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PREPARATION AND SPECTRAL CHARACTERIZATION OF NEW CHELATE COMPLEXES DERIVED FROM AZO ETHYL 4-AMINOBENZOATE LIGAND

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Abstract: The current study was conducted to synthesize new azo-dyes and to study their chemical structures in details. Methods: A new azo compounds is prepared by (E)-5-((2-fluorophenyl)diazenyl)-2-hydroxybenzaldehyde with Ethyl 4-aminobenzoate to form ethyl 4-(((Z)-5-((E)-(2-fluorophenyl)diazenyl)-2-hydroxybenzylidene)amino)benzoate. The azo ligand was identified by Mass, ^{1}H-NMR, UV-Vis. and IR spectra, in addition to elemental analysis measurement. Analytical data revealed that all the complexes exhibited 1:2 metal–ligand ratios. On the basis of magnetic susceptibility measurements, suitable geometry was proposed for each complex. IR spectra of complexes showed that the ligand is coordinated to the metal ions in bidentate manner with oxygen and nitrogen donor sites of hydroxy azo and azo nitrogen. These findings suggested octahedral geometry for all complexes. Also, biological evaluation of all synthesized compound showed moderate to good activity against employed strains. All the comp The synthesized derivatives were screened for their *in-vitro* antibacterial activity against three gram-positive bacterium, *Enterococcus fecalis (E. fecalis), Staphylococcus aureus (S. aureus) and Bacillus subtilis (B. Subtilis)* and two gram-negative bacteria *Klebsiella pneumonia (K. pneumoniae) and Pseudomonas aeruginosa (P. aeruginos)* strains using streptomycin as standard references. *In-vitro* antifungal activity was screened against four fungal strains *Aspergillus Niger* (A. *Niger*) and *Aspergillus flavus* (A. *flavus*) using Fluconazole as standard references. The ligands and Schiff bases exhibited significant activity toward both Gram-positive, Gram-negative bacterial and fungal strains. Further, all the Complexes were stable, non-ionic and exhibited octahedral geometry around the metal centre.

***IndexTerms* - Azo ligand, Metal complexes, Ethyl 4-Aminobenzoat, Chelate complexes.**

1. Introduction

Azo compounds are the oldest and largest class of industrially synthesized organic dyes due to their versatile application in various fields and have attracted much attention in both academic and applied researches [1–3]. The latter included dyeing textile fiber, biomedical studies, advance application in organic synthesis and high technology areas such as laser, liquid crystalline displays, electro-optical devices and ink-jet printers. The N=N group is called an azo group and the name of azo came from azote, the French name of nitrogen that is derived from the Greek (a, which means not, and zoe, which means to live). A large number of (N,N′)- donor ligands in azo imine family have been prepared in the last few years [4-6].

Many azo-compounds have been applied as chromogenic reagents for the determination of several metal ions [7,8].The use of such reagents was found to depend essentially on their UV–vis spectral properties. Many articles have been published concerning the spectral characteristics of azo compounds [9,10] which studied the spectral structure correlations as well as the effects of medium on the band position. However, it seems that no studies were carried out concerning azo-compounds based on Ethyl benzoate moiety.

The coordination complexes of transition metals with azo-ligands are of current attraction due to the interesting physical, chemical, photo-physical and photo-chemical properties. The p-acidity and metal binding ability of azo nitrogen have drawn attention to the exploration of the chemistry of metal complexes incorporating azo-ligands [11–13]. Coordination chemistry of transition metal complexes with azo ligands is an important and fascinating branch of chemistry, and plays a pivotal role in industry, technology and life processes [14-16]. Therefore, current study was conducted to synthesize new azo dyes by bringing together two important chemical compounds, **(E)-5-((2-fluorophenyl)diazenyl)-2-hydroxybenzaldehyde** and **Ethyl 4-Aminobenzoate**. In addition, the chemical structures of both azo dyes and azo metal complexes were studied in details.

2. MATERIAL AND METHODS

2.1 Materials

All chemicals used in the preparation of azo ligand and metal complexes A. R. products from BDH and Merck.

2.2 Methods

Melting points were determined by open capillary tube method and are uncorrected by using Raaga melting point model 9001-2000. Elemental analyses (C, H, N,O,F,Cl) were carried out using a C.H.N.S EA-3000 mth instrument. IR spectra were recorded on PerkinElmer IR E S Version 10.6.1 FTIR spectrophotometer in the (3800-650) cm−1 range using KBr discs. UV-Vis spectrophotometer is employed for the absorbance measurement using ethanol as reference solvent over the range of 200 to 1000 nm. Magnetic susceptibilities are determined by Gouy balance at room temperature utilizing $Hg[Co(NCS)_4]$ as the calibrant. Molar conductivity were determined in (DMF) using Digital conductivity Series Ino. Lab- 720 at 25°C, the concentration of the solutions was (10^{-3} mol L^{-1}).

2.3 Synthesis of azo ligand

(L2) azo ligand is prepared according to the following general procedure [17] (**Fig. 1**), A mixture of (E)-5-((2-fluorophenyl)diazenyl)-2-hydroxybenzaldehyde (0.1 mol) and Ethyl 4-amino benzoate (0.1 mol) in ethanol 30 ml) were refluxed on water bath for about 5-8 hrs. in presence of few drops of glacial acetic acid. The product which was separated out as crystalline solid on cooling was collected and recrystallized from ethanol.

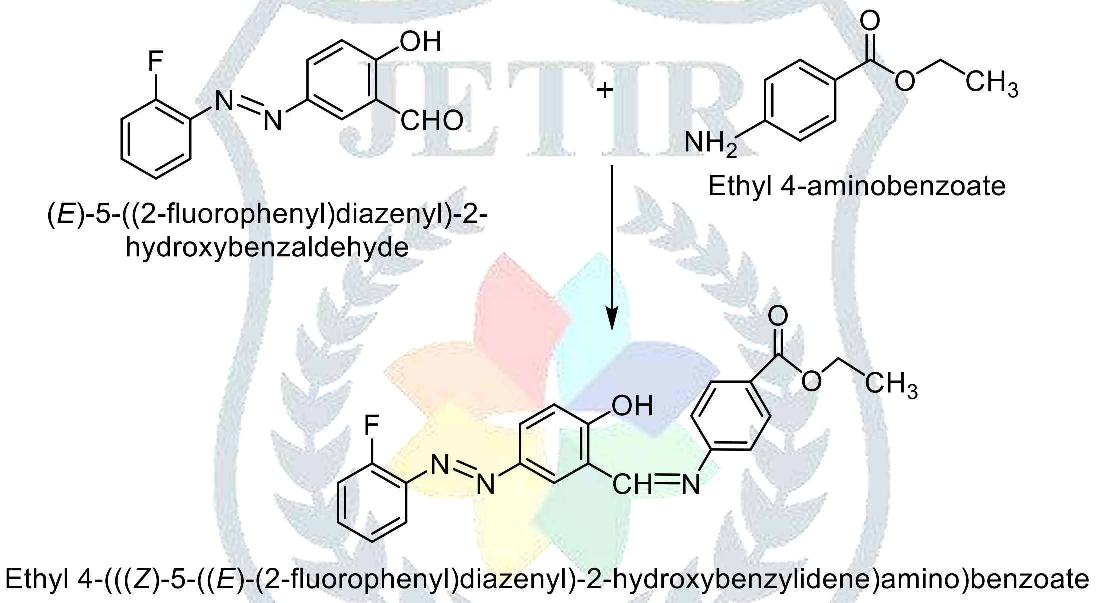


Fig. 1: Structure of Azo ligand (L2)

2.4 Synthesis of metal complexes

The Complexes were prepared by adding appropriate amount of the ethanolic metal salt (10 ml), namely, Co (II), Ni (II) and Cu (II) hydrated metal chloride and anhydrous Zn (II), Cd (II) and Hg (II) chloride and (4 mmol) to an ethanol/chloroform (1:1 v/v) solution containing 8 mmol of the ligand (LH) and the mixture was refluxed for 6 hr. The obtained solution was left at room temperature and the resulting precipitates were filtered off , washed with ethanol and then recrystallized from ethanol / chloroform (1:3 v/v) solvent mixture.

3. RESULTS AND DISCUSSION

Azo ligand was reddish brown, but the chelate complexes of this ligand vary in color depending on metal ion. The metal complexes were characterized by elemental analysis, molar conductivities, IR, UV-Vis and ^{1}HMNR spectra. The magnetic susceptibility of the chelate complexes at room temperature was consistent with octahedral geometry. The experimental results of elemental analyses of prepared ligand and its metal chelates were in good agreement with theoretical expectations. The elemental analyses of complexes indicated that the metal-ligand ratios were 1:2 in the (L2), M = Co (II), Ni (II), Cu (II) Zn (II), Cd (II) or Hg (II), metal complexes. The ligand and its complexes were quite air-stable, insoluble in water but soluble in common organic solvents such as chloroform, ethanol, Dimethyl Sulphoxide and Dimethyl Formamide giving stable solutions at room temperature. Complexes prepared in this work showed lower conductivity values indicating the non- electrolytic nature of these complexes. The synthesized derivatives were screened for their *in-vitro* antibacterial activity against three gram-positive bacterium, *Enterococcus fecalis (E. fecalis), Staphylococcus aureus (S. aureus) and Bacillus subtilis (B. Subtilis)* and two gram-negative bacteria *Klebsiella pneumonia(K. pneumoniae) and Pseudomonas aeruginosa (P. aeruginos)* strains using streptomycin as standard references. *In-vitro* antifungal activity was screened against four fungal strains *Aspergillus Niger* (A. *Niger*) and *Aspergillus flavus* (A. *flavus*) using Fluconazole as standard references. The ligands and Schiff bases exhibited significant activity toward both Gram-positive, Gram-negative bacterial and fungal strains.

3.2 Fourier transform - infrared [FT-IR] spectra of azo dyes

The IR spectra provided valuable information regarding the nature of functional group attached to the metal atom. The infrared spectral data of the Schiff base ligand show a medium intensity absorption band at 3457 cm^{-1} due to ν(O-H) stretching and a band around 1702 cm^{-1} due to a ν(C=O) stretching vibration of ethyl benzoate moiety (**Fig. 2**) . Further the appearance sharp band at 1486 cm-1 indicate the presence of ν(N=N) stretching. Moreover, the appearance medium intensity band at 1618 cm^{-1} is, due to ν(C=N) a vibration of azomethine linkage. However, A broad absorption band is appeared at 3449 cm^{-1} in the IR spectra of the complexes of cobalt(II) chloride, nickel(II) chloride, and copper(II) chloride due to the ν(O-H) stretching of associated water molecule. The strong band that was assigned to ν(C=O) at 1702 cm^{-1} in the ligand emerges in the complexes at the same location but with far less intensity in the metal(II) chloride complexes. The ν(C=N) detected at 1618 cm^{-1} remains in same place in the case of metal complexes. Finally, the IR spectra of complexes exhibited new non-ligand bands in the range of 559–518 cm^{-1}, 497–422 cm^{-1} and 390-348 cm^{-1} assigned as υ (M─O), υ (M─N) and υ (M─Cl) stretching vibrations, This result makes it clear that both "N" atoms of the ν(C=N) linkage are coordinated to a metal atom in chloride complexes [18-20].

Table 1: Physical properties and elemental analysis of azo ligand and their metal complexes, Including molar conductance and magnetic susceptibility.

Compound	**Color**	**M.P °C**	**Yield %**	**Formula**	**Formula Found (Calculated) %)**							**μeff (B.M)**	**Conductivity $S·mol^{-1}·cm^{2}$**
					C	**H**	**N**	**O**	**F**	**Cl**	**M**		
L2	Reddish Brown	145	87	$C_{22}H_{18}FN_3O_3$	67.51	4.64	10.74	12.26	4.85	----	----	-----	----
HTL2 Cu	Brown Powder	180	83	$CuC_{44}H_{36}Cl_2F_2N_6O_6$	57.62	3.96	9.16	10.47	4.14	7.73	6.93	1.56	11.36
THL2 Ni	Yellowish Brown	298	79	$NiC_{44}H_{36}Cl_2F_2N_6O_6$	57.92	3.98	9.21	10.52	4.16	7.77	6.43	3.01	16.34
STL2 Co	Light Brown	260	72	$CoC_{44}H_{36}Cl_2F_2N_6O_6$	57.91	3.98	9.21	10.52	4.16	7.77	6.46	4.30	12.02
CTL2 Zn	Yellow	210	86	$ZnC_{44}H_{36}Cl_2F_2N_6O_6$	57.50	3.95	9.14	10.44	4.13	7.71	7.11	Dia	9.22
ATL2 Cd	Light Yellowish	275	68	$CdC_{44}H_{36}Cl_2F_2N_6O_6$	54.70	3.76	8.70	9.94	3.93	7.34	11.64	Dia	8.65
MTL2 Hg	Brown	230	76	$HgC_{44}H_{36}Cl_2F_2N_6O_6$	50.13	3.44	7.97	9.11	3.60	6.72	19.03	Dia	10

Table 2: Characteristic IR absorption bands of the ligand and its complexes in cm^{-1} units

Sl. No	**Chemical formula**	**υ (O-H)**	**υ (C=N)**	**υ (N=N)**	**υ (M-N)**	**υ (M-O)**	**υ (M-Cl)**
01	L2= $C_{22}H_{18}FN_3O_3$	3457	1618	1486	----	----	----
02	$CuC_{44}H_{36}Cl_2F_2N_6O_6$	3449	1618	1486	497	549	390
03	$CoC_{44}H_{36}Cl_2F_2N_6O_6$	3434	1619	1486	458	534	362
04	$NiC_{44}H_{36}Cl_2F_2N_6O_6$	3420	1599	1498	422	528	348
05	$ZnC_{44}H_{36}Cl_2F_2N_6O_6$	3419	1560	1489	483	518	369
06	$CdC_{44}H_{36}Cl_2F_2N_6O_6$	3417	1578	1480	476	537	363
07	$HgC_{44}H_{36}Cl_2F_2N_6O_6$	3413	1587	1481	492	540	352

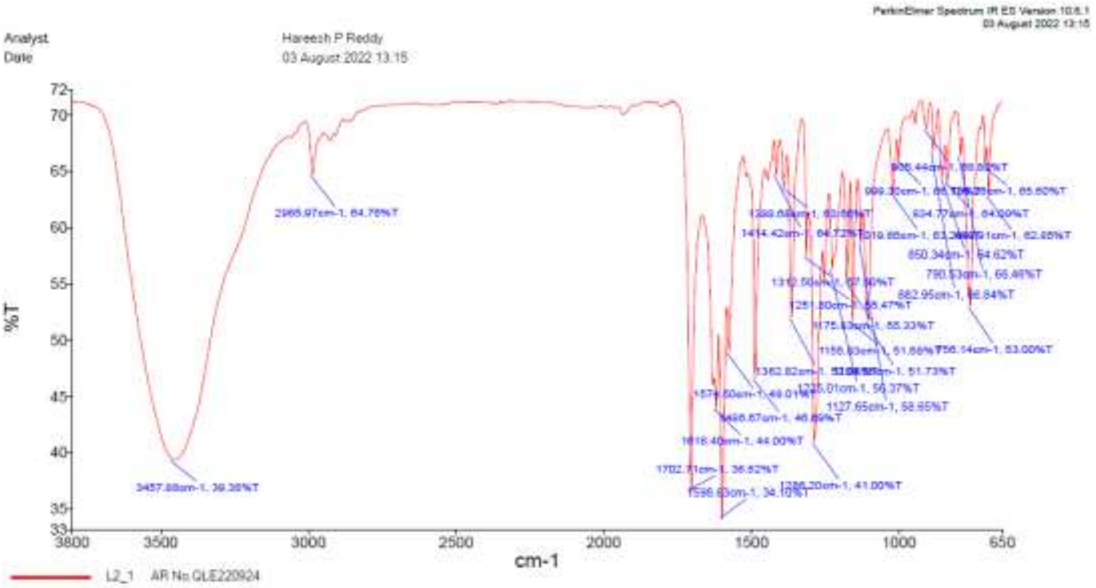


Fig. 2: a) IR spectrum of the azo ligand L2

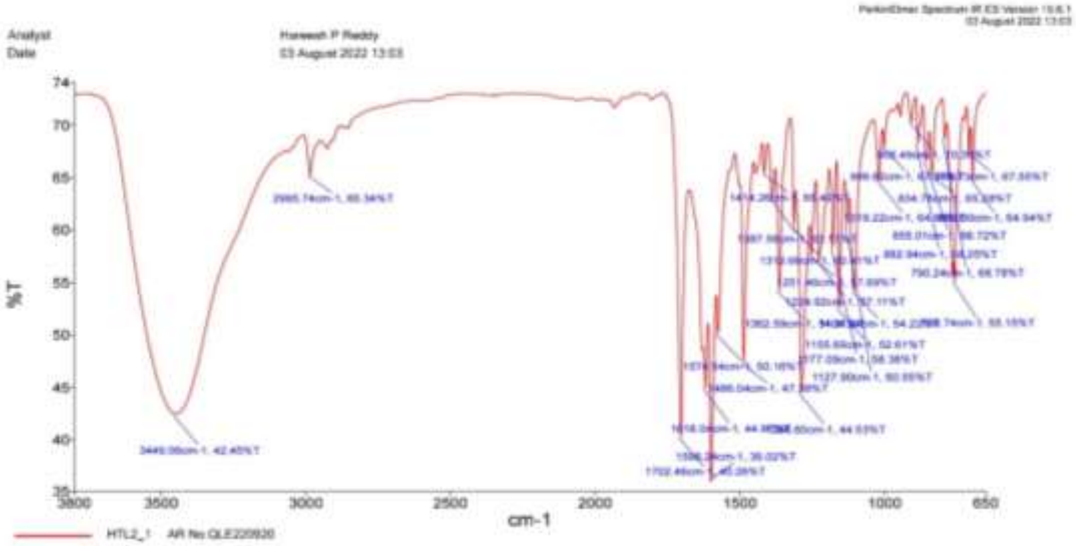


Fig. 2:b) IR spectrum of Cu (II) complex.

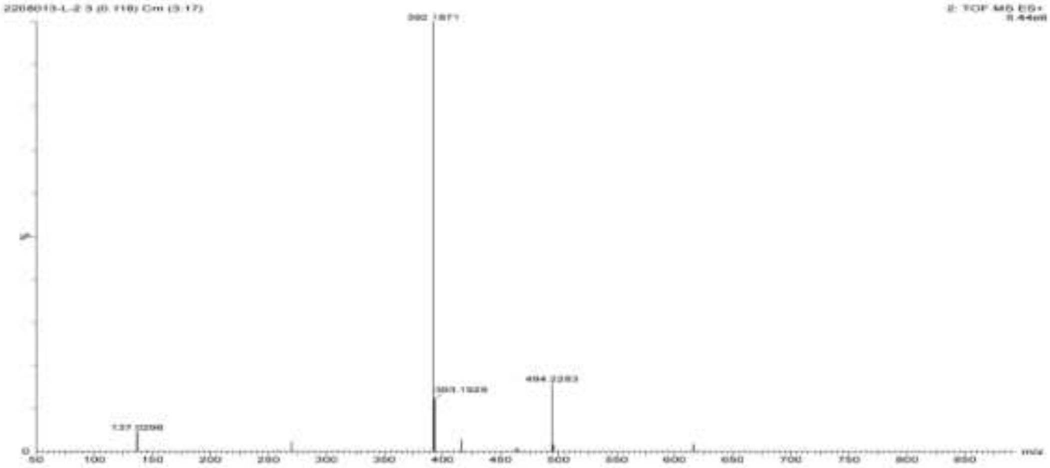


Fig. 3: Mass spectrum of azo ligand (L2)

3.3 Mass spectrum of azo ligand (L2)

The mass spectra of synthesized azo ligand (L2) (**Fig. 3**) Confirms the proposed formula by showing a molecular ion peak (m/z) at 391 (M^+) which is slightly higher than the actual molecular weight of a azo ligand, showing the predicted structure.

3.4. 1 H-NMR spectrum of azo dye

The 1 H-NMR spectrum of azo-compound (L2) under study displayed a group of signals corresponding to the protons of each molecule. The spectrum of this compound was produced using d6- DMSO as a solvent and (TMS) as a reference. The phenyl multiples at 7.1-8.3 ppm were assigned to the aromatic protons. In general, the compounds exhibited chemical shifts during the formation of complexes. As previously reported, the compounds shown in **Fig. 4** were present in solution as proton transfer equilibrium. In all cases, their 1 H-NMR spectrum showed a signal with a chemical shift in the range of 13-11 ppm, corresponding to the O–H·····N proton involved in the relevant intramolecular hydrogen bond. The signal at higher field, at 13.38 ppm for azo compound, was due to the free OH group [21].

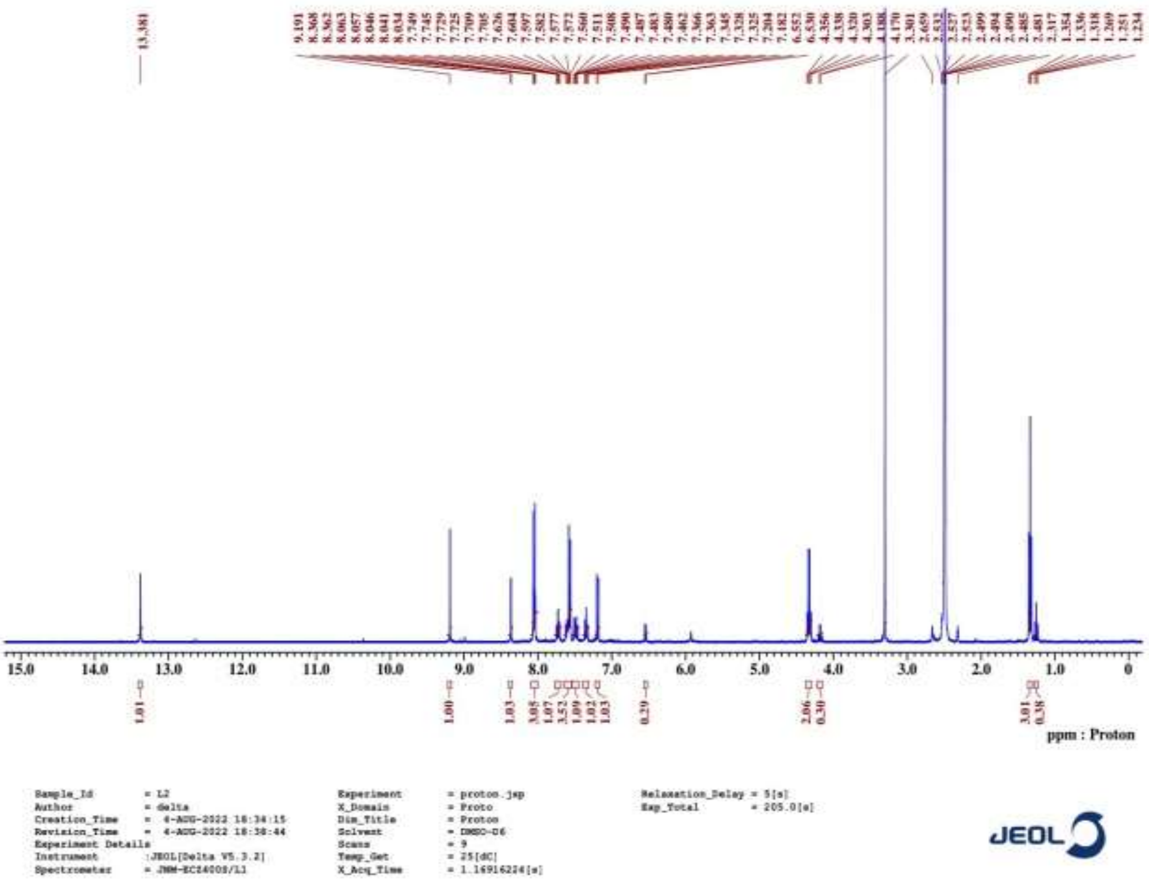


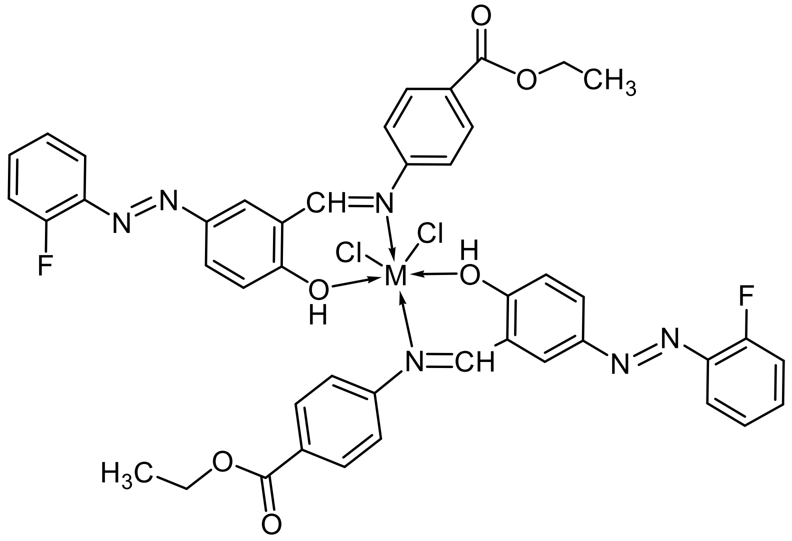
Fig. 4: ^{1}H-NMR spectrum of azo ligand (L2).

3.6 Magnetic measurements

The high spin magnetic moment value of Co (II) complex has a magnetic moment of 4.30 B.M in the high spin state which is in agreement with the reported value for octahedral Co (II) complexes [22]. The present Ni (II) complex showed a magnetic moment value of 3.01 B.M within the range 2.9–3.3 B.M for a high-spin Ni (II) complex depended on the magnitude of the orbital contribution [23] suggested an octahedral environment. The Cu (II) complex shows a magnetic moment value of 1.56 B.M monomeric and consistent with a distorted octahedral geometry. The Zn (II), Cd (II) and Hg(II) are diamagnetic and according to the empirical formulae of complexes, an octahedral geometry was proposed [24]. Based on the above results, we can deduce the probable structures of the complexes as shown in **Fig. 5.**

3.7 Molar conductivity measurement

Molar conductance of the metal complexes was measured in DMSO as a solvent at room temperature. All chelate complexes prepared in this wok showed conductivity values were ranged from 8.65 to 16.34 S.mol^{-1}.cm^{2} that were non-electrolyte and no conductive species [25]. According to these results, the structural formulas of this ligand and chelate complexes can be proposed as in **Fig. 5**.



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

Fig. 5: The proposed Structure of Complexes.

3.8 Biological Evaluation

3.8.1 In-vitro Antimicrobial activity

The investigation of antimicrobial screening revealed that, test compounds showed varying degrees of activity against all the tested microorganisms to quantify the antimicrobial potency of the compounds and the results have been given in (**Table 1**). The investigation of the tested compounds revealed that the series of compounds tested was found to be the most active when compared with the standards *Streptomycin*.

Table 1: *In-vitro* antimicrobial activity.

Compounds	**Conc. (µg/ml)**	**MIC value**				
		Antibacterial activities				
		B. Subtilis	**E. *fecalis***	**S. *aureus***	***K. pneumoniae***	***P. aeruginosa***
L2	100	---	09	12	06	02
	0.75	---	14	---	02	03
	0.50	06	05	06	---	02
	0.25	06	09	12	---	---
HTL2	100	---	05	---	06	02
	0.75	---	07	---	04	02
	0.50	06	06	---	---	02
	0.25	03	07	02	---	02
THL2	100	04	05	03	06	02
	0.75	---	06	---	---	06
	0.50	06	05	06	---	03
	0.25	---	04	03	---	04
STL2	100	---	03	06	04	---
	0.75	03	03	06	03	02
	0.50	---	05	---	05	---
	0.25	02	04	---	06	02
CTL2	100	14	14	14	14	14
	0.75	11	11	11	11	11
	0.50	11	11	11	11	11
	0.25	09	09	09	09	09
ATL2	100	02	04	03	04	05
	0.75	03	05	02	03	04
	0.50	05	02	05	06	07
	0.25	06	01	06	07	08
MTL2	100	08	03	04	03	04
	0.75	06	06	07	06	07
	0.50	04	07	08	09	08
	0.25	02	03	04	05	04
Std I	100	15	15	15	15	15
	0.75	10	10	10	10	10
	0.50	10	10	10	10	10
	0.25	08	08	08	08	08

Key for interpretation: '---'Not shown any zone of inhibition; Inactive: <1 mm, weakly active: 2-4 mm, moderately active: 4-6 mm, highly active: more than 6mm, Std I; Streptomycin.

3.8.2. In-vitro Antifungal activity

The investigation of antifungal screening revealed that, test compounds showed varying degrees of activity against all the tested microorganisms to quantify the antifungal potency of the compounds and the results have been given in (**Table 2**). The investigation of the tested compounds revealed that the series of compounds tested was found to be the most active when compared with the standards *fluconazole.*

Table 2: *In-vitro* antifungal activity.

Comp No	**Zone of inhibition in mm at 25, 50 and 100 (µg/ml)**					
	A. *Nizer*			**A. *flavus***		
	25	**50**	**100**	**25**	**50**	**100**
L2	5	9	15	6	9	12
HTL2	---	9	15	---	9	13
THL2	---	9	11	---	9	12
STL2	---	9	11	---	7	9
CTL2	9	11	15	7	12	14
ATL2	9	12	14	9	10	15
MTL2	5	9	10	---	9	12
Std II	12	13	18	14	18	23

CONCLUSIONS

In the current study we had explored the synthesis and coordination chemistry of some monomeric complexes obtained from the reaction of the didentate azo ligand L2 with some metal ions. The mode of bonding and overall structures of the complexes were determined through physico-chemical and spectroscopic methods. All the complexes were stable, non-ionic and exhibited octahedral geometry around the metal centre.

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Disclosure of conflict of interest

The authors declare that they have no conflict of interest.

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