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Preparation and Characterization of New Ligand Azo-Schiff-2- Naphthol and Mixed Complexes With Ortho- Aminophenol and Ortho- Aminobenzoic Acid

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Abstract

The work covered the synthesis and characterization many complexes of mixed ligands with some ions such as Co(II), Ni (II), Cu(II) and Zn(II) metals with new homocyclic azo - azomethine ligand 1-((E)-(4-((Z)-1-(p-tolylimino) ethyl) phenyl) diazenyl) naphthalen-2-ol(TEPDN) and ligand (HL_2 =4-Aminoacetophenone) at (1:1:1) ratio of ($M: L_1: L_2$) the complexes was characterized by using elemental analysis Uv-Vis and infrared spectra also their prepared complexes war measured by using the same methods in addition of molar conductance measurements, magnetic susceptibility and determined of metal percent in complexes. The physic- chemical studies and spectra data indicate that (TEPDN) ligand and another ligand acts as monobasic bidentate ligand after deprotonated of hydroxyl group .

Keywords: Schiff base , azomethine , Thermal analyses .

1. Introduction

Azo-azomethine ligands and their metal complexes have attracted considerable attention due to their impressive and useful chemical and physical properties [1–4]. Apart from their purely chemical interest, azo-azomethine ligands have also received special attention because of their mixed soft hard donor characters (O, N and S donor sites), versatile coordination behavior [5–7], pharmacological properties [8, 9] and optical and thermal properties [2, 10, 11]. Transition metal complexes of azo-azomethine ligands have also attracted special interest because of their optical and absorption properties and also high thermal stability[12]. Metalized azo-azomethine compounds are more stable against light, can provide easier control of the wavelength according to the substituted groups, and have good solubility in many organic solvents. They have been widely used in many practical applications such as printing systems [13, 14], photoelectronic materials [15, 16] and also as biological active compounds [2, 17, 18].Transition metal-complexes azomethine compounds have been studied in great detail in the literature for understanding their optical and electronic properties, structure-redox relationships, and misogynic characteristics[19, 20]. It could be expected that design and synthesis of transition metal complexes derived from azo Schiff base ligands might be a possible way to obtain the applicable nonlinear optical materials [21].

2. Experimental

2.1 Materials

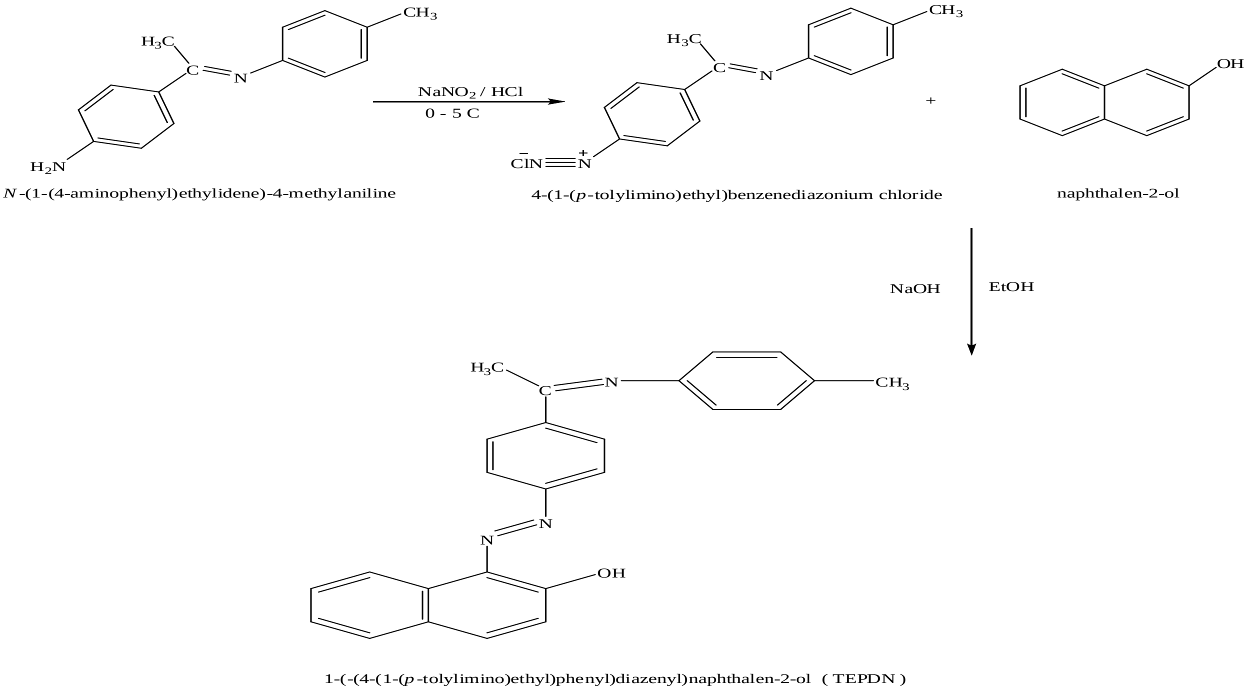
All of the reagents and solvents involved in synthesis were of analytically grade and used as received without further purification. *P*-Aminoaceto-phenone, *P*-Toluidin , The metal saltCoCl$_2$. 6H $_2$O, CuCl$_2$ .2H$_2$O ,NiCl$_2$. 6H$_2$O , ZnCl$_2$ were obtained from Aldrich and Merck.

2.2 Instrumentation

FT-IR spectra were recorded as pressed KBr discs, using Shimadzu FTIR 8400S spectrophotometer in the region of 400–4000 cm^{-1}. Melting points of all newly prepared compounds were determined on Electro thermal 9200 apparatus. Thermal analyses were performed on a Perkin-Elmer Thermogravimetric Analyzer TG/DTA6300 instrument. C. H. N analy- ses were performed on a Vario EL III elemental analyzer. Metal analyses were made on a Perkin-Elmer 2380 atomic absorption/flame emission spectrophotometer. Electronic spectral measurements were carried out using Perkin-Elmer Lamda spectrophotometer in the range 200–800 nm .Molar conductance of the complexes was measured in ethanol at room temperature using a Digital Conductivity SeriesIno.Lab.720.Magnetic susceptibility of the complexes was performed on a Balance Magnetic Susceptibility Model-M.S.B Auto. mass spectra were recorded byMSD Direct Probe. Using Acq Method low energy.

2.3 Synthesis

2.3.1 Synthesis of Azoligand (TEPDN). The diazoniumsalt, N-(1-(4-aminophenyl)ethylidene)-4-methylaniline(2.24 g, 10mmol)was added to mixed of2-Aminophenol (1.44g ,10 mmol) in ethanol and (50ml) of 10% NaOH, the reaction mixture was concentrated to one-half of the volume and refrigerated for one day. The obtained bright orange colour solid product was filtered and recrystallized from ethanol. The yield obtained was 78%, m.p. 177°C the Synthesis of azo Schiff base ligand shown in (Scheme 1).



SCHEME 1: Synthesis of azo Schiff base ligand.

2.3.2. Synthesis of Metal(II) Complexes. To a solution of mixed ligands(0.1895 g, 0.5mmol) 1-((E)-(4-((Z)-1- (p-tolylimino) ethyl) phenyl) diazenyl) naphthalen-2-ol (TEPDN) and 4-Aminoacetophenone(0.0545, 0.5mmol)in 50 mL ethanol wasadded to 0.5mmol of metal salts($CoCl_2$·6H2O, $NiCl_2$·6H2O, $CuCl_2$·$2H_2O$, and $ZnCl_2$)solution was stirred for 2 h at 80 C. The solution was allowed to settle for 10 min at ambient temperature . The resulted product was collected by filtration and washed successively with warm EtOH. The obtained solid was dried in air and stored at 50 C overnight.The yield obtained was70‑80%.

3. Results and Discussion

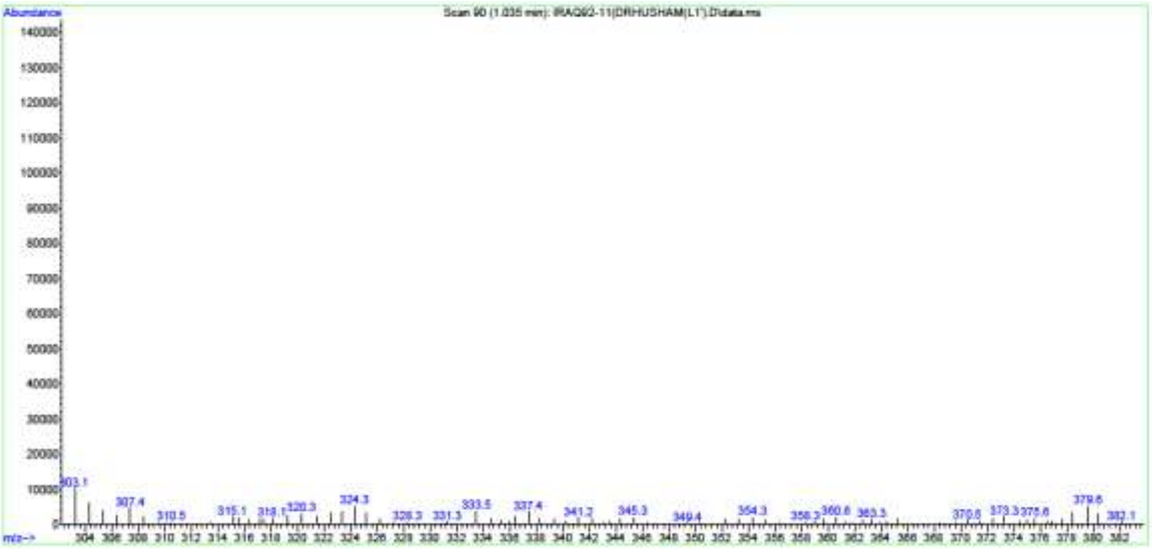
The analytical data and physical properties of (TEPDN) and metal(II) complexes are presented in Table 1The complexes are partially soluble in ethanol but soluble in polar coordinating solvents such as DMF The molar conductivities of all the complexes are in the (10.60‑12.55)(Ω−1 cm2 mol^{-1}) range indicating a non electrolyte nature[22].The obtained data showed that the stoichiometry of the chelates is(1 : 1: 1) (M : L_1 :L_2) and the analytical data of the complexes are in good agreement with the general formula [ML_1L_2].nH_2O for Cu(II), Ni(II), Co(II), and Zn(II) complexes where n=1,2,4 .

TABLE 1: Physical characterization, analytical and molar conductance data of the ligands and its metal(II) complexes.

3.1. Mass Spectral Studies. The mass spectra of the ligand TEPDN (L_1) and its complexes were recorded at room temperature, and they are used to compare their stoichiometry composition. The azo Schiff base shows a molecular ion peak at 379 m/z. Molecular ion peak for the Zn(II) complex observed at597m/z confirms the stoichiometry of metal chelates as[ML_1L_2]·H_2O type. The mass spectra of the ligand and its zinc (II) complex are

Cheimiecal formul	**Symbole**	**M.wt**	**m.p ^{0}C**	**Found (calc.) %**				**ΛM (Ω−1 cm2 mol−1)**
				C	**H**	**N**	**M**	
($C_{25}H_{21}N_3O$) =HL_1	**) TEPDN (**	**379**	**176-177**	**76.83 (79.13)**	**5.42 (5.58)**	**10.89 (11.07)**	**-------**	**------**
($C_7H_7NO_2$) = HL_2	**2-Amino-benzoic acid**	**137.14**	**146**	**------**	**----**	**----**	**------**	**--------**
[Cu ($C_{32}H_{26}N_4O_3$)].4H_2O	**M_1**	**650.12**	**198-199**	**58.91 (59.11)**	**5.13 (5.27)**	**8.46 (8.62)**	**9.58 (9.77)**	**12.55**
[Co ($C_{32}H_{26}N_4O_3$)].2H_2O	**M_2**	**609.51**	**165-166**	**62.87 (63.05)**	**4.84 (4.96)**	**8.82 (9.19)**	**9.72 (9.67)**	**11.31**
[Ni ($C_{32}H_{26}N_4O_3$)].H_2O	**M_3**	**591.27**	**-185 183**	**64.78 (65.00)**	**4.65 (4.77)**	**9.21 (9.48)**	**9.61 (9.93)**	**12.21**
[Zn ($C_{32}H_{26}N_4O_3$]. H_2O)	**M_4**	**615.98**	**-172 170**	**62.17 (62.39)**	**4.78 (4.91)**	**8.93 (9.10)**	**10.39 (10.62)**	**10.60**

shown in Figure1.



(a)

(b)

FIGURE1: Mass spectra of (a) [TEPDN], (b) [Zn(L_1)(L_2)· H_2O].

3.2. IR Spectral Studies. The characteristic IR spectral data of the ligands and its complexes are given in (Table 2).The detected band at 1598 cm^{-1} is assigned to the stretching vibration of the azo group of the ligand TEPDN. This band is shifted in the complexes toward lower frequencies(1530-1566 cm^{-1}) because of the participation of the nitrogen atom to coordinate with metal ion. This fact can be explained by the withdrawing of electrons from nitrogen atom to the metal ion due to coordination process [23].The bands around 3440 cm^{-1} and 1261 cm^{-1} are assigned to(O‑H) vibration and the carboxylic C‑O vibration, respectively. However, in the spectra of the metal complexes the C‑O bands underwent a shift towards higher frequencies ∼40 cm^{-1}, and this shift confirms the participation of oxygen in the C‑O‑M bond .Cu(II), Co(II), Ni(II), and Zn(II)complexes show a broadband at ∼3400 cm−1 due to the vibrations of hydrated water molecules [24].The band at1676 cm^{-1} is assigned to the stretching vibration of the azomethine group and the spectra of the complexes did not show any frequency shift of the C=N‑ band, which may be explained by nonparticipation of azomethine group in complex formation [25].The band of medium intensity observed for the complexes in the region580‑594 cm^{-1} is attributed toν (M‑N) and in the region480‑500 cm^{-1} to ν (M‑O) [26].

TABLE2: IR spectral data of ligands and its mixed metal(II) complexes (cm^{-1}).

Comp.	**ν(O-H) H_2O hyd-**	**ν(C-H)$_{ar.}$**	**ν (C-H)$_{al.}$**	**ν (N-H)**	**ν (C=N)**	**ν (N=N)**	**ν (C-O) carboxylic**	**ν(M-N)**	**ν(M-O)**
HL_1	**3442 w**	**3047 w**	**2958 w**	**---------**	**1676 m**	**1598 w**	**1261 s**	**---**	**---**
HL_2	**3323 w**	**3050 w**	**------**	**3238**	**------**	**-------**	**1260 s**	**------**	**-------**
$[CuL_1L_2].4H_2O$	**3423 w**	**3055 w**	**2935 w**	**3176**	**1678 m**	**1530 w**	**1311 w**	**501 w**	**582 w**
$[CoL_1L_2].2H_2O$	**3481 w**	**3057 w**	**3000 w**	**3421**	**1674 m**	**1539 w**	**1315 w**	**489w**	**584 w**
$[NiL_1L_2].H_2O$	**3483 w**	**3059 w**	**2875 w**	**3408**	**1680 m**	**1544 w**	**1305 w**	**499 w**	**588 w**

[ZnL_1L_2]. H_2O	**3522 w**	**3055 w**	**2920 w**	**3388**	**1670 m**	**1566 w**	**1315 w**	**487 w**	**590 w**

3.3 Thermal Properties

Thermal stability and decomposition behavior of (TEPDN) and Cu(II) complex have been studied TGA in the flowing atmosphere of air in the temperature range 50–900 °C, Table 3.The TGA curves of (HL_1) and (M_1) are presented in Fig. 3From the TGA data it can be seen that the (HL_1) show no any mass loss up to290 °C, indicating the absence of water and any other adsorptive solvent molecules in the coordination sphere [26,27].Whereas, the TG curves of (M_1) show a mass loss of 10.7% within the temperature range 50–145°C corresponds to the loss four molecules of hydration water (calc. 11.07).The complex (M_1) was thermally decomposed in two successive decomposition steps. The second decomposition step of estimated mass loss 25.48% above 300 °C may be attributed to the loss of the ($C_{10}H_6N_2O$)(calc. 26.10%).

TABLE 3: Thermal analyses data for (TEPDN=HL_1) and (M_1)

Compound (M.Wt)	Dissociation stages	Temp.range In TG (C°)	Weight loss Found (calc.)	Decomposition assignment
($C_{25}H_{21}N_3O$) =HL_1 (379)	Stage I Stage II	50 – 280 290 – 577	4.21 (4.23) 61.48(62.26)	Loss of (CH_4) Loss of($C_{15}H_{14}N_3$)
[Cu($C_{31}H_{26}N_4O_2$)].$4H_2O$ = M_1 (650)	Stage I Stage II	50 – 145 155 – 299	10.7 (11.07) 25.48 (26.10)	Loss of ($4H_2O$) Loss of ($C_{10}H_6N_2O$)

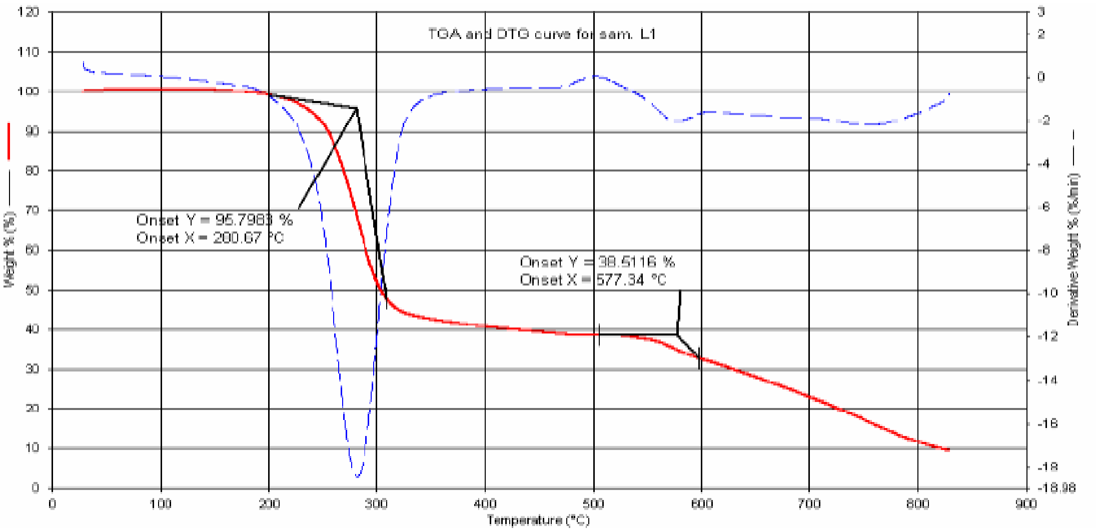


FIGURE 2: TGA analyses curves of (HL_1) ligand .

3.4. Electronic Spectral and Magnetic Susceptibility Studies .The electronic spectra of TEPDN (HL_1) and its complexes were recorded in ethanol. The absorption spectrum of the ligand shows strong peaks at 317 and 286nm which may be assigned to ($n \rightarrow \pi^*$)(transitions of the-CH=N-and -N=N- groups) and ($\pi \rightarrow \pi^*$) (transition of -N=N- azo group) transitions respectively[28,29],the spectral data of the ligand and its complexes given in Table 4.The spectra of the mixed ligands of Cu(II) ,Co(II) ,Zn(II) complexes show peaks in the region at 489-500 nm which can be assigned to charge transfer L→ M bands[30,31].The nickel(II) complex exhibits d-d bands at 487 nm, due to$^1A_{1g} \rightarrow {}^1B_{1g}$transitions which arises from an square- planer structure. The magnetic moment value of the cobalt(II) complex 3.63 B.M. confirms the tetrahedral geometry [32].The magnetic moment value1.37 B.M. falls within the range normally observed for square planar Cu(II) complexes [33]. The Zn(II) , Ni(II) complexes has been found to be diamagnetic in nature confirms the tetrahedral geometry for Zn(II) mixed ligands complex[34]and square planar for Ni(II) complex[34]

TABELE 4: Electronic spectral data of ligands and its metal(II) mixed ligand complexes.

Compound	Assigument	Absorption band(n.m)	μ_{eff} (B.M)	Proposed Structure

HL_1	$n\rightarrow\pi^*$& $\pi\rightarrow\pi^*$	317 , 488 227 , 286	----	----
HL_2	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	336 260	----	----
$[Cu(L_1)(L_2)].4H_2O$	C. T.	508	1.37	Sq.P
$[Co(L_1)(L_2)].2H_2O$	C. T.	488	3.63	Td
$[Ni(L_1)(L_2)].H_2O$	$^1A_{1g}\rightarrow{}^1B_{1g}$	487	Dia	Sq.P
$[Zn(L_1)(L_{32})].H_2O$	C. T.	489	Dia	Td

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