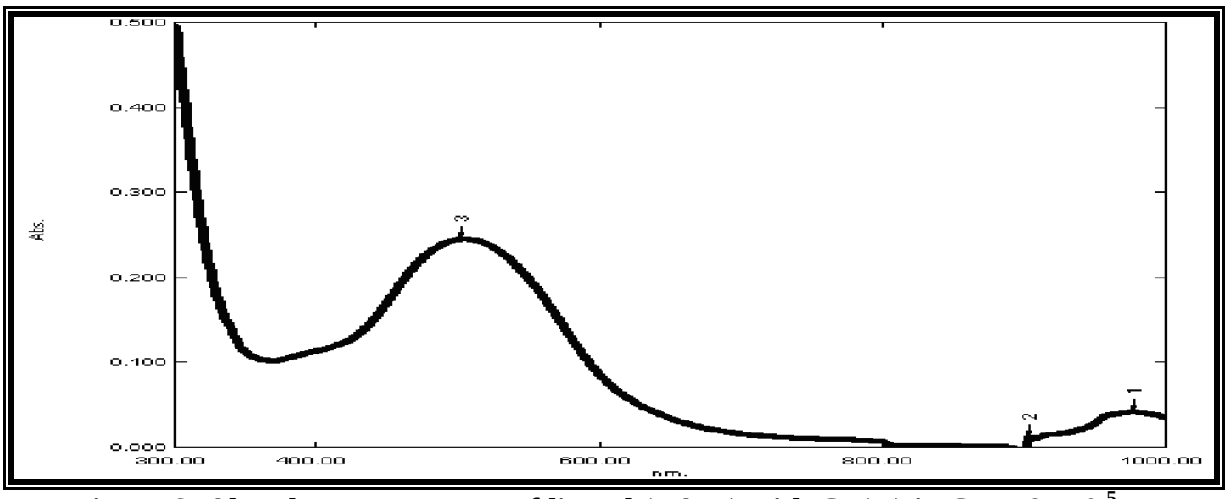


Figure 6: Absorbance spectrum of ligand (BABI) with Cu(II) in Conc.9x 10^{-5} M

Table 2: The optimal pH values, optimal molar concentration and wavelength (λ_{max}) metal ions

Metal Ions	Optimal pH	Optimal molar conc.	Optimal wave length ()nm	Δ_* Nm
Co(II)	8.5	9×10^{-5}	546	+125
Ni(II)	8.5	9×10^{-5}	564	+143
Cu(II)	9	9×10^{-5}	524	+103

Infrared spectra

The infrared spectra data of the free ligand (BABI) and its complexes with Co(II),Ni(II),Cu(II) ions are given in Table.3. These spectra are complicated owing to the extensive overlap of number of bands arising from υ(N─H), υ(C═N), υ(N═N) and other bands due to the phenyl and imidiazole rings[22] which appeared in the region below 1680 cm^{-1} The comparison between the IR spectral data of the free ligand with that of its complexes are discussed as follow:

1-The spectrum of azo ligand (BABI) show absorption band around 3390cm^{-1}due to the υ(N─H) of imidiazole ring [23]. The same band in Zn(II), Cd(II), Hg(II) ions complexes indicates that this band didn't share in complexation.

2-The spectrum of ligand shows absorption band at 1602 cm^{-1} due to υ(C═N) of imidiazole ring[24]. This band is observed with a little change in shape and shifted to higher.

3-frequencies υ(1600-1614) cm^{-1} in complexes. These differences may suggest the linkage of metal ions with nitrogen of hetrocyclic imidiazole ring.

4-The azo group (N═N) appears at (1442) cm^{-1} in the free ligand spectrum. This band has been shifted to a higher frequencies (1444-1456) cm^{-1} in complexes spectra; this means that some linkage of metal ion with nitrogen atom of azo group which is the farthest of imidiazole ring takes place[25].

5-Finally a new weak bands appears at (420-551) cm^{-1} in the complexes spectra which may suggest the linkage of metal ions with nitrogen atom[26]. Figs.(7-10) shows the spectra of ligand (BABI), and it's complexes spectra.

Table 3: Characteristic IR absorption bands of the ligand (BABI) and it complexes in cm^{-1} units.

Compound	υ(N─H)	υ(C═N)	υ(N═N)	υ(M─N)
$C_{36}H_{26}N_8$	3390	1602	1442	─
[Co ($C_{36}H_{26}N_8$)Cl_2]	3396	1600	1456	501
[Ni ($C_{36}H_{26}N_8$)Cl_2]	3399	1614	1448	420
[Cu ($C_{36}H_{26}N_8$)Cl_2]	3358	1600	1444	492

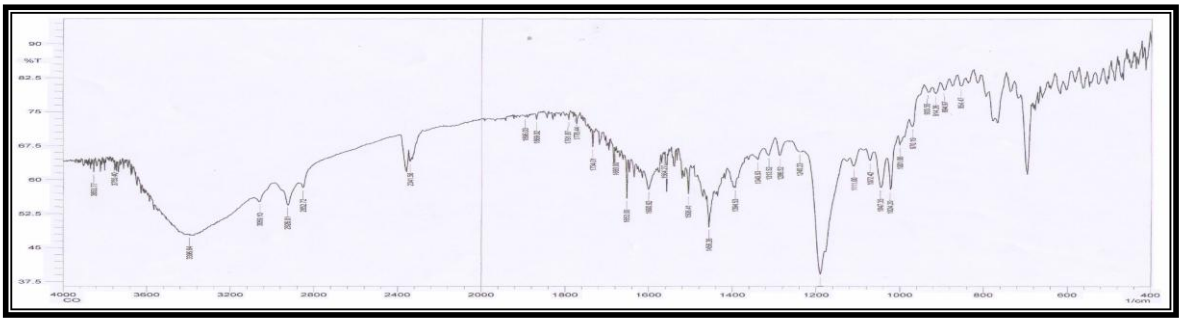


Figure 7: FT-IR spectrum of (BABI)

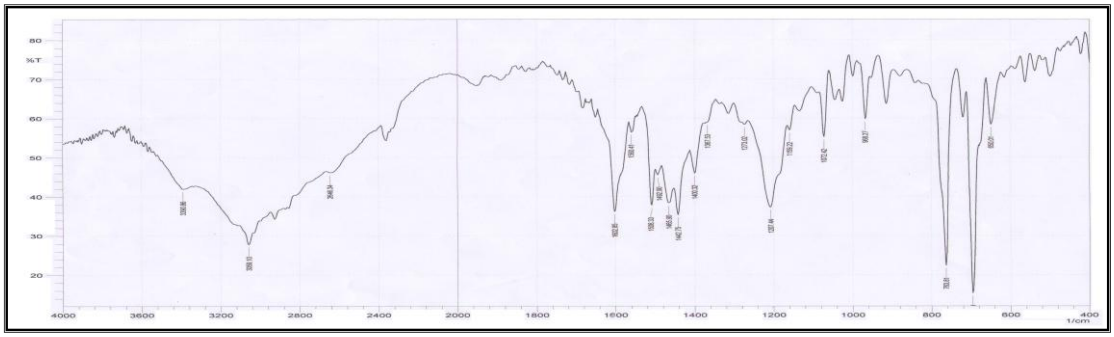


Figure 8: FT-IR spectrum of ion complex of Co (II) with (BABI)

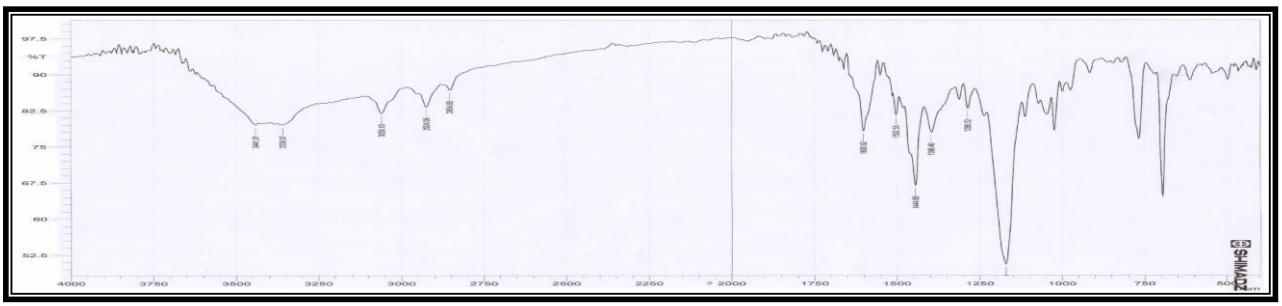


Figure 10: FT-IR spectrum of ion complex of Cu (II) with (BABI)

Table 4: Magnetic moment and

Complex	Conductivity S.cm^2.mol^{-1}	μeff B.M
[Co ($C_{36}H_{26}N_8$)Cl_2]	16.3	4.42
[Ni ($C_{36}H_{26}N_8$)Cl_2]	13.1	2.95
[Cu ($C_{36}H_{26}N_8$)Cl_2]	12.2	1.69

Magnetic susceptibility and electronic spectra measurements

The magnetic momentum and electronic spectra studies have been used to confirm geometry of the complexes .These data are listed in Table.4. Cobalt (II) complex The value of magnetic moment of Co (II) was found to be 4.42B.M, which can be a normal value for octahedral [27,28]. The magnetic momentum of the Co (II) complex has been found to be paramagnetic and the high spin behavior of this complex indicates that Co (II) is not oxidized to Co (III) during complexation.Nickel (II) complex The value of magnetic moment of Ni (II) was found to be 2.95 B.M, which can be a normal value for octahedral Ni (II) complex [29].Copper (II) complex The magnetic moment value of this complex was found to be 1.69 B.M, suggest the presence of one unpaired electron in this complex. It is reasonable to assign distorted octahedral structure[30].

Conductivity measurements

All complexes show the conductivity measurement values ranging between (12.2–16.3) S.cm2. mol-1 in ethanol solution at room temperature ,these values indicating nonionic structure of these complexes. The conductivity values are listed in Table 4.

Conductivity measurements of complexes in ethanol

According to the results , the elemental analysis(C.H.N) and the percentage of metal ions by using atomic absorption technique, the coordination number of metal ions is found to be six with bonding through the (N) of bis azo group and the two (N) atoms of imidazole additionally two Chloride ions. The structural formula of prepared complexes is most probably octahedral as shown in fig.11

Theoretical Study:

The program Hyper Chem-8 was used for the semi-empirical and molecular mechanical calculation at optimized energies, the result of ZINDO/1 method of calculation in gas phase for heat of formation ($\Delta H^{\circ}f$), binding energy (ΔE_b) and dipole moment (μ) for free ligand and its complexes of Co(II),Ni(II) and Cu(II) are listed in table(5). PM3 was used for evaluating the wave number for the ligand and compared with the experimental frequencies to predict the deviation, table (6). ZINDO/S method was used to calculate electronic transitions for the ligands and compared with experimental transition to explain the transitions.

Table (5): Conformation energetic (in K.J.mol^{-1}) and dipole moment (in Debye) for ligand(BABI) and its metal complexes.

	ZINDO/1		
Comp.	$\Delta H^{\circ}f$	ΔE_b	μ
L	-68979.73	-104170.06	8.215
CoL	-86481.62	-118741.44	13.48
NiL	-83721.51	-114216.22	7.811
CuL	-87351.33	-119846.02	11.47

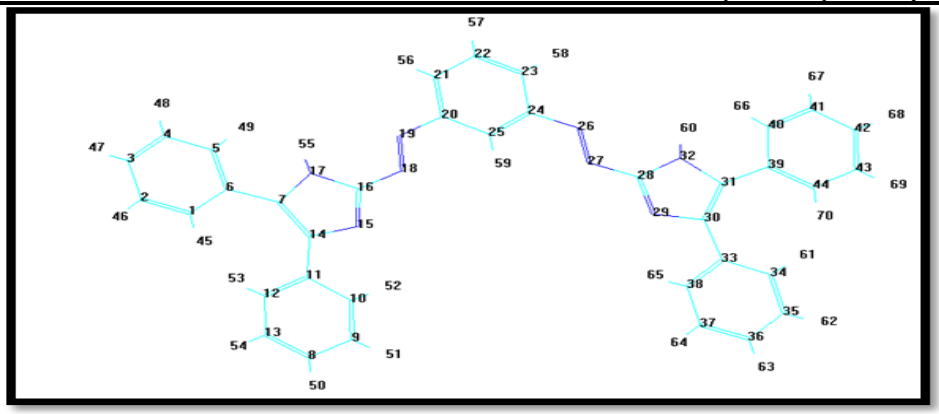
The table above shows that the heat of formation of complexes is smaller than that for ligand, and the binding energy also smaller than that for ligand thus, we expected that the complexes are to be thermodynamically more stable than ligand.

Table (6): Comparison of experimental and theoretical vibrational frequencies for BABI ligand.

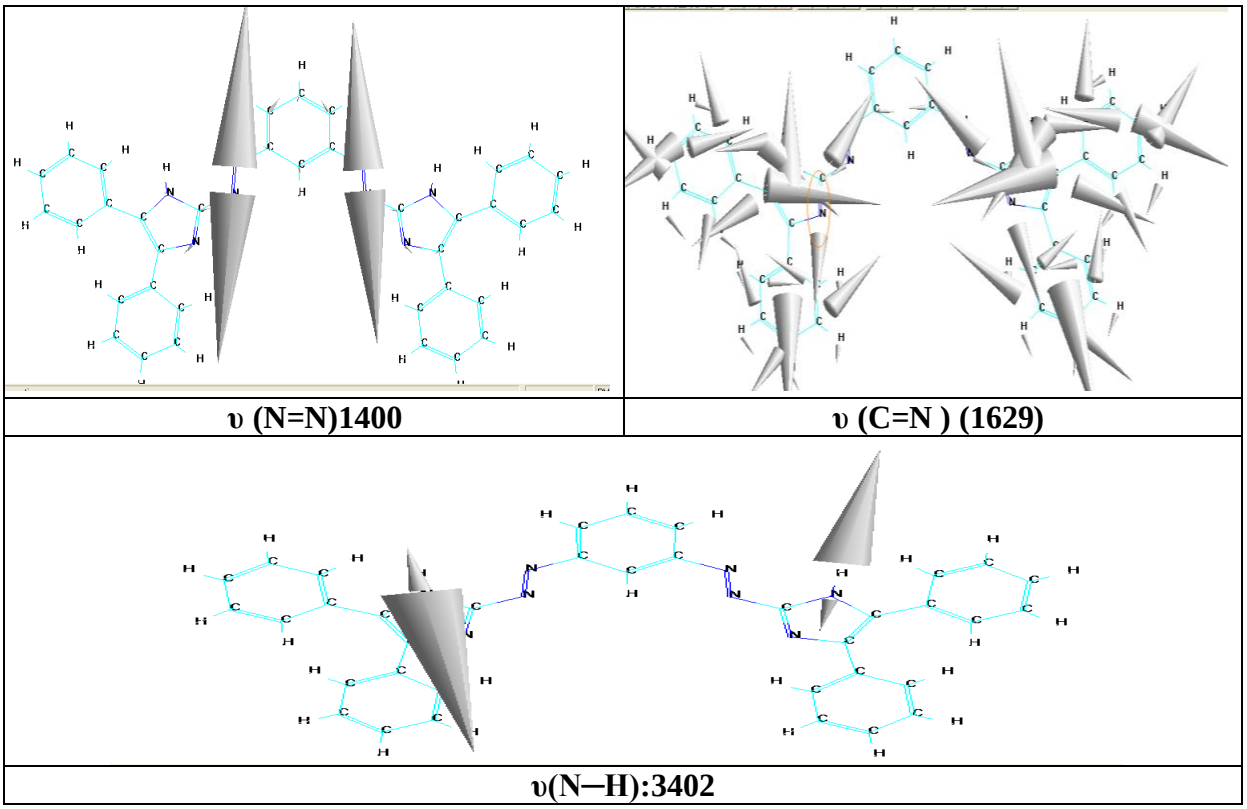
Symb.	***υ(N-H)***	***υ(C=N)***	***υ(N=N)***
L	3390*	1602*	1442*
	3402**	1629**	1400**
	(0.35)***	(1.65)***	(-2.91)***

Where:*Experimental frquency,**theoretical frequency,***Error% due to main different measurements and theoretical treatment of vibrational spectra.

The theoretical UV-spectrum of ligand was calculated using ZINDO/S method and showed some deviations from the experimental values .These deviations are generally acceptable in theoretical calculations(31).The serial number of atoms was plotted in the structure of ligand in order to determine the type orbitals than type of transition figure(12).The theoretical UV-spectrum of ligand BABI showed two absorption peaks at 314.9 and 431.5 nm. The quantum data indicate that these peaks are generated mainly from $\pi \rightarrow \pi^*$ transition (N15→C16 or N29→C28) and $n \rightarrow \pi^*$ transition (N26→N27 or N29→N28).The experimental spectrum also showed two peaks at 313.00 and 421.00 nm



Figure(12):Serial number of atoms view of (BABI).ligand



Figure(13):Calculated vibrational frequencies of the ligand (BABI).

References

1-Bulent Kirkan and Ramazan GVP,Turk J Che 32 (2008).

2-W.Catelen., and G.Koller., J. Phys. Chem.198, 2879(2006).

3-K.Hunger, Industrial Dyes: Chemistry, Properties, Applications,ed. Wiley-VCH, Weinheim, Germany, (2003).

4-R.D.Athey Jr.,Eur.Coat.J.,3, 146,(1998).

5-W. J. Sandborn, Am. J. Gastroenterol, 97, 2939(2002).

6-F. Cisnetti, R. Ballardini, A. Credi, M. T. Gandolfi, S. Masiero, F. Negri, S. Pieraccini and G. P. Spada, Chem.–Eur. J., 2004, 10,2011.

7-A.Jain,Y.Gupta and S.K. Jain, Crit. Rev. Ther. Drug Carrier Syst, 23, 349, (2006).

8-J.-S Bae., H. S Freeman., El-Shafei A.Dyes and Pigments: Vol. 57, 121(2003).

9-F. T.Sanjay, M. P Dinesh., P. P Manish., G. P Ranjan., Saudi Pharmaceutical Journal: Vol. 15(1),48-54(2007).

10-R.G Child, R.G. Wilkinson, and A .Tomcu-Fucik.,Chem. Abstr. : Vol. 87, 6031(1977).

11-H.G. Garg, and Praksh, C. J. Med. Chem: Vol. 15(4), 435-436 (1972).

12-W. Zhen, H. Han, M. Anguiano, C. Lemere, C.-G. Cho and P. T. Lansbury, J. Med. Chem., 42, 2805(1999).

13-AK Singh and Lown JW. Design,Anti Cancer Drug.;15:265-275(2000).

14-H Kucukbay, U Yilmaz , N Sireci and AN Onganer. Synthesis and antimicrobial activities of some bridged bis-benzimidazole derivatives. Turk J Chem.;35: 561– 571(2011).

15-H Kucukbay, R Durmaz, N Okuyucu , S Gunal and C Kazaz. Synthesis and antibacterial activities of new bisbenzimidazoles Arzneimittelforschung.;54(1):64-68 (2004).

16-A Thoraya, Farghaly and ZA.Abdallah ,Synthesis, azo-hydrazone tautomerism and antitumor screening of N-(3-ethoxycarbonyl-4,5,6,7- tetrahydro-benzo[b]thien-2-yl)-2-arylhydrazono-3-oxobutanamide derivatives. Arkivoc.;17:295(2008).

17-S.Shibata,M.Furukawa and R. Nakashima; Anal. Chem. Acta.,81,131 (1976).

18-A. M. Ali and R. T. Mehdi, Al-Mustansiriya ; J. Sci., 16(4), 1, (2005).

19-F. A.Carey ,Organic Chemistry, 3rd .ed., McGraw-Hill, Inc. America, (1134):453 , 454(1996) .

20-E.Yousif, H. Adil and Y. Farina, J. Appl.Scien.Res.6(7):879-882(2010).

21-K. B. Pandega and R. P. Singh; Ind. J. Chem; 14 ,681-682(1976).

22-K Nejeti etal. Dyes and Pigments 75,653-657(2007).

23-Robert.M. Silverstein and Franeis X . Webster" Spectrometric Identification of Onganic Compounds " New York, Wiely and Sons , Iuc 6 th Ed (1996).

24-S.Pal,D.Das,P.Chattopadhyay,C. Sinha,K.Pan neerselvam and T.H.Lu, Polyhedron .,19,1263,(2000).

25-R.T.Mehdi and A.M.Ali ; Ibn Al-Haitham J.for pure and appl.sci,118 (3),50,(2005).

26-N. B.Colthup; L. H .Daly; S. E.Wiberley,; Introduction to Infrared and Raman Spectroscopy, 3rd ed. New York: Academic Press, (1991).

27-S. K. Ibrahim. 22. Figgis B.N , and Lewis .J,Interscience ,New York,37,6,(1964),141-153.

28-Lever .A.B.P.Amesterdam,Elsevier, London, New York The Netherlands 225-243 (1968).

29-A..MohamadAli , M.S. Mohamad and M.A.Hadi ,J.of Kufa for Chemical Science,2, 64-71,(2011).

30-Nicholas.D,Pergamon Press Oxford .1 stEd,24,1152-1154,(1973).

31-T. A. Clark, "Hand Book of Computational Chemistry"John Wiley and Sons, New York,(1985).

تحضير وتشخيص ودراسة نظرية لمعقدات أيونات الكوبلت (II) والنيكل (II) والنحاس (II) مع ليكاند ثنائي ازو مشتق من ميتا- فنيلين ثنائي الأمين و 5,4- ثنائي فنيل اميدازول

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الخلاصـــة

تم تحضير وتشخيص معقدات ايونات الكوبلت(II) والنيكل(II) والنحاس (II) مع الليكاند 3,1 بس (5,4- ثنائي فنيل اميدازول آزو) بنزين. وقد تم التحضير بعد تثبيت الظروف المثلى من تركيز ودالة حامضية من خلال دراسة أطياف الأشعة فوق البنفسجية– المرئية لمزج محاليل الايونات الفلزية الثنائية مع محلول الليكاند ولمدى واسع من الدالة الحامضية والتراكيز الخاضعة لقانون لامبرت– بيير .وقد تم التعرف على تركيب المعقدات المحضرة عن طريق إيجاد النسبة المولية لعلاقة (الفلز : الليكاند) بوساطة دراسة أطياف (UV-Vis.) لمحاليل خلط الايونات الفلـزية المدروسة مع الليكاند ، وبينت الدراســـة إنهـــا (L:M)(1 :1) لهذه المعقدات. شخص الليكاند والمعقدات الصلبة المحضرة بالوسائل التحليلية والطيفية المتاحة فقد تم تشخيصها بوساطة ألاطياف الالكترونية ، كما تم دراسة أطياف الأشعة تحت الحمـــراء (F.T.IR) للمعقدات المدروسة. وقد بينت دراسة التوصيلية المولارية انعدام الصفة الأيونية للمعقدات المذكورة كما تم إجراء التحليل الدقيق للعناصر وحساب نسبة الايونات الفلزية لهذه المعقدات ، وبالاعتماد على النتائج المستحصلة استطعنا الاستنتاج بان المعقدات الكيليتية المحضرة تتخذ الشكل الهندسي الثماني السطوح. أجريت دراسة تكون المعقدات نظرياً في الطور الغازي باستخدام برنامج (Hyperchem-8) باستخدام الطرق شبه التجريبية PM3,ZINDO/S , ZINDO/1 لحساب حرارة التكوين وطاقة الترابط والعزم ثنائي القطب عند درجة حرارة 298 كلفن لليكاند ومعقداته المحضرة. كذلك تم حساب الترددات الاهتزازية والانتقالات الالكترونية لليكاند المحضر.