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## Synthesis, Characterization, Antimicrobial and Theoretical Studies of V(IV), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) Complexes with Bidentate (NN) Donor Azo Dye Ligand

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### Abstract:

The new 4-[(7-chloro-2,1,3-benzoxadiazole)azo]-4,5-diphenyl imidazole (L) have been synthesized and characterized by micro elemental and thermal analyses as well as  $^1\text{H}$ .NMR, FT-IR, and UV-Vis spectroscopic techniques. (L) acts as a ligand coordinating with some metal ions V(IV), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II). Structures of the new compounds were characterized by elemental and thermal analyses as well as FT-IR and UV-Vis Spectra. The magnetic properties and electrical conductivities of metal complexes were also determined. Study of the nature of the complexes formed in ethanol following the mole ratio method.. The work also include a theoretical treatment of the formed complexes in the gas phase, this was done using the (hyperchem-8) program for the molecular mechanics and semi-empirical calculations. The heat of formation ( $\Delta H_f^\circ$ ), binding energy ( $\Delta E_b$ ) and total energy ( $\Delta E_T$ ) for ligand and their metal complexes were calculated by (PM3) method at 298 K. The electrostatic potential of the ligand (L) was calculated to investigate the reactive sites of the molecules. PM3 were used to evaluate the vibrational and electronic spectra for the ligand (L) and their metal complexes then comparing with the experimental values. The antibacterial activity for the (L) and its metal complexes were studied against two types of pathogenic bacteria *Pseudomonas aeruginosa* as gram negative and *Bacillus subtilis* as gram positive. Furthermore, the antifungal activity against two fungi *Candida albicans*, and *Aspergillus flavus* was studied for (L) and its metal complexes.

**Key words:** Azo compounds, coordination compound of Azo, spectral data, antimicrobial activity, synthesis and crystal structure of Azo compounds.

### Introduction:

Azo compounds are highly colored and very important class of chemical which have been used as dyes and pigments for a long time, as well as

they have been studied widely because of their excellent thermal and optical properties in applications [1,2]. A large number of (N,N')-donor ligands in azo imine family have been prepared in the last few years [3-6]. This azo imine family contains aryl azo pyridines [7], aryl azoimidazoles [8], and aryl azopyrimidines [9]. The coupling reaction of imidazole with aryl diazonium ion gives 2-(aryl azo) imidazole [9, 10]. Aryl azoimidazoles have attracted special attention because of the synthetic simplicity of the system and the biochemical ubiquity of imidazole [11]. This type of molecules has several advantages, one of the most important uses is as an analytical reagents [12, 13], and assstaining agents [14]. This class of azo compounds possess active ( $\pi$ -acidic) azo imine ( $-N=N-C=N-$ ), function and efficient agents to stabilize low valent metal oxidation states [15, 16] due to the presence of azo-centered  $\pi^*$ -molecular orbital. For this reason a number of these azo compounds were synthesized and their abilities as chelating ligands [16-18] were investigated. The metal complexes of these azo compounds are also found to be acting as dyes which are light fast due to their stable nature [18]. In this work, we synthesized new azo dye ligand (L) in an attempt to introduce the azo ( $-N=N-$ ) moiety in the structure of 2,1,3-benzoxadiazole ring to investigate the coordination behavior of the new (L) ligand towards some metal ions {V(IV), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II)}, which have been chosen to react with (L) and to compare the biological activity of (L) ligand and its metal complexes with the main ring structure.

## Materials and Methods:

### Materials and Measurements:

All the used reagents and solvents had at least analytical grade, except of 4,5-diphenyl imidazole was prepared as

reported procedure [19]. The buffer solutions were prepared as described earlier [20]. Melting points were determined by open capillary tube method and were uncorrected by using a Stuart melting point (digital SMP 30) apparatus. The micro analytical data for (C.H.N) were obtained using EA-034 mth.  $^1\text{H.NMR}$  measurement was taken ( $^1\text{H.NMR}$  300 MHz, using DMSO, PPM). The metal contents of the complexes were measured using Flame atomic absorption technique using Shimadzu AA-6300. FT-IR spectra were recorded on a Shimadzu 8000 FT-IR spectrophotometer in the (4000-400)  $\text{cm}^{-1}$  range using KBr discs. Electronic spectra were obtained using Shimadzu 1700 UV spectrometer using chloroform as a solvent in the (800-200) nm range. Magnetic susceptibility measurements were obtained on the solid state applying Magnetic susceptibility Balance of Sherwood Scientific (England). Thermal analysis studies of the ligand and their metal complexes were performed on Perkin-Elmer pyris Diamond DTA/TG Thermal system under nitrogen atmosphere. Molar conductance of the prepared metal complexes was determined in (DMF) as a solvent using concentration of  $10^{-3}$  M at  $25^\circ\text{C}$  using corning conductivity meter 220.

### Preparation of Azo ligand (L):

#### A. Preparation of 4-amino-7-chloro-2,1,3-benzoxadiazole (AB):

4-nitro-7-chloro-2,1,3-benzoxadiazole (400mg) was dissolved in a mixture of (8ml) of methanol and (2ml) of concentrated hydrochloric acid. After the addition of (400mg) of iron powder the reaction mixture was stirred for (30) mints, poured into (100ml) of (1M) NaOH solution and extracted with (100ml) of methylene chloride. The organic layer was dried with anhydrous ( $\text{Na}_2\text{SO}_4$ ) and concentrated in vacuo. The residue was chromatographed on

Silica gel (methylene chloride-hexane) to afford (180 mg) of amine as a yellow powder [21], Scheme (1).

### B. Preparation of Azo ligand (E)-4[(7-chloro-2,1,3-benzoxadiazole)azo]-4,5-diphenyl imidazole (L):

Azo ligand (L) was prepared according to the following general procedure [22]:

(1.695 gm, 0.01 mol) from (AB) was dissolved in a mixture of (10ml) hydrochloric acid and (20ml) distilled cold water and diazotized below 5°C with (0.80 gm, 0.011 mol) of sodium nitrite dissolved in (10ml) of distilled water. The resulting diazonium chloride solution was mixed with coupling agent 4,5-diphenyl imidazole (2.2 gm, 10mmol) dissolved in alcoholic NaOH solution (10%). After leaving it in the refrigerator for overnight, the solid was filtered off, washed with cold water, and crystallized from ethanol and dried over CaCl<sub>2</sub>, Scheme 1. The analytical and physical data of the ligand and its metal complexes are listed in Table (1).

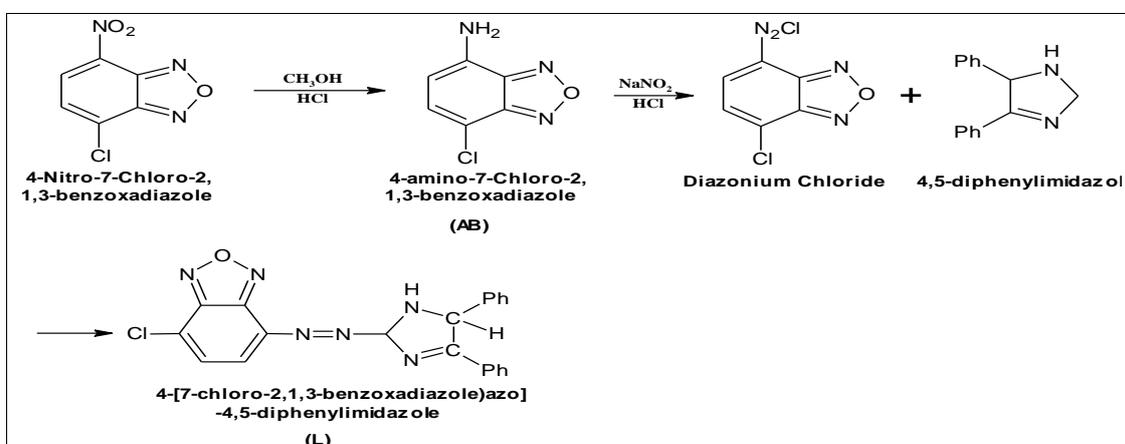
#### Preparation of AzoComplexes:

The metal complexes (1-6) were prepared by mixing the ethanolic solution of the ligand (L) (0.01 mol) with the appropriate metal ion salt (0.01 mol) [VOSO<sub>4</sub>.5H<sub>2</sub>O, CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, and ZnCl<sub>2</sub>.2H<sub>2</sub>O], while (0.02 mol) with (0.01 mol) of

FeCl<sub>3</sub>.9H<sub>2</sub>O and CuCl<sub>2</sub>.2H<sub>2</sub>O. The pH of the reaction mixture was adjusted to ~8 and it was refluxed for (2-3hrs.) on a water bath. The obtained solution was left at room temperature. The precipitated complex was filtered, washed with ethanol and then recrystallized from ethanol-chloroform (1:3 V/V) and dried in vacuum. The yields of all complexes were almost quantitative and the proposed structure of these complexes is as predicted in Figure (1).

#### Antimicrobial Studies:

The synthesized ligand (L) and metal complexes were screened for their antimicrobial activity by well plate method in nutrient agar (antibacterial activity) and sabouraud dextrose agar (antifungal activity). The *in Vitro* antibacterial activity was carried out against 24hrs old cultures of pathogenic bacteria like *Pseudomonas aeruginosa* as gram negative and *Bacillus Subtilis* as gram positive at 37°C. Antifungal activity was carried out against 72hrs old cultures of fungal strains like *Candida albicans* and *Aspergillus flavus*. In order to ensure that solvent had no effect on bacteria or yeast growth, a control test was performed with only DMSO and found inactive in culture medium.



Scheme 1: Preparation of Azo Ligand (L)

### Results and Discussion:

The analytical and physical properties of the (AB), (L), and metal complexes of (L), which are summarized in table (1), indicate [1:1] [Metal:Ligand] stoichiometry in case (1, 3, 4, and 6) complexes, whereas the molar ratio are [1:2] for (2, and 5) complexes. The new (L) ligand was soluble in common

organic solvents such as ethanol, acetone and methanol, whereas (1-6) of the new Azo colored crystalline solid complexes were soluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , DMF, and DMSO, they are thermally stable and unaffected by atmospheric oxygen and moisture. The elemental analysis data are in agreement with the proposed stoichiometry.

**Table 1: The Physical Properties of the Prepared Ligand (L) and its Metal Complexes<sup>1</sup>H.NMR**

Comp. No.	Color	Melting Point °C	Yield %	Elemental Analysis Found (calc.)				Suggested Formula for Compounds
				C	H	N	M	
(AB)	Yellow	164-165	85	42.60 (42.48)	3.04 (2.36)	25.11 (24.78)	-	$\text{C}_6\text{H}_4\text{N}_3\text{OCl}$
(L)	Reddish Brown	128-130	90	63.03 (62.69)	3.94 (3.73)	21.06 (20.89)	-	$\text{C}_{21}\text{H}_{15}\text{N}_6\text{OCl}$
(1)	Dark Green	215	77	44.68 (44.61)	3.04 (2.66)	15.13 (14.87)	9.11 (9.02)	$[\text{VO}(\text{C}_{21}\text{H}_{15}\text{N}_6\text{OCl})\text{SO}_4]$
(2)	Dark Brown	238	70	52.51 (52.18)	2.98 (3.11)	18.01 (17.39)	9.98 (10.35)	$[\text{Fe}(\text{C}_{21}\text{H}_{15}\text{N}_6\text{OCl})_2\text{Cl}_2]\text{Cl}$
(3)	Greenish Blue	219	86	47.50 (47.37)	3.11 (2.82)	15.94 (15.79)	10.89 (11.08)	$[\text{Co}(\text{C}_{21}\text{H}_{15}\text{N}_6\text{OCl})\text{Cl}_2]$
(4)	Green	218	80	47.31 (47.39)	2.69 (2.82)	15.83 (15.79)	11.16 (11.04)	$[\text{Ni}(\text{C}_{21}\text{H}_{15}\text{N}_6\text{OCl})\text{Cl}_2]$
(5)	Dark Brown	242	83	54.13 (53.69)	3.25 (3.19)	16.99 (17.89)	6.82 (6.77)	$[\text{Cu}(\text{C}_{21}\text{H}_{15}\text{N}_6\text{OCl})_2\text{Cl}_2]$
(6)	White	209	94	45.95 (46.80)	3.05 (2.79)	15.71 (15.60)	12.22 (12.15)	$[\text{Zn}(\text{C}_{21}\text{H}_{15}\text{N}_6\text{OCl})\text{Cl}_2]$

The synthesized ligand (L) has been characterized by <sup>1</sup>H.NMR, FT-IR spectroscopic techniques as well as elemental analysis. The <sup>1</sup>H.NMR spectral data of azo ligand in d<sup>6</sup>DMSO showed sharp single peak at ( $\delta=13.2$ ), ( $\delta=3.8$ ), and ( $\delta=1.9$ ), which are assigned to (NH), (-N-CH-N), and (-CH-Ph) respectively, due to protons of imidazole ring. The aromatic protons due to diphenyl at 4,5-position of imidazole ring have resonated in region ( $\delta=6.9-6.4$ ) (m, 5H\*2,Ar-H) as a multiplet. On the other hand, the doublet at ( $\delta=7.3-7.5$ ) due to proton of benzo-2,1,3-oxadiazole ring [23,24].

### Infrared Spectra:

The IR spectra of the free ligand (L) and its metal complexes were carried out in 4000-400 $\text{cm}^{-1}$  range, (Table (2)). The strong and broad band 3360  $\text{cm}^{-1}$  in the spectrum of the ligand (L) may be attributed to the ( $\nu\text{NH}$ ) of imidazole

group. This band remains in the same position in free ligand and in complexation. Thus, the remaining of amine hydrogen group in act in solid complexes, indicating its non-involvement in coordination of the ligand to the metal ions. The spectra of ligand (L) shows absorption band at 1615  $\text{cm}^{-1}$  due to ( $\nu\text{C}=\text{N}$ ) of (N3) imidazole nitrogen. It is observed with a little change in shape and shifted to lower frequencies (1600-1588)  $\text{cm}^{-1}$  in the prepared complexes spectra. These differences suggest the linkage of metal ion with nitrogen heterocyclic ring as shown in table (2). The ( $\nu\text{N}=\text{N}$ ) stretching vibration appears at 1498  $\text{cm}^{-1}$  in the free ligand spectra, this band appear at 1485-1480  $\text{cm}^{-1}$  with decreased in intensity in the spectra of complexes[24]. On the basis of this evidence, it is concluded that (L) acts as bidentate ligand in all complexes. The complexes spectra exhibited new weak

bands at frequency range (489-510) and (400-408)  $\text{cm}^{-1}$  assigned to stretching frequency of ( $\nu_{\text{M-N}}$ ) and ( $\text{M-Cl}$ ) respectively [24]. A strong band was observed at (980)  $\text{cm}^{-1}$  due to ( $\nu_{\text{V=O}}$ )

stretching mode [25], furthermore, a band related to ( $\text{SO}_4$ ) sulfate anion in complex (1) was observed at (1508)  $\text{cm}^{-1}$ , which indicated a bidentate behavior [25,26].

**Table 2: The Main Frequencies of the (AB),ligand (L)and itsComplexes (1-6)**

Comp. No.	$\nu_{\text{NH}_2}$ (as, s)	$\nu_{\text{NH}}$	$\nu_{\text{C=N}}$	$\nu_{\text{N=N}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-Cl}}$	Other
(AB)	3270 3238	-	1620	-	-	-	
(L)		3360	1615	1498	-	-	
(1)		3360	1600	1485	489	400	980 ( $\nu_{\text{V=O}}$ ), 1508 ( $\text{SO}_4$ ) anion coordination
(2)		3359	1592	1480	508	408	
(3)		3360	1589	1483	495	400	
(4)		3360	1600	1481	500	401	
(5)		3360	1588	1480	510	405	
(6)		3359	1596	1483	499	400	

### Thermal analysis:

The results for thermo gravimetric analysis of (L) and its metal complexes are given in Table (3). The thermo grams have been carried out in the range 25-900  $^{\circ}\text{C}$  at a heating rate of 20  $^{\circ}\text{C}/\text{min}$  in nitrogen atmosphere, they showed the following features:

1) There was an agreement in weight loss between results obtained from the thermal decomposition and calculated values, which supports the results of elemental analysis and confirms the suggested formulae.

2) The ligand (L) and all the studied complexes showed a common general behavior, in which the first pyrolysis step was the loss of diphenyl of 4,5-diphenyl imidazole substituted followed by the other part of the ligand except donor atom which were left with the metal atom depending on the type of metal ion.

3) The final step of the thermolysis reactions of the all complexes were found to give metal nitrogen as a final residue, which indicates the stability of such residues [27].

**Table 3: Thermal analysis by (TG-DTG) for (L) and its metal complexes**

Stable phase	Temp. range of decomposition $^{\circ}\text{C}$	% weight loss Found (Calc.)
(L)		
-2C <sub>6</sub> H <sub>5</sub>	68-280	39.09 (38.26)
-C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> OCl	280-388	38.55 (38.13)
-C <sub>3</sub> H <sub>3</sub> N <sub>2</sub>	388-438	17.02 (16.64)
-N <sub>2</sub>	438-500	6.99 (6.95)
Nothing		
1)[VO(L)SO <sub>4</sub> ]		27.79 (27.23)
-2C <sub>6</sub> H <sub>5</sub>	66-288	27.58 (27.14)
-C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> OCl	288-395	17.02 (16.97)
-SO <sub>4</sub>	395-479	16.99 (16.80)
-C <sub>3</sub> H <sub>3</sub> N <sub>4</sub> VO	479-900	12.11 (11.83)
2)[Fe(L) <sub>2</sub> Cl <sub>2</sub> ]Cl		35.79 (35.50)
-4C <sub>6</sub> H <sub>5</sub> +Cl	68-368	32.58 (31.73)
-2C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> OCl	368-415	7.62 (7.33)
-2Cl	395-483	16.99 (16.74)
-2C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> FeN <sub>2</sub>	483-900	9.01 (8.66)
3)[Co(L)Cl <sub>2</sub> ]		29.04 (28.92)
-2C <sub>6</sub> H <sub>5</sub>	66-300	28.95 (28.83)
-C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> OCl	300-412	13.56 (13.33)
-2Cl	412-593	15.86 (15.21)
-C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> CoN	593-900	13.93 (13.69)
4)[Ni(L)Cl <sub>2</sub> ]		28.99 (28.93)
-2C <sub>6</sub> H <sub>5</sub>	65-310	28.90 (28.84)
-C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> OCl	310-422	13.51 (13.34)
-2Cl	422-598	15.43 (15.22)
-C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> NiN	598-900	13.82 (13.65)
5)[Cu(L) <sub>2</sub> Cl <sub>2</sub> ]		32.92 (32.78)
-4C <sub>6</sub> H <sub>5</sub>	65-388	33.08 (32.67)
-2C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> OCl	388-452	7.69 (7.55)
-2Cl	452-510	17.79 (17.24)
-2C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> CuN <sub>2</sub>	510-900	9.91 (9.74)
6)[Zn(L)Cl <sub>2</sub> ]		28.76 (28.57)
-2C <sub>6</sub> H <sub>5</sub>	67-300	28.63 (28.48)
-C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> OCl	300-452	13.91 (13.17)
-2Cl	452-578	15.43 (15.03)
-C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> ZnN	578-900	13.89 (14.73)

### Electronic absorption Spectra, Magnetic susceptibility and Conductivity measurements:

Table (4) gives the electronic spectra of the metal complexes were recorded for their solution in chloroform, in the range (200-1100) nm, and magnetic moments at room temperature as well as the molar

conductance values of the complexes in (DMF).

The (L) ligand exhibit two bands around 34000 and 30000  $\text{cm}^{-1}$ , these intense bands are due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions respectively [24].

[1]:- The spectrum of VO(II) complex show two main absorption bands, which are assigned to the two transition  ${}^2B_2 \rightarrow {}^2E$  and  ${}^2B_2 \rightarrow {}^2B_1$  respectively in a square pyramidal geometry[28,29]. The magnetic moment (2.01B.M) is higher than spin value of the vanadium metal only, this result indicate a higher orbital contribution[30]. Measurement in (DMF) showed that the complex was non-ionic.

[2]:- This complex showed three bands related to octahedral iron complex[31]. They were observed at (11593,18666 and 26327)  $\text{cm}^{-1}$  that refer to  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  (G),  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  (G) and  ${}^6A_{1g} \rightarrow {}^4A_{1g} + {}^4E_g$  (G) respectively [28,31]. The ligand field (10Dq,  $B^-$ , Dq/ $B^-$ ,  $15B^-$  and  $\beta$ ) came out to (10015,766,1.22,10325 and 0.40) respectively. The magnetic moment is (5.23B.M.) indicated a high spin octahedral complex [28,30]. Conductivity in (DMF) showed that the complex was ionic.

[3]:-The greenish-blue cobalt(II) complex gave a magnetic moment value of (4.53B.M), which indicates a high-spin type complex[30]. Electronic spectrum in chloroform solvent exhibited a splitted band in the range of (17452-14184)  $\text{cm}^{-1}$  [28,31,32]. These bands can be assigned to the transition  ${}^4A_2 \rightarrow {}^4T_1$  (P) ( $\nu_3$ ). A broad band was observed at 3244 $\text{cm}^{-1}$  in infrared spectrum can be assigned to the  ${}^4A_2 \rightarrow {}^4T_2$  (F) ( $\nu_1$ ), while the transition of ( $\nu_2$ ) expected in the range (5000 - 6000)  $\text{cm}^{-1}$  can not be measured<sup>(35)</sup>. The various ligand field parameters(10Dq,  $B^-$  and  $\nu_2$ ) have been calculated by refer to Tanaba-Sugano diagram for ( $d^7$ ) configuration [28,33], to be (3244, 720.8 and 5453)

respectively, as well as the calculation of the spin-orbit coupling constant ( $\lambda$ ) was calculated. The resulting value ( $\lambda = -198.4$ ) show the present complex to be distorted tetrahedral[32,33]. The nephelauxetic factor ( $\beta$ ) was calculated and found to be (0.64) indicating high degree of covalence in bonding of ligand donor atoms with cobalt (II) ion [28,29]. The molar conductance showed that the complex was non ionic.

[4]:- The diamagnetic Ni(II) complex exhibit a medium intensity band at 16673 $\text{cm}^{-1}$  and a high intensity band at 28810  $\text{cm}^{-1}$  corresponding to transitions from  ${}^1A_{1g} \rightarrow {}^1A_{2g}$ ,  ${}^1E_g$  and the high intensity of the latter band may be due to over lap of L  $\rightarrow$  Ni(II) charge transfer band respectively in square planar disposition[28,31,34,35]. Conductivity measurement in Table (4) showed that the complex was non electrolyte.

[5]:- The UV-Vis spectrum of Cu (II) complex in ( $\text{CHCl}_3$ ) solution displays a broad band at 16130  $\text{cm}^{-1}$ , can be assigned to  ${}^2E_g \rightarrow {}^2T_{2g}$ , transition and the other to a charge transfer band in distorted octahedral geometry [28, 29, 33, 36]. This is further supported by the magnetic susceptibility value (1.74B.M), which agree well with distorted octahedral structure[30,32,36]. Conductivity in (DMF) solution, Table (4) showed that the complex was non ionic.

[6]:- The prepared complex is colorless in ( $\text{CHCl}_3$ ) solution and diamagnetic which is expected for  $d^{10}$  ion, since the spectra of this complex show some shifting and change in the shape of the bands were compared with those of the free ligand (L). The UV-Vis. spectrum of Zn(II) complex in ( $\text{CHCl}_3$ ) solution show some transition found in the region (200- 443 nm), can be assigned as intra ligand transition [28,31-34]. Conductivity showed that the complex was non electrolyte.

**Table 4: Electronic spectra (CHCl<sub>3</sub>), Magnetic moment (B.M) and Conductance in (DMF) for metal complexes**

Comp. No.	Bands cm <sup>-1</sup>	Assignment	10Dq	Molar cond. μs. Cm <sup>-1</sup>	μ <sub>eff</sub> . B.M	Suggested structure
[1]	11229 23988	<sup>3</sup> B <sub>2</sub> → <sup>2</sup> E <sup>2</sup> B <sub>2</sub> → <sup>2</sup> A <sub>1</sub>	-	17.68	2.01	Square Pyramidal
[2]	11593 18666 26327	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (G) <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> (G) <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> A <sub>1g</sub> + <sup>4</sup> E <sub>g</sub> (G)	10015	82	5.23	Octahedral
[3]	3244 5453 (cal) 15733(av.)	<sup>4</sup> A <sub>2</sub> → <sup>4</sup> T <sub>2</sub> (F) <sup>4</sup> A <sub>2</sub> → <sup>4</sup> T <sub>1</sub> (F) <sup>4</sup> A <sub>2</sub> → <sup>4</sup> T <sub>1</sub> (P)	3244	18.21	4.53	Tetrahedral
[4]	16673 28810	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> A <sub>2g</sub> , <sup>1</sup> E <sub>g</sub> L→Ni(II) (C.T)	-	17.96	0.0	Square planar
[5]	16130 30894	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub> L→Cu(II) (C.T)	-	14.03	1.74	Octahedral
[6]	20989,27854 29200	Zn(II)→L (C.T)	-	18.72	0.0	Tetrahedral

**Biological Studies:**

The new synthetic compounds were screened *in vitro* for their ability to inhibit the growth of representative *Pseudomonas aeruginosa* as gram negative and *Bacillus Subtilis* as gram positive]. Also the study was done against *Candida albicans* and *Aspergillus flavus* fungus, in DMSO as a solvent at two different concentrations. The results showed that the (AB) compound is moderate activity against the studied bacteria and fungus as compared with their Azo Dye ligand (L) against the same microorganisms and under the identical experimental conditions, Table(5), this difference

attributed to effect of introducing the pharmacologically important Azo moiety in the structure of the prepared free ligand. The complexes were found to be more toxic than the corresponding parent ligand (L) against all the types of the microorganisms table(5), this was attributed to the synergetic effect between the metal ion and the ligand [37]. Furthermore the results in Table(5), indicate that some of the new compounds exhibited antibacterial activity against the studied bacteria at lower concentration, while they don't show such activity at higher concentration [37-39].

**Table 5: Antibacterial and antifungal activities for (AB), free ligand [L] and their Metal Complexes (μgm.ml<sup>-1</sup>)**

Compo.	<i>Pseudomonas aeruginosa</i>		<i>Bacillus Subtilis</i>		<i>Candida albicans</i>		<i>Aspergillus flavus</i>	
	100 ppm	200 ppm	100 ppm	200 ppm	100 ppm	200 ppm	100 ppm	200 ppm
Control (DMSO)	-	-	-	-	-	-	-	-
[AB]	6	4	8	6	12	8	10	10
[L]	10	6	12	10	12	8	10	10
[1]	11	23	15	20	10	12	8	10
[2]	13	16	18	14	12	16	18	14
[3]	12	10	20	12	14	23	18	18
[4]	14	14	10	17	10	16	10	12
[5]	11	23	15	20	10	12	8	10
[6]	25	12	10	13	12	18	8	16
Where :[6-8: (+),8-10: (++) ,>10: (+++)]					30-40: (+++), 20-30 :(++++) , 10-20: (++++)			

### General Proposed Stereo Chemistry Structure of Complexes:

According to the results obtained from the elemental analysis, spectral studies,

magnetic and conductivity measurements, the general structure of the above mentioned complexes can be illustrated as follows, Fig.(1):

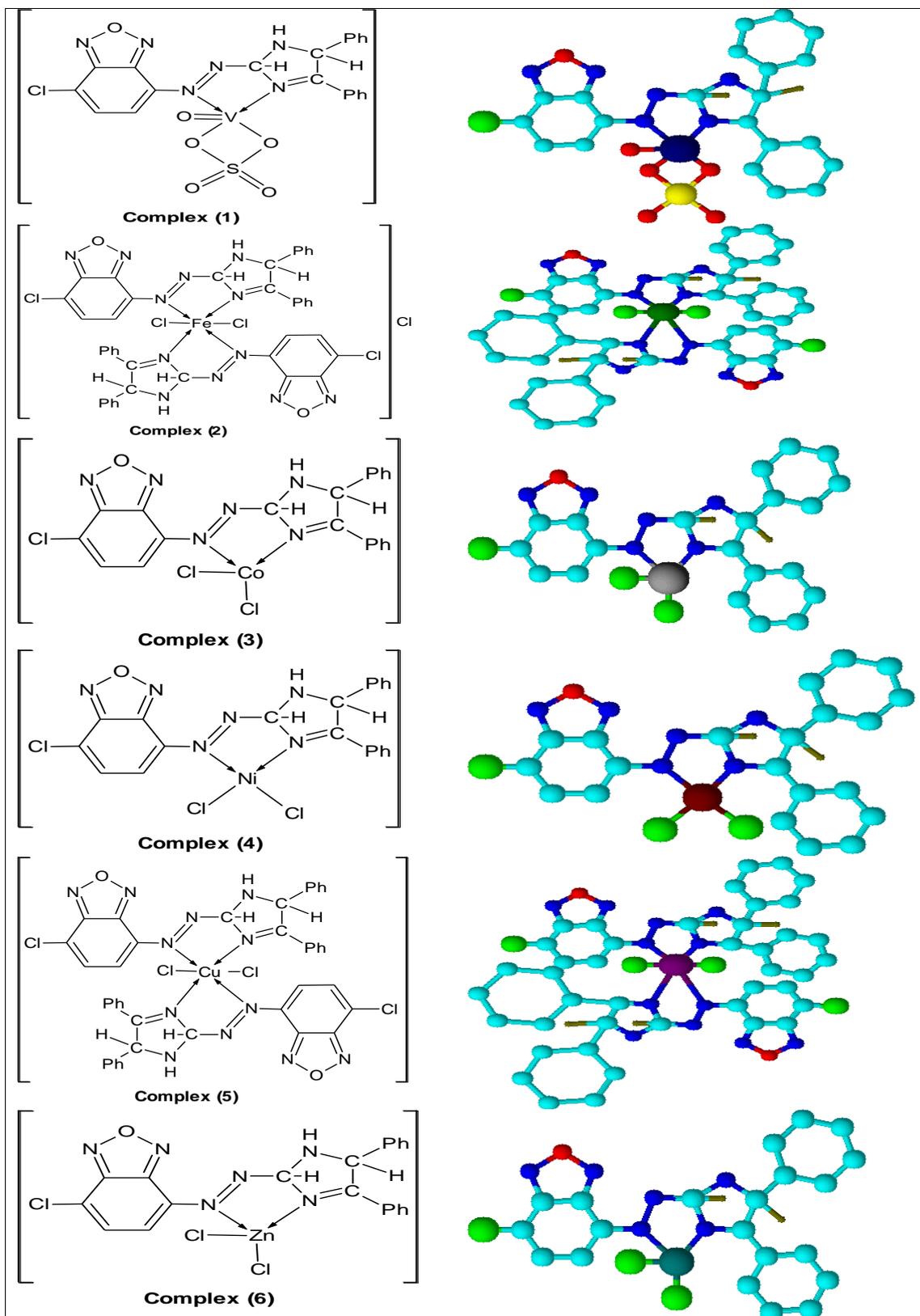


Fig. 1: Suggested structures of complexes of Azoligand

### Theoretical Studies of (L) ligand and their metal complexes:

#### a) Electrostatic potential (E.P)

Electron distribution governs the electrostatic potential of the molecules and describes the interaction of energy of the molecular system with a positive point charge, so it is useful for finding sites of reaction in a molecule positive charged species tend to attack a molecule where the electrostatic is strongly negative electrophilic attack [28,40,41]. (E.P) of free ligand (L) was

calculated and plotted as 2D contour to investigate the reactive sites of the molecules, fig. (2), and one can interpret the stereochemistry as well as rates of many reactions involving "soft" electrophiles and nucleophiles in terms of the properties of frontier orbital (HOMO and LUMO). The results of calculation showed that the LUMO of transition metal ion prefer to react with the HOMO of azo nitrogen (N=N) and (C=N) of imidazole nitrogen ring.

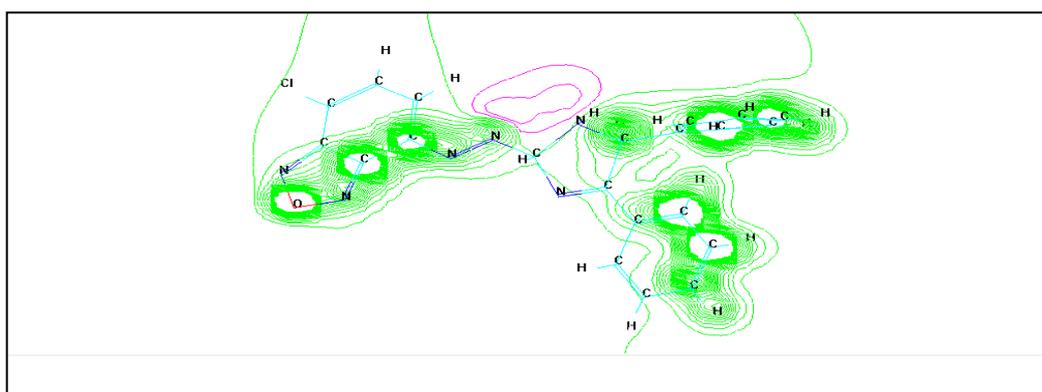


Fig .2: Electrostatic Potential (HOMO and LUMO) as (2D) contours for (L) ligand

#### b) Optimized geometries and energies:

The program hyperchem-8 was used for the semi-empirical and molecular mechanic calculations in gas phase to estimate the binding energy ( $\Delta E_b$ ), heat of formation ( $\Delta H_f^\circ$ ) and total energy ( $\Delta E_T$ ) for the ligand (L) and their metal complexes (1–6), were calculated by (PM3) method at 298 K, and at a value of geometry optimization constant (0.01 Kcal/mol) as tabulated in Table (6).

Table 6: Conformation energetic values for ligand and its metal complexes

Symb.	$\Delta H_f^\circ$	$\Delta E_b$	$\Delta E_T$
L	168.38	- 8003.39	- 5161.31
[1]	- 92.42	- 5537.21	- 4589.28
[2]	- 188.69	- 4428.07	- 5001.56
[3]	- 52.99	- 7273.11	- 5538.43
[4]	- 79.72	- 6954.82	- 3897.37
[5]	- 200.78	- 6522.14	- 6073.60
[6]	- 49.29	- 9103.09	- 5804.90

#### c) Optimized vibrational spectra for (L) and its metal complexes :

The theoretical calculations of the frequencies of  $\nu_{N=N}$ ,  $\nu_{C=N}$ , and  $\nu_{N-H}$  for free ligand (L), and (1-6) complexes as well as  $\nu_{M-N}$ , and  $\nu_{M-Cl}$  have been calculated, (Table (8)). The theoretically calculated wave numbers for all compounds showed some deviations from the experimental values. These deviations are generally acceptable in theoretical calculations [41-44]. The results obtained for the theoretical calculations of the frequencies for (L) and metal complexes, agreed well with those obtained for the experimental values.

**Table 8: Comparison between the experimental and theoretical vibrational frequencies for (L) ligand and complexes (cm<sup>-1</sup>)**

Symb.	$\nu_{\text{NH}}$	$\nu_{\text{C=N}}$	$\nu_{\text{N=N}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-Cl}}$
(L)	3360* 3344** [0.48]***	1615* 1620** [0.31]***	1498* 1490** [0.34]***	-	-
[1]	3360* 3356** [0.12]***	1600* 1610** [0.62]***	1485* 1480** [0.34]***	489* 488** [0.20]***	-
[2]	3359* 3355** [0.12]***	1592* 1585** [0.44]***	1480* 1488** [0.27]***	508* 504** [0.79]***	408* 388** [1.729]***
[3]	3360* 3357** [0.09]***	1589* 1580** [0.57]***	1483* 1475** [0.54]***	495* 493** [0.41]***	400* 392** [0.93]***
[4]	3360* 3357** [0.09]***	1600* 1611** [0.68]***	1481* 1478** [0.20]***	500* 502** [0.39]***	401* 390** [0.86]***
[5]	3360* 3357** [0.09]***	1588* 1590** [0.13]***	1480* 1478** [0.14]***	510* 504** [1.12]***	405* 403** [0.49]***
[6]	3359* 3355** [0.12]***	1596* 1600** [0.25]***	1483* 1480** [0.20]***	499* 497** [0.40]***	510* 512** [0.39]***

Where:

\* Theoretical frequency, \*\* Experimental frequency, \*\*\* Error % due to main difference in the experimental measurements and theoretical treatment of vibration spectrum.

#### d) Theoretical electronic spectra for the (L) and its metal complexes:

The electronic spectra of the free ligand (L) and its metal complexes have been calculated and the wave number for these compounds showed some deviations from the experimental values as shown in Table (9). These deviations in theoretical calculation are generally acceptable due to couplings between the electronic spectra modes and the approximation that each normal mode of the electronic spectra inter acts independently electronic spectra beam [41,43,44]. The most diagnostic calculated electronic spectra were chosen for the assignment of the free ligand (L) and its metal complexes. Experimental electronic modes are shown in Table (4). All the theoretical electronic spectra of all compounds were calculated by using the semi-empirical (PM3) method at geometry optimization (0.01 K.Cal. Mol<sup>-1</sup>) was used, as is shown in Table (9).

**Table 9: Comparison between experimental and theoretical of the electronic spectra metal complexes of (L)**

Symb.	Bands (nm)	Assignment
[1]	890*,888**,[0.23]*** 416*,420**,[0.95]***	<sup>2</sup> B <sub>2</sub> → <sup>2</sup> E <sup>2</sup> B <sub>2</sub> → <sup>2</sup> A <sub>1</sub>
[2]	862*,859**,[0.35]*** 535*,529**,[1.13]*** 379*,380**,[0.26]***	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (G) <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> (G) <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> A <sub>1g</sub> + <sup>4</sup> E <sub>g</sub> (G)
[3]	3082*,3088**,[0.19]*** 1833*,1840**,[0.38]*** 635*,639**,[0.63]***	<sup>4</sup> A <sub>2</sub> → <sup>4</sup> T <sub>2</sub> (F) <sup>4</sup> A <sub>2</sub> → <sup>4</sup> T <sub>1</sub> (F) <sup>4</sup> A <sub>2</sub> → <sup>4</sup> T <sub>1</sub> (P)
[4]	599*,594**,[0.84]*** 347*,350**,[0.86]***	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> A <sub>2g</sub> , <sup>1</sup> E <sub>g</sub> L→Ni(II)(C.T)
[5]	620*,615**,[0.81]*** 323*,327**,[1.53]***	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub> L→Cu(II)(C.T)
[6]	476*,470**,[1.28]*** 359*,362**,[0.83]*** 342*,344**,[0.58]***	Zn(II)→L(C.T)

Where:

\* Theoretical transition band of electronic spectra.

\*\* Experimental transition band of electronic spectra

\*\*\* Error % due to main difference in the experimental measurements and theoretical treatment of electronic spectra.

#### Conclusions:

The new Azo Day ligand and its metal complexes were successfully synthesized and characterized. The mode of bonding and overall structure of the complexes was determined through physio-chemical and spectroscopic methods. Hyperchem-8 program has been used to predict structural geometries of all compounds

in gas phase. The free ligand ( $L_1$ ) and its metal complexes (1-6) show significant antimicrobial activity. The all complexes are found more effective than the free ligand.

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## تحضير و تشخيص ودراسة بايولوجية ونظرية لمعقدات ثنائية السن V(IV) و Fe(III) و Co(II) و Ni(II) و Cu(II) و Zn(II) مع ليكاند واهب (NN) صبغة الأزو

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### الخلاصة:

حضر الليكاند الجديد 4- [ (7-كلورو-3,1,2-بنزوأكسدايازول)أزو] -4,5-ثنائي فنيل أيميدازول (L) وشخص بصورة كاملة بالطرائق الفيزيائية المناسبة [التحليل الدقيق للعناصر (C.H.N.S) والتحليل الحراري وطيف الأشعة تحت الحمراء والأطياف الإلكترونية وأطياف الرنين النووي المغناطيسي (<sup>1</sup>H NMR)]. تم استخدام (L) كليكاند لتحضير عدد من المعقدات الجديدة مع بعض أيونات العناصر الانتقالية V(IV) و Fe(III) و Co(II) و Ni(II) و Cu(II) و Zn(II). شخصت التراكيب الكيميائية للمركبات الجديدة باعتماد التحليل الدقيق للعناصر والتحليل الحراري فضلاً عن اطياف الأشعة تحت الحمراء و الأشعة فوق البنفسجية – المرئية. كما حددت الخصائص المغناطيسية وقيم التوصيلية الكهربائية للمعقدات الفلزية. كذلك تم دراسة طبيعة المعقد المتكون في محلول الايثانول باتباع طريقة النسبة المولية. تضمن العمل أيضاً معالجة تكوين المعقدات نظرياً في الطور الغازي، باستعمال برنامج (Hyperchem-8) وبتطبيق الميكانيك الجزيئي والشبه التجريبي في الحساب وذلك باستخدام الدالة (PM3) لحساب حرارة تكوين ( $\Delta H_f^\circ$ ) وطاقة التأصير ( $\Delta E_b$ ) والطاقة الكلية ( $\Delta E_T$ ) وبدرجة حرارة 298 كلفن لليكاند [L] ومعقداته. كذلك تم حساب الجهد الإلكتروني لليكاند (L) لتحديد المواقع الفعالة ضمن الجزيئة. جرى كذلك حساب قيم الاطياف الاهتزازية و الاطياف الإلكترونية لليكاند (L) ومعقداته نظرياً باستخدام الدالة PM3 ومقارنتها مع القيم المقاسة عملياً، ووجد بأن هنالك توافقاً كبيراً بين القيم العملية و المحسوبة نظرياً. تم تقويم الفعالية المضادة للبكتريا لليكاند (L) ومعقداته واختير نوعان منالبكتريا *Pseudomonasaeruginosa* سالبة الصبغة و *Bacillus subtilis* موجبة الصبغة لهذا الغرض. كما تم اجراء التقويم الحيوي لقاعدة شف ومعقداته ضد نوعين من الفطريات *Candida albicans* و *Aspergillusflavus*

الكلمات المفتاحية: مركبات الأزو، مركبات الأزو التناسقية، البيانات الطيفية، الفعالية البايولوجية، التركيب البلوري والتصنيعي لمركبات الأزو.