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Preparation and Characterization of Some Metal Ions Complexes with Heterocyclic Azo Ligand (Bbai)

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Abstract

The preparation and characterization of the Co(II), Ni(II), Zn(II), Cd(II), and Hg(II) metal complexes of heterocyclic azo ligand 2,2'-[(1,1'-Biphenyl)-4,4'- diyl-bis-(azo)]-bis [4,5-diphenyl imidazole] (Bbai) have been studied by elemental analysis, IR and Spectroscopic, magnetic moment and Molar conductance methods. The analytical data showed that all chelate complexes were prepared with (ligand:metal) ratio of (1:1). The general formula of these complexes was $[M_2L_2Cl_4]$, and the octahedral geometry were suggested for these complexes L:M ratio was 1:1 for all homodinuclear prepared complexes.

Key Words: Heter cyclic azo ligand;Metal chelate complexes.

الخلاصة :-

تم تحضير وتشخيص معقدات ليكاند الازو غير المتجانسة الحلقة -2,2'-[(1,1'-Biphenyl)-4,4'- diyl-bis-(azo)] bis [4,5-diphenyl imidazole] (Bbai) للعناصر الانتقالية Ni(II), Co(II) Zn(II), Cd(II), and Hg(II) . واستخدمت الطرق الطيفية والمغناطيسية والتوصيلية المولارية لتشخيصها وقد وجد أن النسبة المولية(ليكاند: فلز) هي (1:1) ولجميع المعقدات المحضرة .وكانت الصيغة العامة لهذه المعقدات $[M_2L_2Cl_4]$وقد تم اقتراح التراكيب الثمانية السطوح لهذه المعقدات.

Introduction

Azo compound are a very important class of chemical compounds receiving attention in scientific research. They are highly colored and have been used as dyes and pigments for along time[1,2]. Furthermore, they have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium[3-6], toner[7,8], ink-jet printing[9,10], and oil-soluble light fast dyes [11].

The imidazol ring is one of the heterocyclic compounds that related to pyrole ring by substituted on of the ß carbon atoms by nitrogen atom[12].

Azo- imine group (-N=N-CH=N-) which is found in this kind of azo compounds enable it to form a stable form chelating complexes with awide rang of metal ions[13,14].

The present work show the preparation and identification of heterocyclic azo ligand derived from benzidene and 4,5-diphenyl imidazole and its complexes with Co(II), Ni(II), Zn(II), Cd(II),and Hg(II) metal ions.

Experimental

Materials and measurements

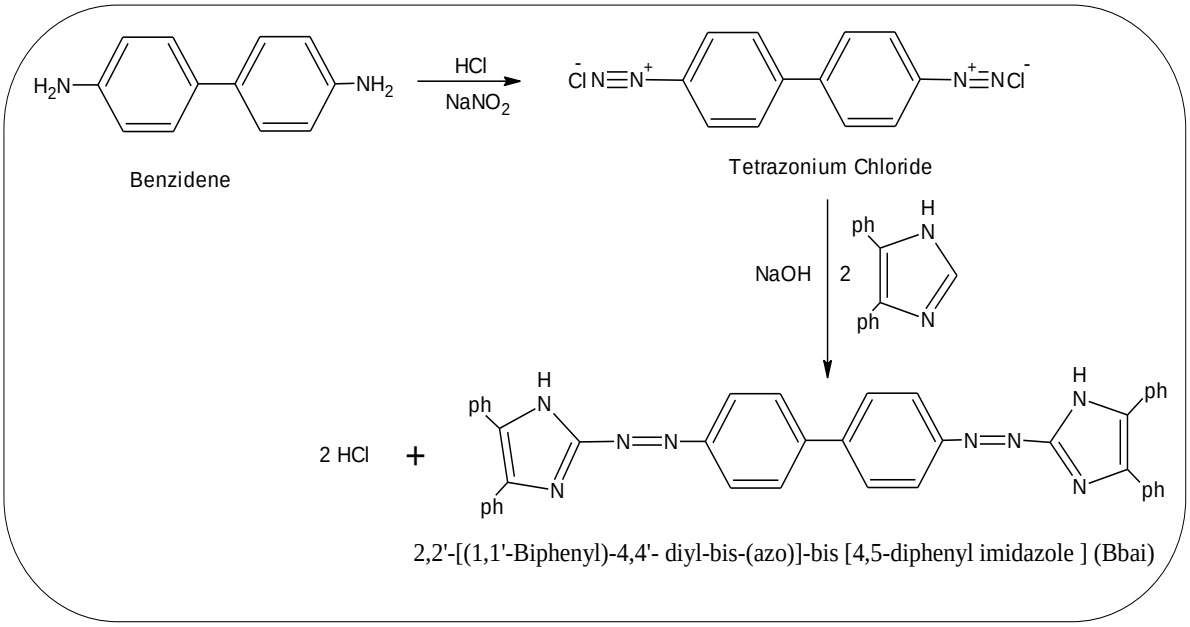
All reagent and solvents were obtained from commercial sources were of highest purity and used as received , except of 4,5-diphenyl imidazole which was prepared as reported [15] . The electro thermal melting point model 9300 was used to measure the melting points of the ligand and its complexes. Elemental analyses were carried out by means of Micro analytical unit of 1108 C.H.N Elemental analyzer. IR spectra were recorded using KBr discs in 4000-400 cm^{-1} range on FT-IR Shimdzu Spectrophotometer model 8400. Uv-Vis spectra were recorded in ethanol on shimadzu Spectrophotometer double beam model 1700 Uv-Vis spectrophotometer. Magnetic Susceptibilities were measured as powder samples using faraday method, Balance Magnetic MSB- MKI was employed for this purpose. The diamagnetic corrections were made by pascal's constants[16]. Molar

conductance measurements were determined in DMF by using a Alpha Digital conductivity meter model 800. Some physical and analytical data of the ligand and its chelate complexes was listed in table 1.

Preparation of the ligand (Bbai)

(Bbai) ligand was prepared according to the following procedure [17,18] (Scheme1). (1.84g, 0.01mol) of benzidene were dissolved in 50ml of water and 4ml of concentrated hydrochloric acid. The solution was treated with 8ml of aqueous (1M) sodium nitrite drop wise, and stirred for 30min at 0C^{o} ,4,5- diphenyl imidazole (2.2g , 0.02mol) was dissolved in 200ml of ethanol and 80ml of 10% sodium hydroxide was added, the tetrazonium chloride solution prepared above was then added drop wise for coupling after the mixture had been stirred for 3hrs at 0-5C^{o}, it was acidified with dilute hydrochloric acid until (pH=5).

The precipitated was filtered, air dried and recrystallized twice from hot ethanol and then dried in the oven at 100 C^{o} for two hours.



Scheme. 1: Preparation of the ligand (Babi).

Preparation of complexes

Theappropriatemetalchloride of $CoCl_2.6H_2O$(0.237g,1mmol), $NiCl_2.6H_2O$ (0.237g, 1mmol), $ZnCl_2$ (0.137g, 1mmol), $CdCl_2$ (0.183g, 1mmol),and $HgCl_2$ (0.271g, 1mmol) in ethanol:water (1:1) 25ml mixture was added to the solution of the azo ligand (0.646 g,1mmol) in ethanol 70ml. The resulting solution was stirred at 50C° for 30min, then the complexes were precipitated, they were removed by filtration, washed with hot ethanol and dried over anhydrous $CaCl_2$.

Results and discussion

The azo ligand was red semicrystals, but its chelate complexes were vary in color depending of metal ions. The ligand and its complexes were insoluble in water but soluble in most organic solvents such as methanol, ethanol, chloroform, ether. The conductivity values (6.95- 5.34) S. cm^2. mol^{-1} indicate that all chelate complexes are non-electrolytes in solution. The elemental analysis are in agreement with theoretical values. The formula of the ligand and its complexes given in table 1.

Metal : ligand ratio

The metal: ligand ratios of chelates were determined by the method of molar ratio method at the wavelengths of maximum absorption. The ligand (Bbai) found to form 1:1 chelates with metal ions under studies, these results are in agreement with the values reported for some azo complexes[19] .Figure 1.

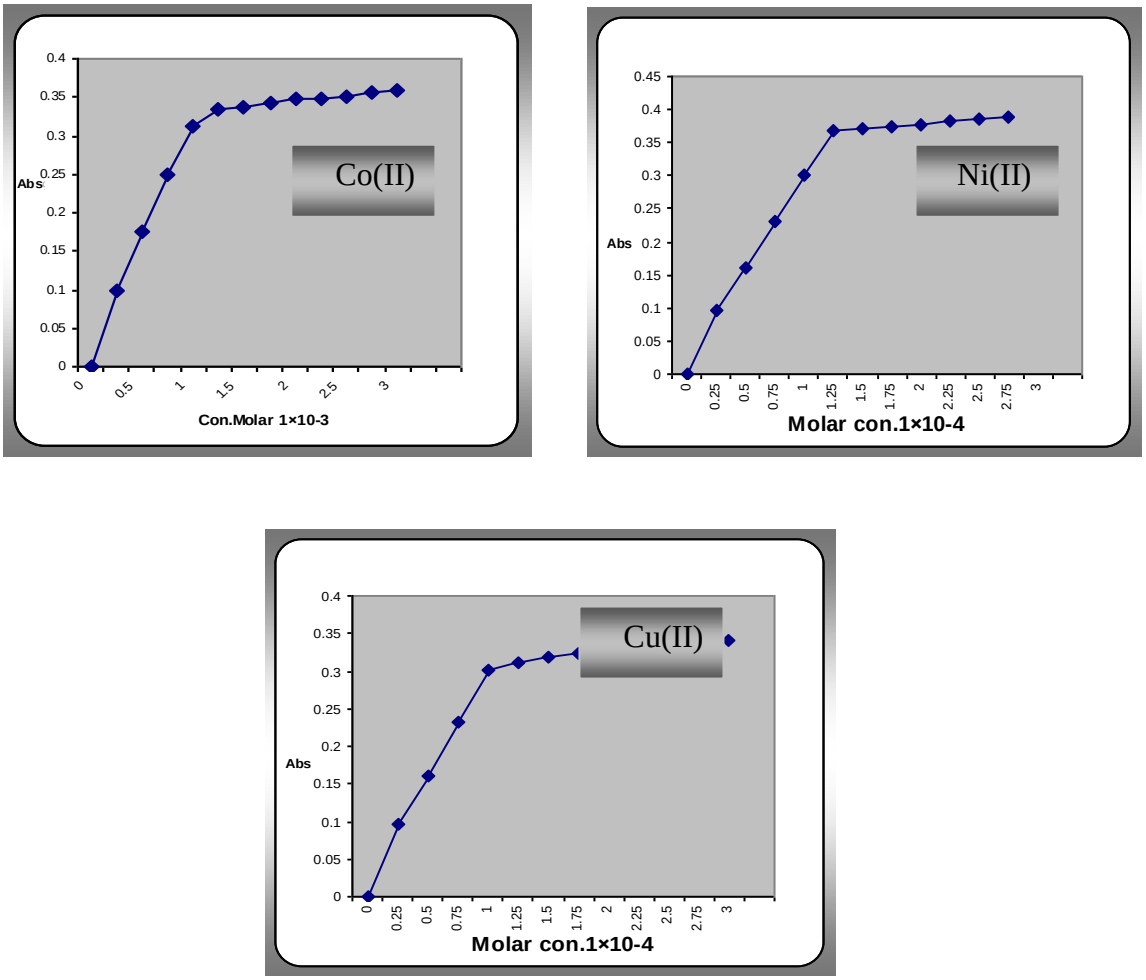


Figure (1) :Mole ratio method for Co(II), Ni(II) and Zn (II) ions.

Infrared spectra

The most important IR bands, presented and assigned in table(2) reported from the Figure(2) show the following characteristics:

The three bands appearing at 3360 cm^{-1}, 1600 cm^{-1},and 1480 cm^{-1} in the free ligand spectra, were assigned to stretching vibration modes υ(N-H), υ(C=N) and υ(-N=N-) respectively.[20,21]

The υ(N-H) of imidazole group this band remains in the same region free ligand and in complexes. Thus, the remaining of amine hydrogen band in solid complexes, indicating its non-involvement in coordination of the ligand with the metal ions . While the υ(C=N) and υ(-N=N-) bands were shifted to lower frequency and recorded at (1620- 1595)$cm^{-1}$and (1470-1400)cm^{-1} respectively. The shifted in frequency and different in the sharp and intensity of these function groups means that these groups involve in coordination with metals ions.

The formation of (M-N) band is further supported by the appearance of υ(M-N) in the region (480-410)cm^{-1} in the spectrum of chelates [22] , therefore. The IR spectra indicate that (Bbai) ligand behaves as aneutrat tetradentate chelating agent, and the coordinating sites are (-N=N-) and N_3 atom of the imidazole ring.

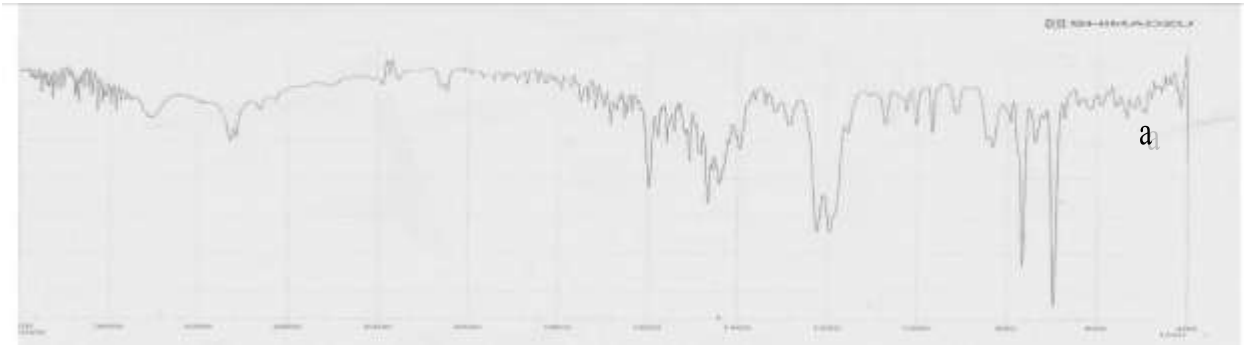


Figure.(2): IR spectra of ; (a) the ligand (Bbai) & (b) [$Ni_2L_2Cl_4$]

Electronic spectra and magnetic moments

The magnetic moment values measured at room temperature and electronic spectra peaks of the complexes which were studied are given in table 3.

The magnetic moment of Co(II) complex 4.35B.M suggest a high-spin octahedral configuration[23]. The high values of (μeff) may be due to orbital contribution. The electronic spectrum of this complex shows three absorption bands at 14765, 16535 and 23800 cm^{-1}, there are assigned to $^4T_1g(F) \rightarrow {}^4T_2g(F)$ (υ_1) $^4T_1g(F) \rightarrow {}^4A_2g(F)$ (υ_2) and $^4T_1g(F) \rightarrow {}^4T_1g(p)$ (υ_3) transition respectively, which are characteristic of octahedral stereo geometry[24].

The Ni(II) complex gave a magnetic moment value of 3.12 B.M, and d-d spectrum of this complex show bands at 15384 and 24150 cm^{-1}, which are suggesting the existence of $^3A_2g \rightarrow {}^3T_1g(F)$ (υ_2) and $^3A_2g \rightarrow {}^3T_1g$ (P) (υ_3) transition, this suggests that the complex octahedral[23].

The electronic spectra of Zn(II), Cd(II), Hg(II) complexes do show the charge transfer , and the magnetic susceptibility shows that all complexes have diamagnetic moments., magnetic properties and conductivity values of preparaed complexes are listed in tables 3.The electronic spectra of the ligand and the Ni(II) Complex were shown in Figure 3.

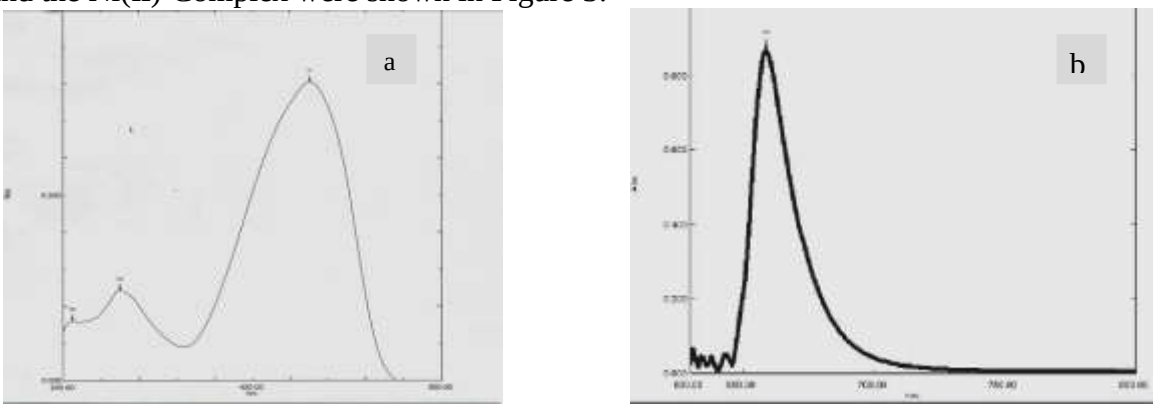


Figure.(3). Electronic spectrum of ; (a) the ligand& (b) [$Ni_2L_2Cl_4$] (Bbai)

Molar conductivity measurement

All chelate complexes prepared in this work showed conductivity values ranged between (6.95-5.34), S. cm^2. mol^{-1} in the DMF at room temperature , all these complexes are non-electrolytic species[25]. According to these results the structural formula of complexes may be proposed in Figure 4.

Table.1: Physical data and analysis of ligand and its complexes.

Compound	υ(N-H)	υ (C-H)	υ (C-H)	υ(C=N)	υ (N=N)	υ (M-N)
L=(Babi)	3360 w	3080w	2929w	1600s	1480	----
$[Co_2L_2Cl_4]$	3410w	3080w	2920w	1620m	1470m	480w
$[Ni_2L_2Cl_4]$	3400w	3080w	2920w	1619m	1400m	475w
$[Zn_2L_2Cl_4]$	3400w	3080w	2920w	1610m	1405m	477 w
$[Cd_2L_2Cl_4]$	3410wbr	3080w	2920w	1600m	1410m	465 w
$[Hg_2L_2Cl_4]$	3412w	3080w	2920w	1595s	1430m	410 w

L = Ligand, d= complex metal with decomposition

Table.2 : IR spectra frequencies for the ligand and its metal complexes in cm^{-1} units

No.	Compound	Colour	M.P °C	Yield %	Formula	Found,(calc.)%			
						C	H	N	M
1	L=(Bbai)	Yellow	158	75	$[C_{42}H_{30}N_8]$	78.9 (78.0)	4.5 (4.6)	17.2 (17.3)	----
2	$[Co_2L_2Cl_4]$	Purple	110	65	$[C_{84}H_{60}N_{16}Cl_4Co_2]$	61.9 (61.4)	3.2 (3.6)	13.8 (13.6)	8.2 (8.7)
3	$[Ni_2L_2Cl_4]$	Dark Purple	175	78	$[C_{84}H_{60}N_{16}Cl_4Ni_2]$	65.5 (64.1)	3.2 (3.8)	14.3 (14.2)	7.4 (8.7)
4	$[Zn_2L_2Cl_4]$	Purple	<200 d	80	$[C_{84}H_{60}N_{16}Cl_4Zn_2]$	64.6 (64.1)	3.0 (3.8)	14.2 (14.2)	8.8 (8.4)
5	$[Cd_2L_2Cl_4]$	Purple	180-183	77	$[C_{84}H_{60}N_{16}Cl_4Cd_2]$	60.2 (60.7)	3.7 (3.6)	13.0 (13.5)	13.4 (13.5)
6	$[Hg_2L_2Cl_4]$	Purple	200 d	72	$[C_{84}H_{60}N_{16}Cl_4Hg_2]$	54.6 (54.9)	3.5 (3.2)	12.8 (12.2)	21.8 (21.8)

L= ligand, s = strong, w = weak, m = medium, br = broad

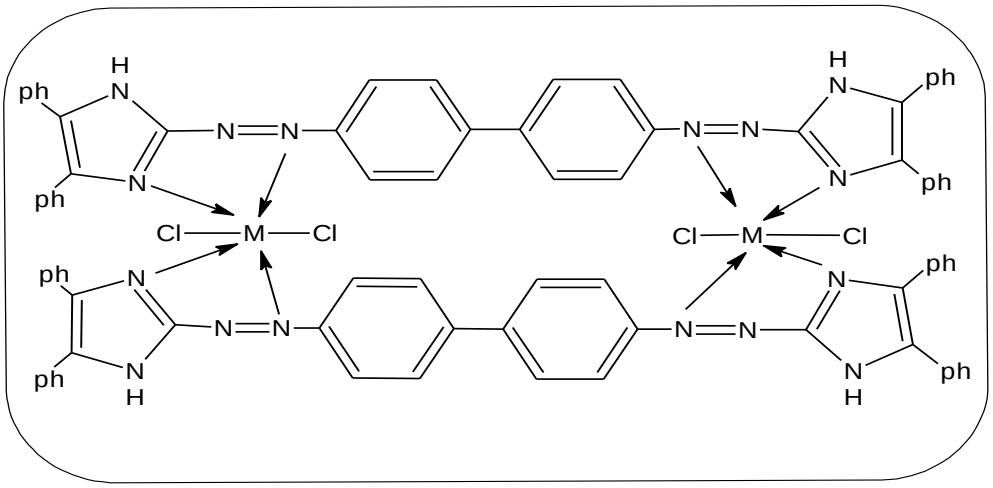
Table.3 : Electronic spectra, conductivity and magnetic moment of complexes

Complexes	λ_{max} nm (cm^{-1})	Transition	Conductivity S. cm^2. mol^{-1}	μeff(B.M)
$[Co_2L_2Cl_4]$	677 (14765) 604 (16535) 420 (23800)	$^4T_1g(F)\rightarrow {}^4T_2g(F)$ $^4T_1g(F)\rightarrow {}^4A_2g(F)$ $^4T_1g(F)\rightarrow {}^4T_1g(p)$	6.13	4.35
$[Ni_2L_2Cl_4]$	650 (15384) 414 (24150)	$^3A_2g\rightarrow {}^3T_1g(F)$ $^3A_2g\rightarrow {}^3T_1g(P)$	6.76	3.12
$[Zn_2L_2Cl_4]$	424 (23584)	LMCT	6.89	Dia
$[Cd_2L_2Cl_4]$	456 (21929)	LMCT	5.34	Dia
$[Hg_2L_2Cl_4]$	455 (21978)	LMCT	6.95	Dia

Conclusion

1- The prepared ligand is a tetradentate and bonding to two metal ion from the nitrogen of azo and the nitrogen of heterocyclic ring.
2- All the complexes an stable and ionic.
3- Some of the complexes are paramagnetic and the other are diamagnetic.
4- All the proposed Geometry of the complexes are octahedral.

The geometry is proposed for all complexes show octahedral stereochemistry . Figure.(4)



M= Co(II), Ni(II), Zn(II), Cd(II), and Hg(II)

Figure.(4) : the proposed structural formula of the metal chelate complexes

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