



Synthesis and Characterization of Resorcinol based Schiff Base Ligand and Its Complexes of CO(III), NI(II), CU(II) and ZN(II) Metal Ions

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Abstract : A hitherto new resorcinol based acyclic ligand (L) was synthesized by Schiff base condensation reaction. The ligand was synthesized by microwave assisted method at enhanced yield and drastically reduced reaction time. The new ligand was completely characterized. A series of Cobalt (III), Nickel(II), Copper (II) and Zinc(II) complexes of the unreported ligand(L) has been synthesized by the direct reaction of the preformed ligand(L) with Cobalt (III), Nickel(II), Copper(II) and Zinc (II) salts in 1:1 mole ratio in ethanol. The free ligand is neutral, but on complexation with metal ions, it tends to lose both the phenolic hydrogen and coordinates with Cobalt (III), Nickel(II) and Copper(II) and Zinc (II) metal ions as dianionic moiety. The ligand(L) being tetradentate in nature coordinates through its two nitrogen donors and two oxygen donors in the equatorial positions, the ligand serves as dianionic tetradentate dioxadiaza moiety. The perchlorate complexes of the ligand were isolated and characterized thoroughly, using elemental analysis, electronic spectroscopy, infrared, molar conductivity measurements, magnetic susceptibility, ¹H NMR and cyclic voltammetry studies. The complexes formed were of mononuclear in nature.

Key words: Resorcinol based ligand, tetradentate ligand, dioxadiaza ligand, resorcinol, Schiff base condensation, dianionic ligand, transition metal complexes.

Introduction

Coordination Chemistry of Schiff base ligand has shown to be an interesting subject of current research in the last two decades^{1,2}. Acyclic ligand having nitrogen, oxygen donor atoms as well as their coordination compounds play important roles in antibacterial, antifungal and antiviral activities^{3,4}. The chemical compound, 2-alkyl resorcinol (where the alkyl group is linear) has been reported to have skin depigmentation properties (Gadgil et al., 2004; Bollinger et al., 1990). Alkyl resorcinol and aromatic resorcinol are reported to possess valuable therapeutic and antiseptic properties. These useful properties present in the precursors tend to get enhanced when they are coupled with other moieties to form ligand. Schiff bases are capable of forming coordinate bonds with metal ions through both azomethine group and phenolic group⁵. Further the complexation of the ligand with the metal ion has enormous enhancement of the built-in properties. In order to enhance these properties an attempt has been made. In this article we have reported the synthesis, characterization of Cobalt (III), Nickel(II), Copper(II) and Zinc (II) complexes derived from the acyclic ligand (L) obtained as a Schiff base condensation of synthesized 4,6-diacetyl resorcinol with 4-methyl-2-amino phenol.

Experimental

Materials and Methods

All the chemicals used in this study were of Analar grade. Metal salts were purchased from Merck and were used as such as received. Elemental analysis carried out on Elemental vario EL III-Germany. ^1H NMR spectrum was recorded used to Bruker model 4276. FT IR spectra recorded on Perkin Elmer on KBr pellets in the range of 4000 to 400cm^{-1} . The electronic spectrum recorded on Lambda 35 in the range of 200 to 800 nm using 10^{-3}M concentration solution in DMF. NMR spectrum was recorded using Bruker model 4276. The new ligand (L) was synthesis from 4,6-diacetyl resorcinol and 4-methyl-2-amino phenol⁶.

Synthesis of Schiff Base Ligand(L)

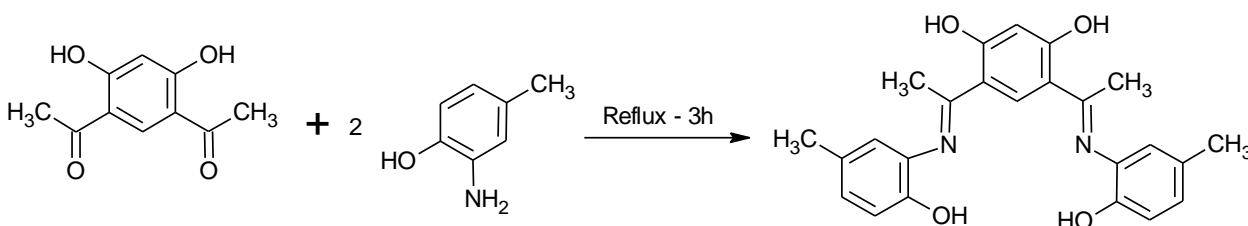
To a solution of 4,6-diacetyl resorcinol 9.7g (50 mmol) and 4-methyl-2-aminophenol 12.2g (100 mmol) dissolved separately in absolute ethanol with molar ratio (1:2) were mixed together and the solution mixture was left under reflux for three hours. The reaction mixture was then cooled and yellow precipitate which separated out was collected by filtration and washed several times with a small amount of ethanol. The ligand was recrystallized, in absolute alcohol. The crystals were dried over anhydrous calcium chloride under vacuum.

Yield was 83%.m.p.-272°C.

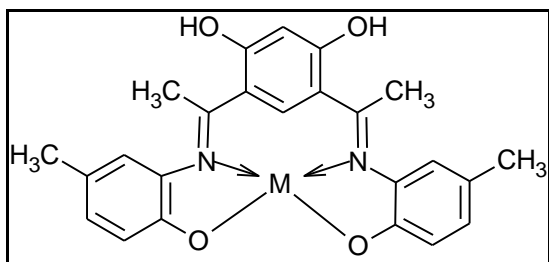
Anal. Cal.($\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_4$): C(71.27), H(5.98), N(6.93). Found: C (71.20), H (6.03), N(6.88).

IR (KBr Pellets) (C=N) 1652cm^{-1} , (C=C)_{Aro} 1490cm^{-1} , (C-O) 1250cm^{-1} , (OH) 3416cm^{-1} , (OH) 3200cm^{-1} , **^1H NMR**: 12.71(s, 2H, OH), 9.49(s, 2H, OH), 8.41, 8.26(d, 2H, Ph), 6.9-6.2(m, 6H, Ph), [2.65(s), 2.50(s), 2.37(s), 2.22(s), 12H, CH₃]. Mass value $m/z = 388(\text{P-OH})^+$

The synthesis of the ligand (L) is depicted in **Scheme.1**



Scheme -1: Formation of Schiff base



Scheme - 2: Formula of the metal complexes M= Ni(II), Cu(II) and Zn (II)

Synthesis of Metal Complexes

To a refluxing solution of the ligand(L) (10mmol) in 30 mL of the ethanol was added an equivalent mole ratio of the corresponding perchlorate salts $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Co(III)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II)) dissolved in 20 mL of ethanol. The resulting mixture was refluxed for 3hrs. The colored precipitate which separated due to low solubility was filtered, washed repeatedly with absolute ethanol and diethyl ether and dried over anhydrous CaCl_2 in vacuum.

The nature of bonding exhibited by metal ions with the ligand is depicted in **Scheme 2**.

Result and Discussion

Synthesis and Characterization of the Ligand

The dioxadiazatetradentate acyclic ligand(L), was synthesized by the reaction of 4,6-diacetyl resorcinol and 4-methyl 2-aminophenol in 1:2 mole ratio by both conventional and under microwave assisted reaction conditions. The microwave assisted reaction resulted in high yield and increased purity of the ligand. The corresponding metal perchlorate complexes were synthesized by the reaction of the preformed ligand with the corresponding perchlorate metal salts in 1:1 mole ratio in ethanol, by conventional method. The synthesized dioxadiazatetradentate Schiff base ligand(L) and their metal perchlorate complexes were characterized by elemental analysis, infrared, electronic, NMR, mass, conductance and magnetic measurements. The elemental analysis, color, electronic spectral data of the ligand and the complexes were furnished in **Table-1**.The infrared spectral data of the ligand and the complexes are furnished in **Table-2**.The electronic spectral data of the ligand and the complexes are furnished in **Table-3**.

Tables -2. IR spectral data of ligand and metal complexes

Compound	ν OH (cm ⁻¹)	ν (C=N) (cm ⁻¹)	ν (M-O) (cm ⁻¹)	ν (M-N) (cm ⁻¹)	ClO ₄
L	3425, 3219	1652	-	-	-
[Cu (L)] (ClO ₄) ₂	3426	1639	537	505	1117
[Ni (L)] (ClO ₄) ₂	3428	1592	577	538	1118
[Co (L)(H ₂ O) ₂] (ClO ₄)	3533	1616	590	530	1117
[Zn (L)] (ClO ₄) ₂	3402	1610	592	435	1120

Tables -3 . Electronic spectral data of the compounds

Compound	Solvent	Absorption (cm ⁻¹) / (nm)	Band assignment	Geometry
[Cu (L)] (ClO ₄)	DMF	256 340 550	INCT INCT ² B _{1g} → ² A _{1g}	Square planar
[Ni (L)] (ClO ₄) ₂	DMF	256 340 412 542	INCT INCT ¹ A _{1g} → ¹ A _{2g} ¹ A _{1g} → ¹ B _{1g}	Square planar
[Co (L)(H ₂ O) ₂] (ClO ₄)	DMF	256 360 420 470	INCT INCT ⁴ T _{1g} (F) → ⁴ T _{1g} (P) ⁴ T _{1g} (F) → ⁴ A _{2g} (F)	Octahedral
[Zn (L)] (ClO ₄) ₂	DMF	260 320 360	-	Square planar

Infrared Spectra of Ligand

The infrared spectra provide valuable information regarding the formation the dioxadiazatetradentate acyclic ligand(L) and the coordination behavior of the ligand to the metal ions. The infrared spectrum of the ligand(L), show two broadened bands in the region 3200 cm⁻¹ and 3416 cm⁻¹ has been assigned to ν (O-H) stretching of phenolic groups of 4,6-diacetyl resorcinol and that of the phenolic group comprising the 4-methyl-2-amino phenol moiety. The (C=O) peak around 1700 cm⁻¹ observed in the 4,6-diacetyl resorcinol is absent in the ligand and instead the a sharp peak appears at 1652cm⁻¹ corresponds to the ν (C=N) stretching of newly formed azomethine groups. The infrared spectrum of the ligand is depicted in **Fig.1**.

The proton NMR spectrum of the ligand exhibits a sharp peak at 12.71 ppm assignable to the phenolic protons of 4,6-diacetyl resorcinol and another single sharp signal at 9.49 ppm assignable to the phenolic protons

of 4-methyl 2-aminophenol. A broad band centered around 8.41 and 6.2 ppm has been assigned to the aromatic protons. The quartet centered around 2.65 -2.22 ppm is due to the 12 methyl protons. The ^1H NMR spectrum and the ^{13}C NMR spectrum of the ligand are depicted in **Fig.2** and **Fig.3** respectively. The CIMS spectrum of the ligand revealed a peak at 388 m/e due to the hydroxyl group depleted ligand moiety. The mass spectrum of the ligand is depicted in **Fig.4**.

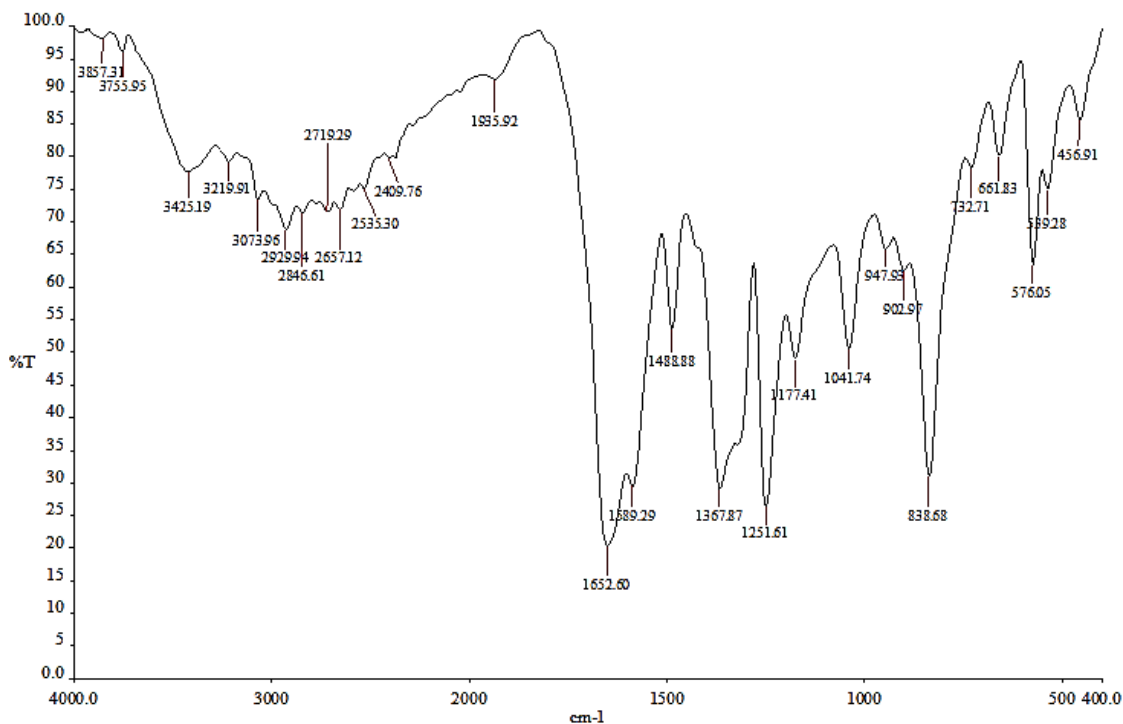


Fig-1: Infrared spectrum of Ligand (L)

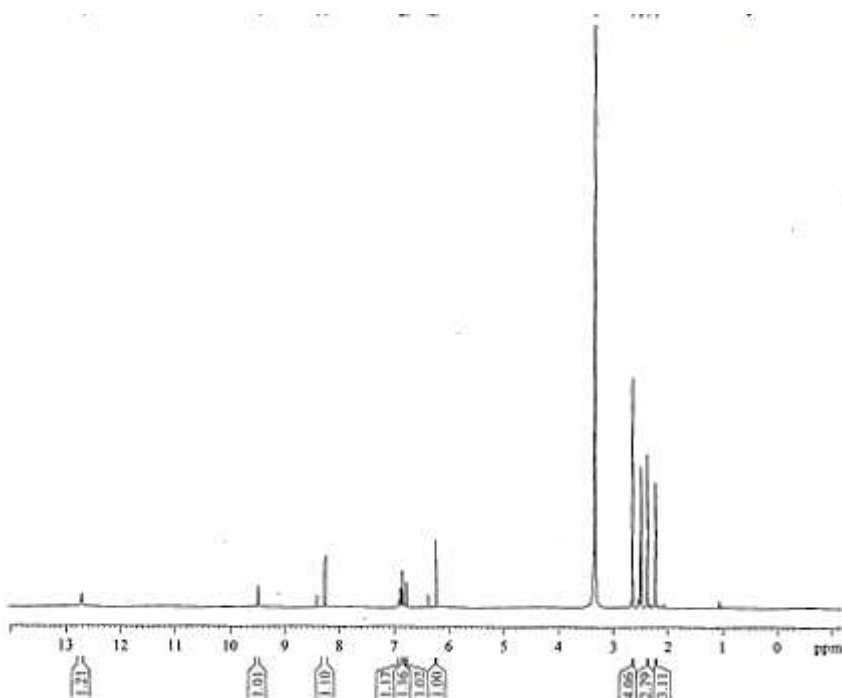


Fig -2: ^1H spectrum of ligand(DARMAP)

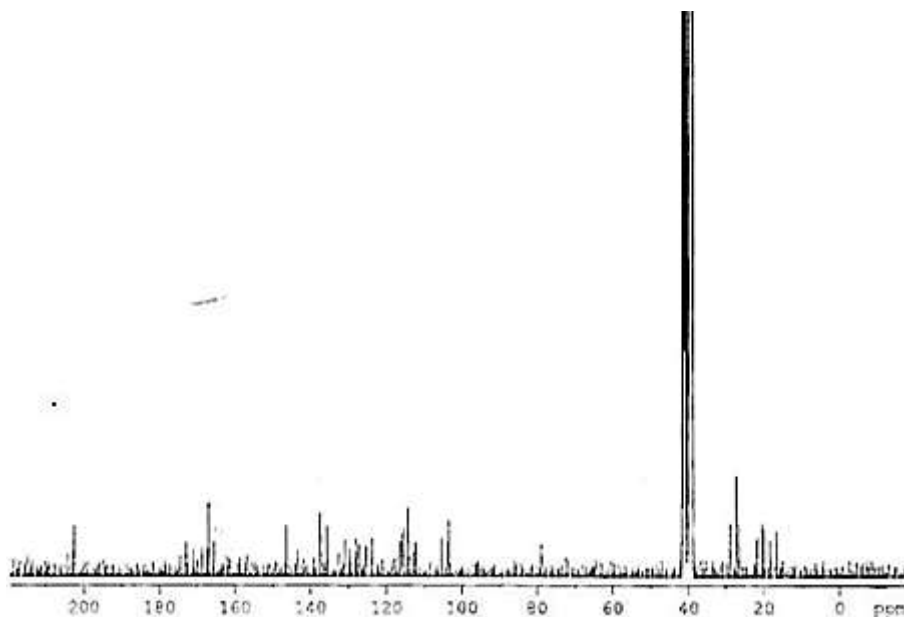


Fig - 3: ^{13}C spectrum of ligand (L)

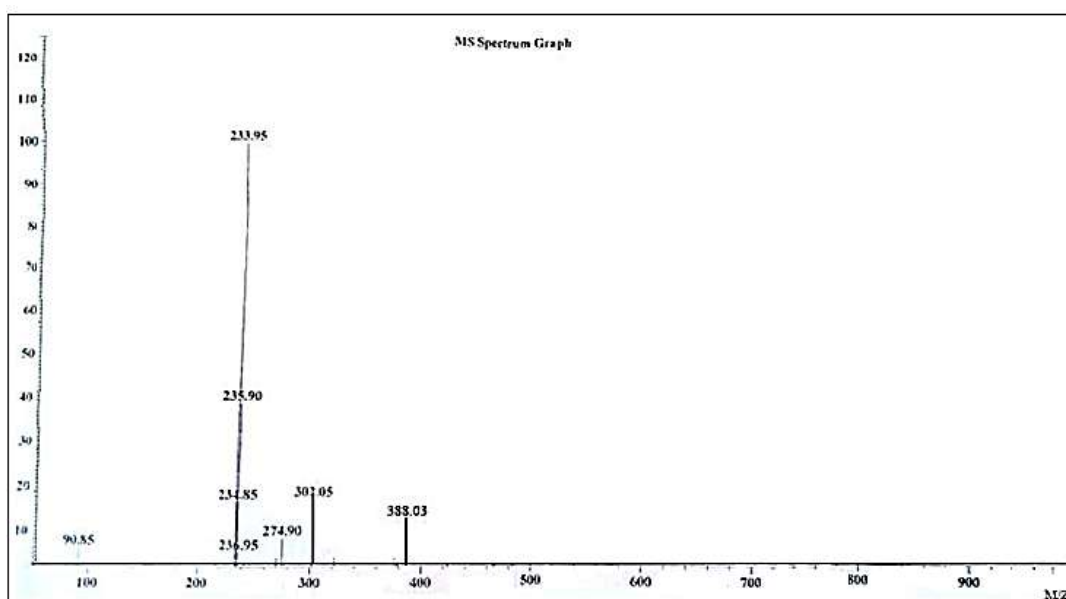


Fig -4: Mass spectrum of ligand(L)

Synthesis and Characterization of the Perchlorate Complexes of the Ligand (L)

The broad hydroxyl band present in the ligand corresponding to the 4-methyl-2-amino phenol moiety disappears in the spectra of the complexes indicating that the hydroxyl groups are coordinated to metal through the deprotonated form^{7,8}. The other band at $3435\text{-}3400\text{cm}^{-1}$ indicates the presence of -OH group from the resorcinol phenolic group are present in the ligand as well as metal complexes. This observation indicates that the hydroxyl group from the resorcinol moiety does not involve in coordination to the metal ions. The azomethine band around 1652cm^{-1} present in the free ligand, has been shifted to lower frequencies in the metal complexes, suggested that coordination took place through the $\text{C}=\text{N}$ moiety. The infrared show stretching frequencies in the region $530\text{-}590\text{cm}^{-1}$ corresponding to $\nu(\text{M-O})$ vibration and also the presence of bands at $435\text{-}540\text{cm}^{-1}$ assigned to $\nu(\text{M-N})$ band respectively, supporting that the bonding of the ligand to the metal ions is achieved by the phenolic oxygen, and azomethine nitrogen atoms of the ligand⁹. Also IR spectra of the metal complexes exhibit an intense band at $1115\text{ to }1120\text{cm}^{-1}$ due to uncoordinated perchlorate anions¹⁰. The infrared spectrum of the Copper complex of the ligand is depicted in **Fig.5**.

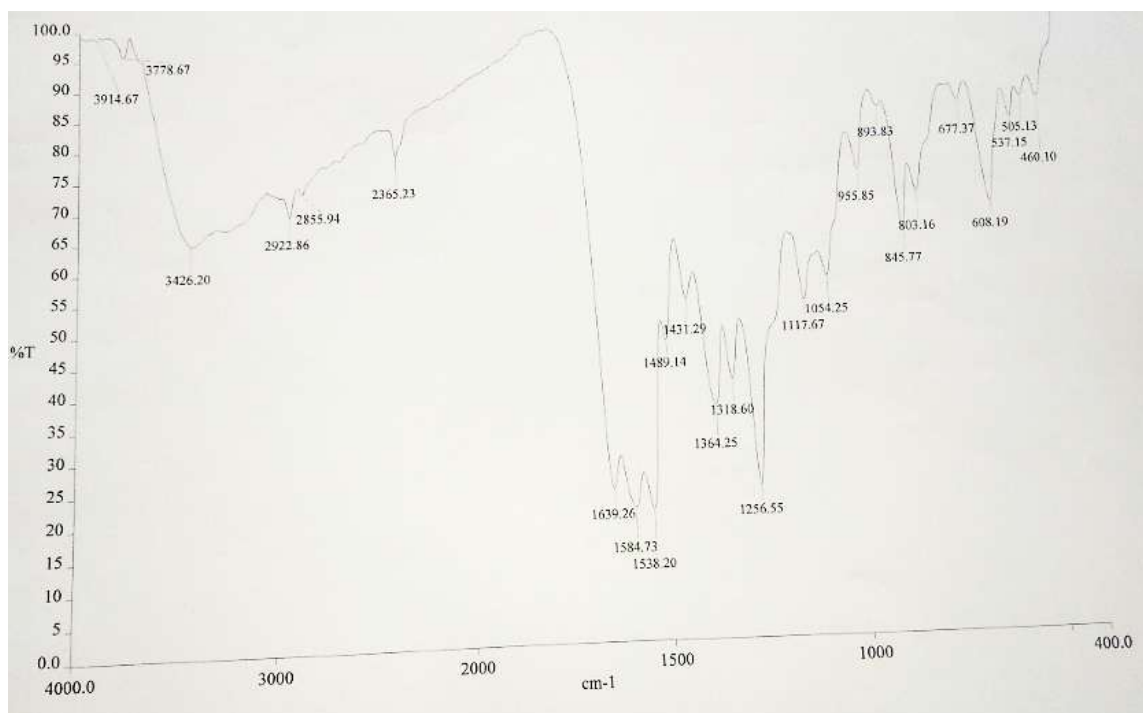


Fig -5: Infrared spectrum of complex $[Cu (DARMAP)] (ClO_4)_2$

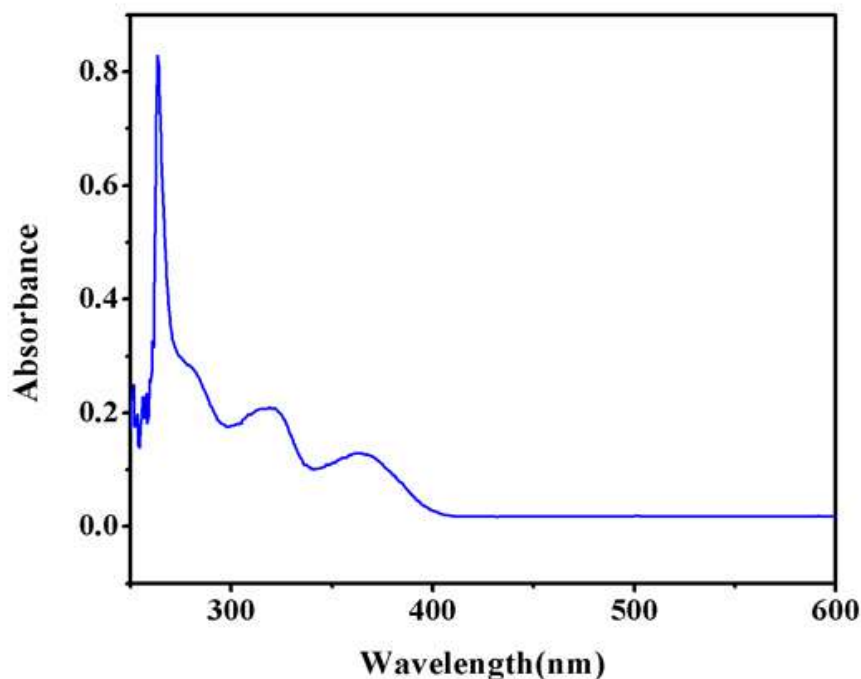


Fig - 6: UV-Spectrum of complex $[Zn (L)] (ClO_4)_2$

Molar Conductance

The molar conductance of the metal perchlorate complexes were measured in DMF as solvent. (Table - 1). The molar conductance value of the complexes indicates that under study was 1:1 electrolytic nature¹¹.

Magnetic Susceptibility

The magnetic susceptibility measurements provide information regarding the structure of the metal complexes. The magnetic values were recorded and discussed Table-1.

Tables -1. Elemental analysis, colour, molar conductance electronic spectra and magnetic susceptibility of the ligand and their complexes

Compound	Mol. Formula	Mol. Weight	Yield %	Calculated / (Founded)					Colour	μ eff (BM)	Molar Cond.
				C	H	N	O	M			
L	C ₂₄ H ₂₄ N ₂ O ₄	404	87	71.27 (71.20)	5.98 (6.03)	6.93 (6.87)	15.82 (15.89)	-	Yellow	-	-
[Cu (L)] (ClO ₄) ₂	C ₂₄ H ₂₂ CuN ₂ O ₄	466	68	61.86 (61.66)	4.76 (4.65)	6.01 (5.62)	13.73 (13.03)	13.64 (13.50)	Greenish Brown	1.7	179
[Ni (L)] (ClO ₄) ₂	C ₂₄ H ₂₄ N ₂ NiO ₄	461	73	62.51 (62.65)	4.81 (4.98)	6.07 (6.37)	13.88 (14.14)	12.73 (12.87)	Pale Brown	2.8	170
[Co (L)(H ₂ O) ₂] (ClO ₄)	C ₂₄ H ₂₈ CoN ₂ O ₆	461	71	62.48 (63.13)	4.81 (5.26)	6.07 (5.86)	13.87 (13.23)	12.77 (12.67)	Violet	4.9	104
[Zn (L)] (ClO ₄) ₂	C ₂₄ H ₂₄ N ₂ O ₄ Zn	467	76	61.62 (61.66)	4.74 (4.65)	5.99 (5.77)	13.68 (13.76)	13.98 (13.87)	Yellow	Dia	162

Conclusion

The synthesized compound and its complexes of Cobalt (III), Nickel (II), Copper(II) and Zinc (II) metal ions were characterized. The structural data established on the basis of ¹H & ¹³C NMR, mass, elemental analysis (C,H,N,O) infrared, ultra violet and magnetic susceptibility analysis of complexes were recorded and discussed.

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