

Preparation and Identification of Co (LI), Ni (LI), Cu (LI) Complexes with a new 4-(4-(1-(2-Hydroxyl Phenyl) Amino) Ethyl Phenyl) Azo-2, 6-Dimethyl Phenol Ligand

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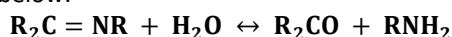
Abstract

The new ligand was prepared in two stages, the first involves the preparation of Schiff base by condensation reaction between p-aminoacetophenone with 2-aminophenol, and the second includes the diazonium coupling of the Schiff base with 2, 6-dimethylphenol. The complexes of this ligand with Cu (II), Ni (II) and Co (II) ions were prepared and characterized by analytical methods like molar ratio, magnetic susceptibility and molar conductivity, spectroscopies methods like Uv. Visible, FT-IR 1H-NMR and flame atomic absorption spectroscopies. From these diagnostic methods, we concluded that the complexes are octahedral in shape.

1. Introduction

Schiff's bases are considered one among the foremost prominent ligands utilized in coordination chemistry, as they enter into the preparation of an outsized number of complexes with metal ions normally and transitional elements specifically, due to their high ability to coordinate with metals and form complexes with different structural structures and multiple uses [1]. Schiff's bases have many names, including Anils, Azomethines, Benzanils, Benzylidene Aniline, Ketimines after they are derived from ketones, and Aldimines after they are derived from Aldehydes [2].

The stability of Schiff bases depends on the carbonyl compounds and amines that are employed in their preparation, whether or not they are aliphatic or aromatic, where it's preferable to withdraw the water molecule first from the reaction when preparing Schiff bases from diaryl or alkyl aryl ketones [3], while it's not done per the water molecule during the condensation process Various aldehydes or di-alkyl ketones with amines [4]. (Daniilof and Reddlien) found that azomethane compounds are stable in aqueous solutions of bases, but they disintegrate rapidly in acidic metallic solutions as shown below:-



Azo dyes are colorful materials that may bind with the materials to be dyed and provides them vibrant hues while being resistant to acids, bases, washing, light, and oxygen [5]. In azo compounds, two nitrogen atoms are bonded together in the molecule by double bonds (-N=N-), which is why it was discovered and named by the scientist (Greiss) in the year 1860 AD, azo dyes to the presence of this bridge group (-N=N-) with a hybrid (SP²) associated with the aromatic system [6, 7]. If the azo dyes are attached to both ends of the bridge group (-N=N-), they are known as aliphatic azo dyes. Because of its high

stability and multiplication, this type is highly significant [8].

The colors of azo dyes are determined by their composition and the type of the compensated aggregates, with the intensity of the color increasing as the aggregation of the color-donating chromophores or the molecular weight increases. The color developers are the axochromic groups, which change the color intensity of the chromophore-bearing benzene ring. It does, however, boost the color's intensity and capacity to adhere to the dyed materials [9, 10].

Azo dyes are linked to tissues through exochromates (aggregates of color-donating and fixing chromophores) [11], where they're linked either directly or through fixative materials through a range of mechanisms, including physical adsorption, mechanical retention of the dye, covalent bonds, the formation of metal complexes, and therefore the formation of solutions with it [12].

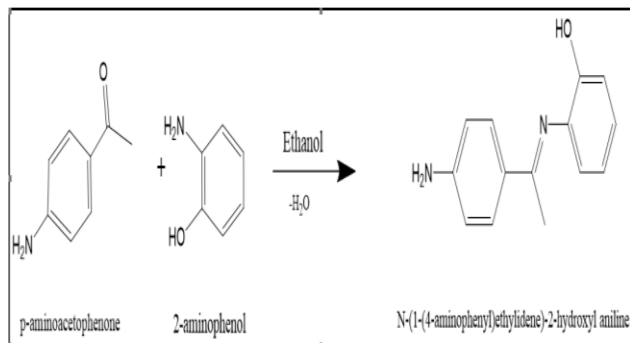
2. Experimental

Materials: - mineral salts CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O and absolute ethanol with high purity supplied from B.D.H company. 2-aminophenol, p-aminoacetophenone and 2, 6-dimethylphenol provide from Merck Company.

Instruments: - UV-visible spectrophotometer type UV 6100PC double beam Spectrophotometer was used to identify the produced ligand and its complexes in the wave length range (200 nm to 800 nm), FT-IR 8400S spectrometer -Schimadzu within the region (4000 cm⁻¹ to 400cm⁻¹). The 1H-NMR Bruker's. The molar conductivity of the metal complexes was measured using the solvent absolute ethanol (1x10⁻³ molar) using the (Glassco-India) apparatus. The magnetic susceptibility of the complexes was measured using an iron balance. Temperature was measured employing a German 9300 thermoelectric freezing point type.

1- Preparation of Schiff Base

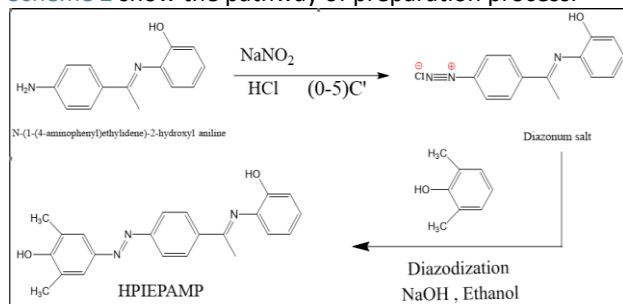
The Schiff base derivative was prepared by dissolving (0.01 mole, 1.35 g) of (4-aminoacetophenone) in 20 ml of absolute ethanol and (0.01 mole, 1.09 g) of (2-aminophenol) in a similar volume of absolute ethanol and mixed these two solutions, and adding three drops of glacial CH₃COOH as a catalyst and refluxed the reaction for 6 hours, after that cooling the reaction mixture, filtered, dried, and recrystallized with hot absolute ethyl alcohol. The pathway of the preparation steps shown in scheme 1.



Scheme.1. Preparation of Schiff Base

2- Preparation of new 4-(4-(1-(2-hydroxyl phenyl) imino) ethyl phenyl) azo-2,6-dimethyl phenol (HPIEPAMP) Ligand

The HPIEPAMP ligand was prepared by dissolving (0.01 mole, 2.26 g) of the schiff base derivative obtained in the first step in a solution of an acidic mixture (4 ml HCl + 20 ml DW), cooling in an ice bath at (0-5)°C, and then it has been added a sodium nitrite solution (0.01 mole, 0.69 g) in 10 ml of distilled water, left the solution with cooling and stirring continuously for 15 minutes to completely prepare the diazonium salt, while the conjugation component is made by dissolving (0.01 mole, 1.22 g) of (2,6-Dimethylphenol) in mixture of 20 ml of ethyl alcohol and 25 ml of 10%NaOH solution at the same temperature (0-5)°C with constant stirring and cooling and then left for 1 hour and then adjusted pH to become equal to 7. Filtrated the solution and washed with deionized water, dried, and recrystallized with hot absolute ethanol. Scheme 2 show the pathway of preparation process.

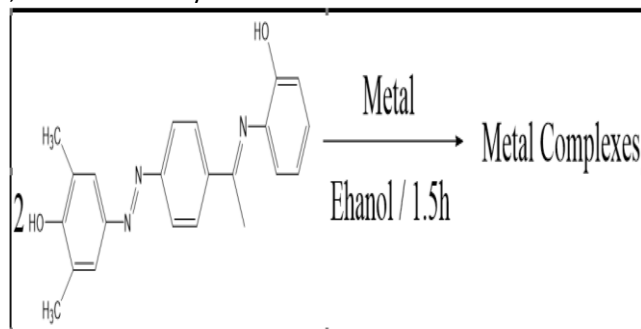


Scheme 2. Preparation of Ligand (HPIEPAMP)

3- Preparation of metal complexes

The Cu (II), Ni (II) and Co(II) complexes were prepared by mixing their metal salts of 0.001 mole dissolved in 20 ml of absolute ethanol with 0.002 mole of ligand (HPIEPAMP) dissolved in 40 ml of absolute ethanol with the ratio of (M:L) (1:2) and refluxed for 1.5 hours, the mixture cooled

, filtered and recrystallized in hot ethanol as in scheme 3.



Scheme 3. Preparation of metal complexes

3. Results and Discussion

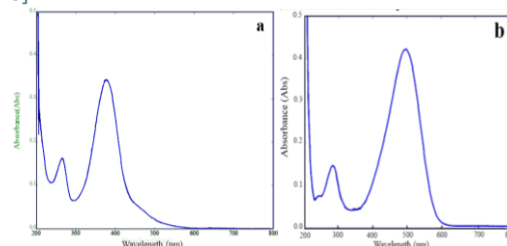
Identification of ligand and its metal complexes

Table 1 summarizes the physical properties, elemental values, magnetic and conductivity properties of the ligand and its complexes, where the conductivity values indicate the absence of chloride ions outside the coordination sphere [13, 14]. The C.H.N. values were found to be identical in both theoretical and experimental coordination sphere of the complex.

Table 1. Elemental values, magnetic and conductivity properties of the ligand and its complexes.								
Compound (M.wt gm/mol)	m.p(°C) (Yield %)	Colour	μ B. M	Am Ohm ⁻¹ . cm ²	Elemental Analysis % Exp.(Cal.)			
					C%	H%	N%	M%
C ₂₂ H ₂₁ N ₃ O ₂ (359)	256 - 259 (84.8)	Red brown	---	---	74 (73.54)	5.8 (5.85)	11.69 (11.69)	---
[Co(L) ₂ (H ₂ O) (778.93)	288 - 290 (71.4)	Dark brown	4.88	24.5	---	---	---	8.13 (6.95)
[Ni(L) ₂ (H ₂ O) ₂ (778.69)	294 - 296 (69.3)	Dark red	3.69	21.2	---	---	---	7.98 (6.96)
[Cu(L) ₂ (H ₂ O) (783.55)	279 - 282 (73.2)	Black	1.83	18.7	---	---	---	7.08 (7.47)

4. Electronic Spectra

Figure.4 and Table 2. Show the Uv. Visible spectrum of the prepared ligand (HPIEPAMP) and their (Cu(II) ,Ni(II) and Co (II) complexes each at a concentration of (1x10⁻⁵) molar. The difference between the ligand spectrum and these complexes spectrum in maximum wavelength (λ_{max}), where the cobalt complex (II) includes a longer wavelength (499 nm), the nickel complex (II) show a maximum wavelength (511 nm), and the copper complex (II) show the maximum wavelength (508 nm) [15, 16].



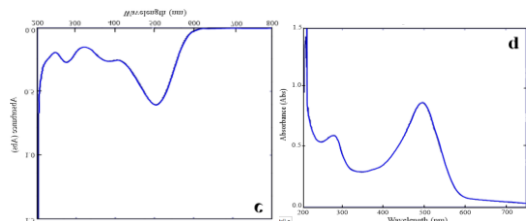


Fig.4. Electronic spectrum of: a-Ligand, b-Co Complex, c-Ni Complex, d-Cu Complex.

No.	Molecular formula	λ_{max}	Wave number (cm^{-1})	Transition type
1	$C_{22}H_{21}N_3O_2$	377	26525	$n \rightarrow \pi^*$
		265	37735	$\pi \rightarrow \pi^*$
2	$[Co(C_{22}H_{20}N_3O_2)_2(H_2O)_2]$	499	20040	CT
		287	34843	$\pi \rightarrow \pi^*$
3	$[Ni(C_{22}H_{20}N_3O_2)_2(H_2O)_2]$	511	19569	CT
		276	36232	$n \rightarrow \pi^*$
		203	49261	$\pi \rightarrow \pi^*$
4	$[Cu(C_{22}H_{20}N_3O_2)_2(H_2O)_2]$	508	19685	CT
		283	35336	$n \rightarrow \pi^*$

FT-IR Spectra

Figures 5, 6, 7, and 8 and table 2 illustrate the FT-IR of ligand and its complexes. The functional bonds of ligand and their ions Co (II) Ni(II) , Cu(II) complexes were demonstrated in FT-IR spectrum [17].The phenolic (O-H) appears within the FT-IR spectrum of the ligand and coordinated water as a ligand in metal ions complexes at ($3144-3339\text{ cm}^{-1}$) [18, 19].

No.	Compound	$\nu(O-H)$	$\nu(C=N)$	$\nu(N=N)$	$\nu(M-N)$	$\nu(M-O)$
1	$C_{22}H_{21}N_3O_2$	(3339)	(1668)	(1589)	---	---
		s	s	s		
2	$[Co(C_{22}H_{20}N_3O_2)_2(H_2O)_2]$	(3362)	(1665)	(1593)	(419)	(659)
		s	s	s	m	w
3	$[Ni(C_{22}H_{20}N_3O_2)_2(H_2O)_2]$	(3358)	(1664)	(1591)	(419)	(649)
		s	s	s	m	w
4	$[Cu(C_{22}H_{20}N_3O_2)_2(H_2O)_2]$	(3144)	(1680)	(1597)	(495)	(651)
		s	s	s	m	w

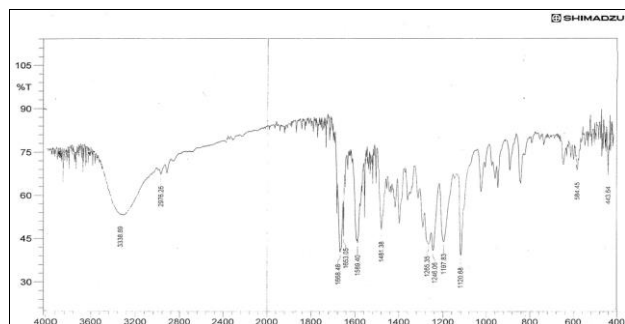


Fig.5. FT-IR spectrum of (HPIEPAMP) ligand.

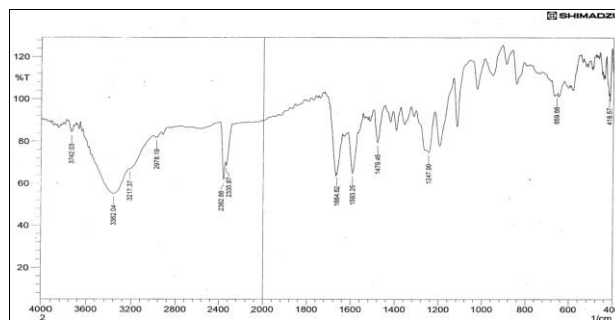


Fig.6. FT-IR spectrum of Co(II) complex.

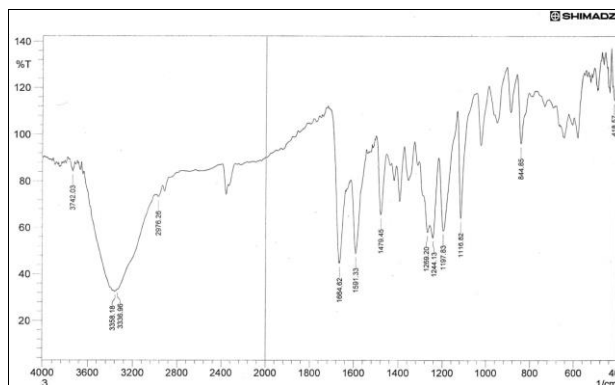


Fig.7. FT-IR spectrum of Ni(II) complex.

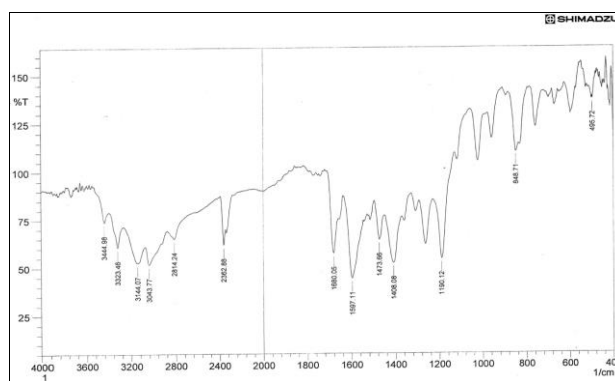


Fig.8. FT-IR spectrum of Cu(II) complex.

¹H-NMR Spectra

Figure (9, 10, 11, and 12) shows the spectra of ¹H-NMR off-ligand (HPIEPAMP) and its complexes in DMSO solution with TMS as an internal standard. The spectrum of the ligand (HPIEPAMP) showed one beam at the chemical shift (2.12 ppm) belonging to the protons of the methyl group (CH₃) connected to the isomethyl group, while one beam appeared at the chemical shift (2.35 ppm) which refers to the protons of the methyl group (CH₃) connected to the aromatic ring, in addition to the appearance of changeable bands at two displacements (4-7 ppm) belonging to the proton of the hydroxyl group (OH) of the aromatic ring. The multiple signals observed in the region (6.35-8.1 ppm) were assigned to the chemical shifts of aromatic protons [20, 21]. In the spectrum of complexes, the absence of a proton beam for the hydroxy (OH) group of the vinyl ring, and this indicates the participation of the oxygen atom in the coordination process after the loss of the proton and the formation of complexes, while one beam appeared at the chemical displacement of (2.27 ppm) for the cobalt complex, (2.38 ppm) for the nickel compound, (2.27 ppm) for the copper compound and (3.3 ppm) for the copper compound all belong to the protons of the methyl group (CH₃)

connected to the aromatic ring, the multiple signals of many proton bundles of the aromatic ring between chemical shifts (6.96-8.11 ppm) for Co(II) and (6.98-8.13 ppm) for Ni(II) and (6.51-8.12 ppm) for Cu(II) complexes [22].

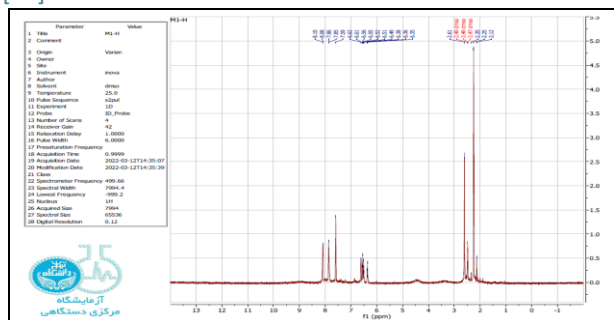
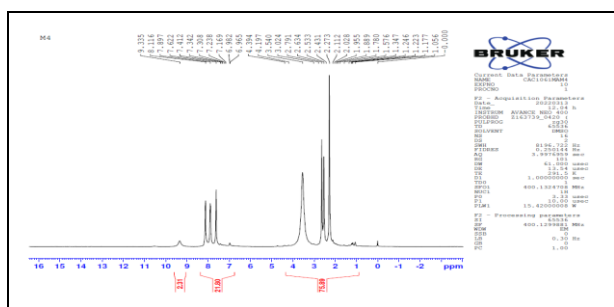


Fig.9. $^1\text{H NMR}$ of the ligand (HPIEPAMP).



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