

Synthesis, Spectroscopic and Biological Studies of Some New Binuclear Thiocyanate Complexes Containing Bidentate Schiff Base Ligands

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Abstract: Two new Schiff bases were synthesized from condensation of 4-nitro benzene diamine with aromatic aldehydes (4-nitro benzaldehyde and 4-hydroxy benzaldehyde). These Schiff bases were reacted with binuclear thiocyanate complexes of $MM(SCN)_4$ [$M = Co(II), Ni(II)$; $M = Cd(II)$] to produce four new complexes. These compounds were identified by elemental analysis, infrared, Ultraviolet-visible, 1H , ^{13}C -NMR, mass spectra, molar conductance, atomic absorption and magnetic susceptibility. The synthesized Schiff bases were regarded as bidentate ligands and formed complexes of the type $LM(NCS)_2M(SCN)_2$. These complexes were non electrolytes and had coordination number equal four. Moreover, these Schiff bases and their complexes were screened for antibacterial and antifungal activity against some microorganisms and compared with standard compounds. It was found that the synthesized compounds had a good antibacterial activity.

Keywords: Schiff base, Binuclear complexes, Thiocyanate, Synthesis, Biological

1. Introduction

Schiff base ligands are defined by the combinations that contain azomethine groups in their structure. These combinations are obtained by means of kind one amine condensation with a one carbonyl group contained molecule [1]. In general Schiff bases are able to form various complexes with different metal ions. Schiff base complexes are used in many fields such as pharmaceutical industry, biological activity, agriculture and organic synthesis [2, 3].

Binuclear metal complexes that contain Schiff base ligands are useful to study the relation between structures and magnetic exchange interaction [4] to mimic bimetallic biosites in various proteins and enzymes [5] and to use as a versatile building unit for constructing various supramolecular assemblies [6-8]. Schiff bases are good ligands and show chemical reactivity and various biological activities when mixed with bimetallic Lewis acid $MM(SCN)_4$ [$M=Ni^{+2}, M=Cd^{+2}, Hg^{+2}$] [9]. Binding mode sensitivity of thiocyanate ion has attained great interest in recent years. The thiocyanate moiety is reported to have an ability to modify the biochemical behavior when present in mixed ligand coordination complexes [10, 11].

In the present paper we report the synthesis, physical, spectral characterization and biological activity of new bidentate Schiff base ligands and their binuclear thiocyanate complexes with general formula of $[L M Cd (SCN)_4] M = Co^{+2}, Ni^{+2}, L =$ Schiff base ligand.

2. Experimental

Chemicals and Solvents

4-Nitro benzaldehyd, Sulfuric acid was purchased from Aldrich. 4-Hydroxy benzaldehyde, Cobalt (II), Nickel (II), Cadmium (II) nitrate, Potassium thiocyanate were purchased from Sigma, 4-Nitro-1, 2-Diamine benzene, Glacial acetic

acid were purchased from Fluka, Ethanol, Methanol were purchased from Scharlau.

Instruments

Melting points of all compounds were determined by Thermo scientific apparatus. Elemental analysis was carried out on Euro Vector EA 3000 A. The molar conductance of Schiff base complexes was determined in DMF at room temperature using HI 2315 Conductivity Meter. The infrared spectra of the compounds were recorded in the range 400-4000 cm^{-1} on FTIR-84005 Shimadzu. Electronic spectra in the 200-600 nm range were obtained in ethanol on UV 1800 Shimadzu. The metal content of the complexes were determined by atomic absorption on Phoenix -986AA Spectrophotometer. The 1H , ^{13}C -NMR spectra of the ligands were recorded in DMSO- d_6 on Varian 500 MHz NMR Spectrometer at room temperature using TMS as an internal reference. The magnetic susceptibility of the complexes was recorded on Balance Magnetic Susceptibility model MSB-MKI at room temperature by Faraday method. Mass spectra of the ligands were determined by MS model: 5975C VL MSD (EI) 70 ev. The biological activity was evaluated using the disc Diffusion method.

Synthesis of Schiff base ligands

The Schiff base ligands (L_1, L_2) were synthesized as in similar method [12] by reaction of (4-nitro-1, 2-diamine benzene, 1.5314 gm, 10 mmol) with (4-nitro benzaldehyde, 3.0224 gm, 20 mmol) or (4-hydroxy benzaldehyde, 2.4424gm, 20 mmol) in ethanol solvent in the presence of drops of catalyst. This mixture reaction was refluxed for some hours then cooled at room temperature. The solid product was filtered, washed and recrystallized then dried over silica.

The suggested structure of these ligands was given in figure (1) and some physical properties were shown in table (1).

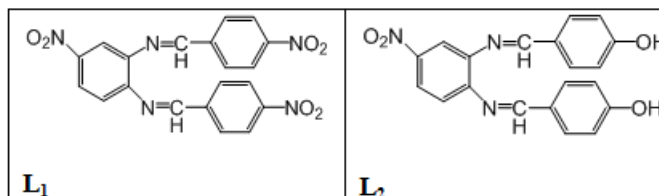


Figure 1: The proposed structure of the synthesized Schiff base ligands

Table 1: Some physical properties of the synthesized Schiff base ligands

Sym.	Molecular formula Molecular weight	Time of reflux (hrs)	Catalyst	Recrystallized Solvent	Physical state and color	Melting Point (°C)	Yield %
L ₁	C ₂₀ H ₁₃ N ₅ O ₆ 419.35	5	Sulfuric acid	Acetone	Orange powder	254-256	74
L ₂	C ₂₀ H ₁₅ N ₃ O ₆ 361.36	8	Glacial acetic acid	Methanol	Yellow crystals	238-239	80

Synthesis of binuclear thiocyanate complexes

These complexes were synthesized as a similar paper [13] by following procedure: metal dithiocyanate [Co(SCN)₂, Ni(SCN)₂, Cd(SCN)₂] were first synthesis by the reaction of metal nitrate with potassium thiocyanate in methanol. The formed potassium nitrate was removed by filtration and solutions of dithiocyanates were kept for further reaction. For the synthesis of tetrathiocyanates MM(SCN)₄ [M = Co, Ni ; M' = Cd]. Solution of M(SCN)₂ and M'(SCN)₂ were mixed in 1:1 molar ratio and stirred for 36 hrs. Solution of these tetrathiocyanates as alone in methanol was mixed with synthesized Schiff base in the same solvent in 1:1 molar ratio and stirred. In each case a solid product formed was filtered and washed with ether. The suggested structure for the synthesized complexes was given in figure (2) and some physical properties were shown in table (2).

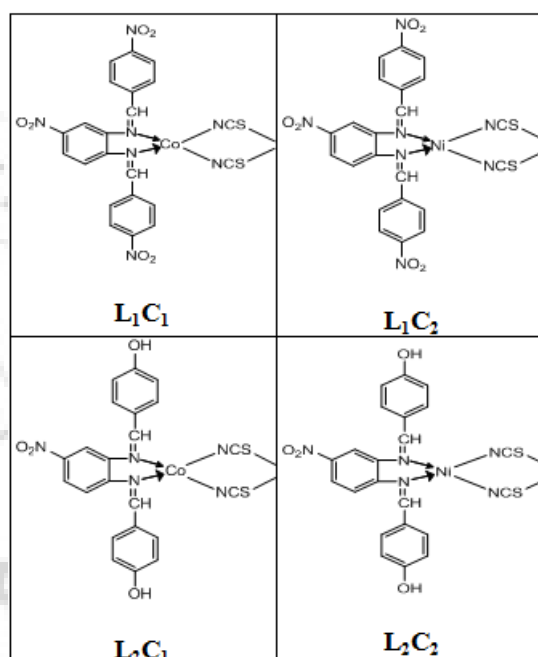


Figure 2: The proposed structure of the synthesized complexes

Table 2: Some physical properties of the thiocyanate complexes containing Schiff base ligands

Sym. of Complex	Molecular formula Molecular weight	MCo(SCN) ₄ (gm) Ligand (gm)	Time of reaction (hrs)	Physical state and color	Melting Point (°C)	Yield %
L ₁ C ₁	CoCd (SCN) ₄ . C ₂₀ H ₁₃ N ₅ O ₆ 823.01	0.40367 0.41934	18	Brown powder	216 ^d	60
L ₁ C ₂	NiCd (SCN) ₄ . C ₂₀ H ₁₃ N ₅ O ₆ 822.77	0.40343 0.41934	14	Blue powder	228 ^d	65
L ₂ C ₁	CoCd (SCN) ₄ . C ₂₀ H ₁₅ N ₃ O ₆ 765.01	0.40367 0.36133	10	Green powder	259 ^d	85
L ₂ C ₂	NiCd (SCN) ₄ . C ₂₀ H ₁₅ N ₃ O ₆ 764.77	0.40343 0.36133	18	Brown powder	>270	85

3. Results and Discussion

Physical and spectroscopic studies

The results of elemental analysis for synthesized ligands and complexes show that the percentages of carbon, hydrogen and nitrogen are equivalent to calculated values as show in table (3). This is evidence that proposed chemical structures of these compounds are true. The most characteristic absorptions in the infrared spectra for the synthesized bidentate Schiff base ligands and their complexes are summarized in table (4) and figures (3-8). The

corresponding complexes exhibit absorptions belonged to ligands at different frequencies. Also the characteristic absorption frequencies of carbonyl and amine groups in the starting materials using in the preparation of Schiff bases including aldehyde and diamines were not observed in the infrared spectra of the ligands indicating condensation of aldehyde with diamine. In the ligandes L₁, L₂ the stretching frequencies at 1614 cm⁻¹ and 1612 cm⁻¹ respectively assigned to azomethine group [14] are shifted by 4-12 cm⁻¹ in complexes indicating coordination of the azomethine nitrogen of the schiff base with metal ion. The infrared

spectra of all complexes show new bands at 2079-2148 cm⁻¹ region which are assigned to C-N in nitrogen bonded thiocyanate (M-NCS) and sulfur bonded thiocyanate (M-SCN) [15, 16]. Also it is observed that bands in the region 734-750 cm⁻¹ and 819-848 cm⁻¹ belong to the stretching vibration of S-C in the bridged thiocyanate [17]. In addition, infrared spectra of the complexes also show new bands at 410-490 cm⁻¹ and 500-520 cm⁻¹ due to the formation of M-N bonds [18].

UV-visible spectra of the ligands and their complexes were recorded in ethanol of 1.0×10⁻⁵ M at room temperature and the spectral data including the ε and λ are summarized in table (5). The free ligands (L₁, L₂) show three bands (307 nm, 339 nm, 435 nm) and (295 nm, 315 nm, 384 nm) respectively. The first and second bands are due to π-π transition in the C=C of phenyl and azomethine groups whether three band is due to intra charge transfer [19]. These bands were shifted to less wavelengths in the complexes. Also the spectra of complexes show new band which assigned to ligand-metal charge transfer [20] as show in figures (9-14).

Moreover, the ¹HNMR and ¹³CNMR spectra of the ligands shown in figures (15-18) are appeared the expected signals as a signed in tables (6, 7). The mass spectra of the ligands L₁, L₂ shown in figures (19, 20) are indicated appearance of molecular ion at 419 m/z and 361 m/z respectively. The rest of the fragments are shown in table (8).

The data of atomic absorption, molar conductivities and magnetic susceptibilities were listed in the tables (9, 10). The results were indicated that the reaction of the ligands L₁ and L₂ with tetrathiocyanate complexes was 1:1 molar ratio and percentage of the metals in the formed complexes was in good agreement with the theoretical values as evidenced by atomic absorption measurements. Moreover the values of the molar conductance for the complexes were low indicating that all the complexes were non electrolytic [21]. The magnetic moment μ_{eff} of the complexes was measured by Faraday method [22] at room temperature. The μ_{eff} values for the complexes L₁C₁ and L₂C₁ was indicated that these complexes are tetrahedral geometry while L₁C₂ and L₂C₂ were square planer [23].

Biological Study

Antibacterial and antifungal activity of the Schiff base ligands and their complexes were evaluated against S.aureus (bacteria) and Alternaria SP (fungi) as shown in table (11). The results were indicated that all synthesized compounds have good activity due to the presence of azomethine group and some functional groups such as (nitro and hydroxyl) which have chelating properties to inhibit growth of bacteria or fungi. Also the antibacterial activity of the compound was compared with Ciprofloxacin and Amoxicillin at concentration 1000 ppm and it was found that synthesized compounds are more activity than Ciprofloxacin and less activity than Amoxicillin.

Table 3: Elemental analysis data of the ligands and their complexes

Sym. of comp.	Formula of Comp. M.wt (gm/mol)	C%		H%		N%	
		Cal.	Found	Cal.	Found	Cal.	Found
L ₁	C ₂₀ H ₁₃ N ₅ O ₆ 419.35	57.28	57.21	31.12	3.23	16.70	16.54
L ₂	C ₂₀ H ₁₅ N ₃ O ₆ 361.36	66.48	66.22	4.18	4.13	11.63	11.69
L ₁ C ₁	CoCd (SCN) ₄ . C ₂₀ H ₁₃ N ₅ O ₆ 823.01	35.03	35.45	1.59	1.84	15.32	15.38
L ₁ C ₂	NiCd (SCN) ₄ . C ₂₀ H ₁₃ N ₅ O ₆ 822.77	35.04	35.38	1.59	1.78	15.32	15.551
L ₂ C ₁	CoCd (SCN) ₄ . C ₂₀ H ₁₅ N ₃ O ₆ 765.01	37.68	37.29	1.98	2.03	12.82	12.97
L ₂ C ₂	NiCd (SCN) ₄ . C ₂₀ H ₁₅ N ₃ O ₆ 764.77	37.69	37.93	1.98	2.06	12.82	12.67

Table 4: Infrared spectra data of the ligands and their complexes

Sym.	νC-H Arom. cm ⁻¹	νC-H Azomethin cm ⁻¹	νHC=N cm ⁻¹	νC=C cm ⁻¹	νC-N in M-SCN cm ⁻¹	νC-N in M-NCS cm ⁻¹	νS-C in M-SCN cm ⁻¹	νS-C in M-NCS cm ⁻¹	νC-N in M-SCN-M ⁻ cm ⁻¹	νM←N cm ⁻¹	νM-NCS cm ⁻¹	νM-SCN cm ⁻¹
L ₁	3075 W 3101 W	2900 W	1614 S	1521 Sh	-	-	-	-	-	-	-	-
L ₁ C ₁	3068 W 3103 W	2875 W	1602 M	1512 M	2090 M	2079 W	744 Sh	846 Sh	2139 M 2148 M	500 W	475 W	440 W
L ₁ C ₂	3080 W 3101 W	2850 W	1610Sh	1514 M	2100 W	2050 W	744 Sh	846 Sh	2144 S	500 W	465 W	420 W
L ₂	3025 W 3115 W	2875 W	1612 S	1506 Sh	-	-	-	-	-	-	-	-
L ₂ C ₁	3100 W 3159 W	2889 W	1608 M	1514 Sh	-	2079 W	734 M	838 M	2137 S 2148 S	514 W	470 Sh	440 Sh
L ₂ C ₂	3100 W 2195 W	2883 W	1606 M	1516 Sh	2110 S	-	750 Sh	819 M	2148 S	520 W	460 Sh	415 W

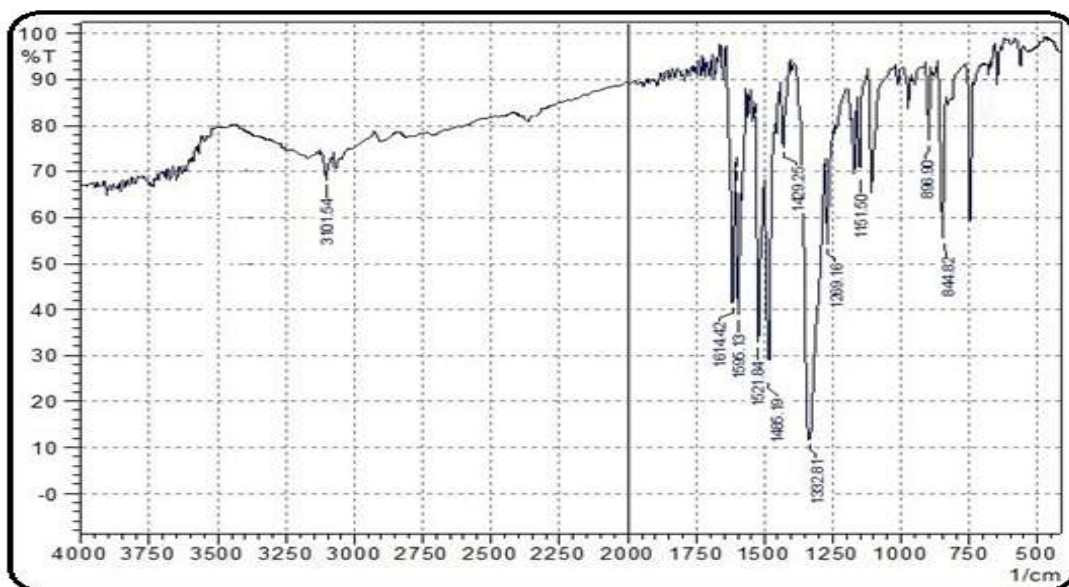


Figure 3: IR Spectrum of the ligand L₁

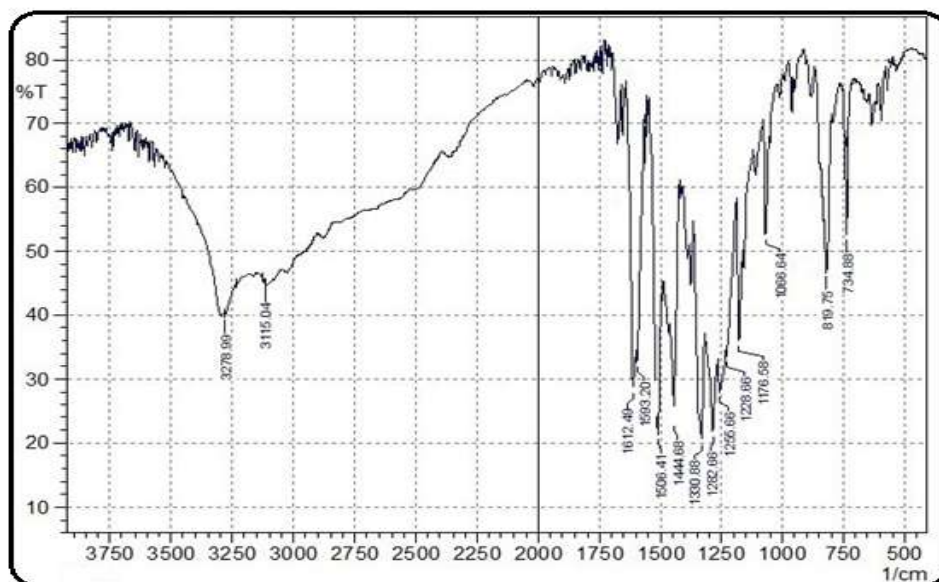


Figure 4: IR Spectrum of the ligand L₂

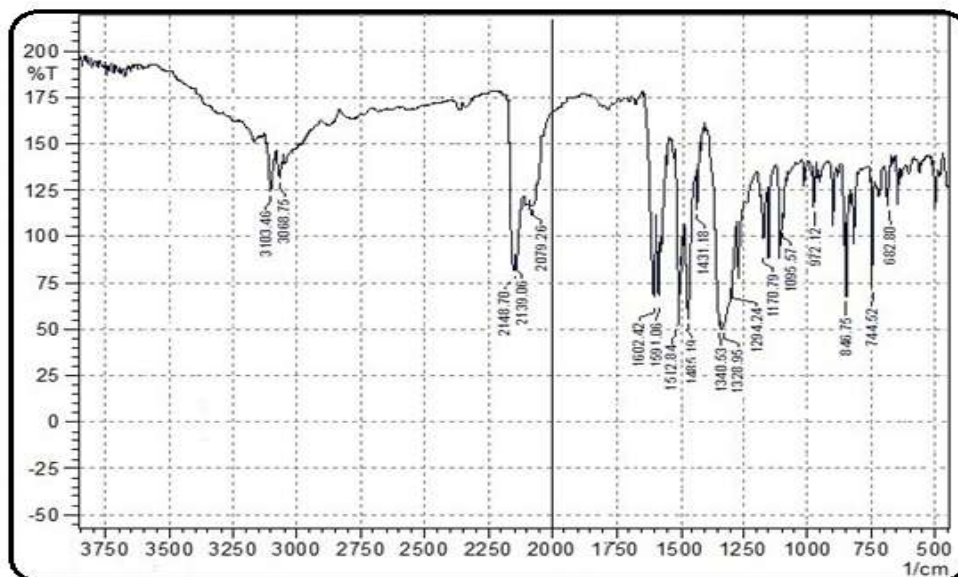


Figure 5: IR Spectrum of the complex L₁C₁

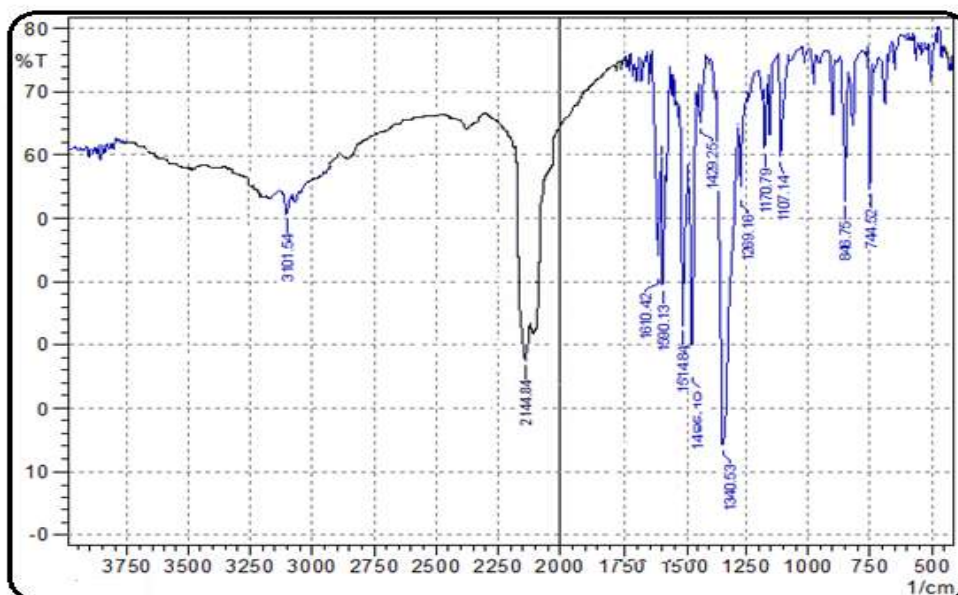


Figure 6: IR Spectrum of the complex L_1C_2

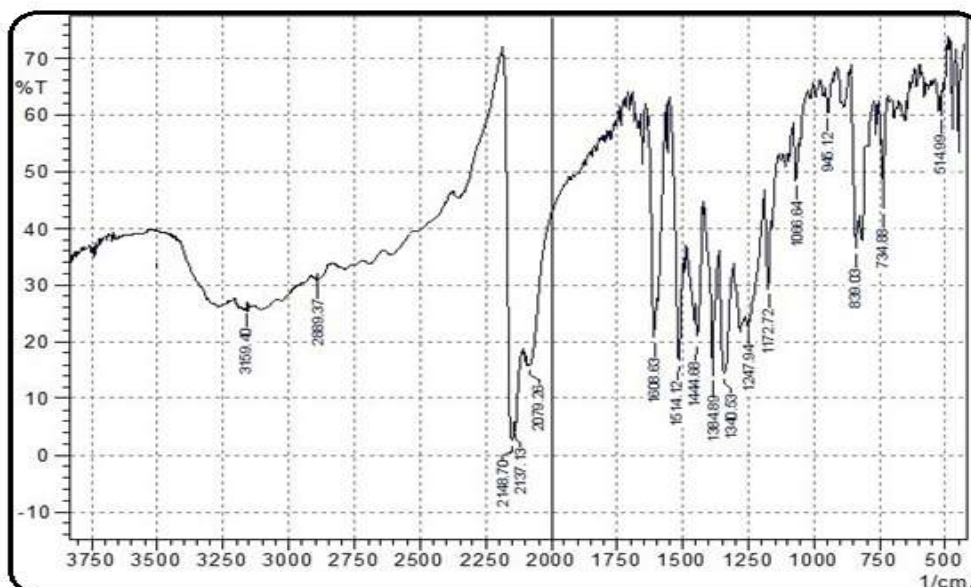


Figure 7: IR Spectrum of the complex L_2C_1

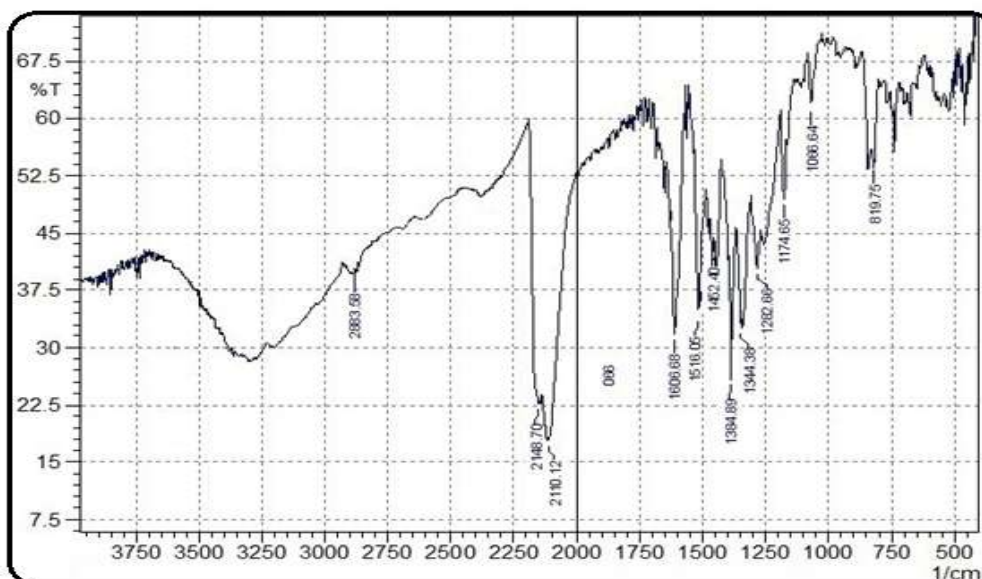


Figure 8: IR Spectrum of the complex L_2C_2

Table 5: Electronic data of the ligands and their complexes

Sym. of compound	(nm) λ	Type of transition	ϵ (L.mol ⁻¹ .cm ⁻¹)
L ₁	307	$\pi - \pi^*$	204500
	339	$\pi - \pi^*$	224800
	435	Intra charge transfer	33900
L ₁ C ₁	277	$\pi - \pi^*$	25400
	327	L \rightarrow M	22100
L ₁ C ₂	280	$\pi - \pi^*$	130700
	315	$\pi - \pi^*$	95000
	384	L \rightarrow M	112600
L ₂	295	$\pi - \pi^*$	194700
	339	$\pi - \pi^*$	178600
	461	Intra charge transfer	8800
L ₂ C ₁	(225) Shoulder	$\pi - \pi^*$	65000
	278	$\pi - \pi^*$	139400
	340	L \rightarrow M	107000
L ₂ C ₂	(220) Shoulder	$\pi - \pi^*$	75000
	277	$\pi - \pi^*$	158400
	338	L \rightarrow M	123000

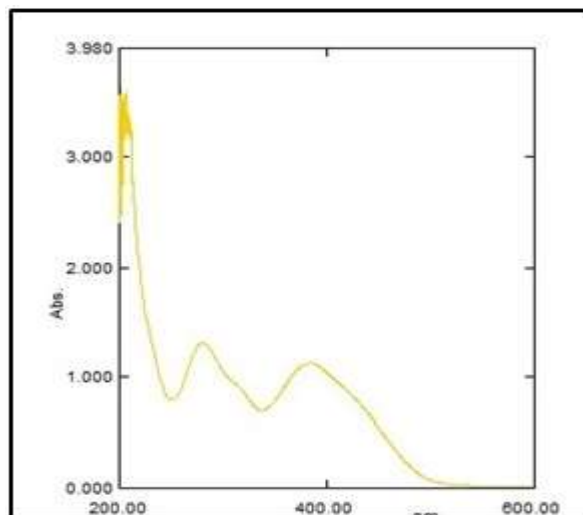


Figure 11: UV -Visible Spectrum of the complex L₁C₂

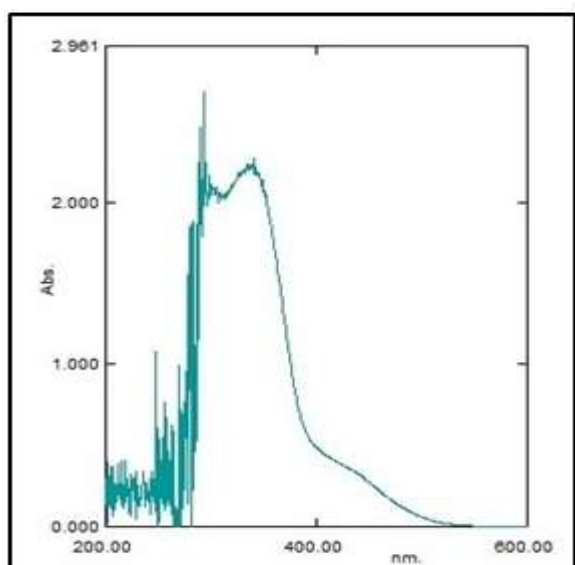


Figure 9: UV -Visible Spectrum of the ligand L₁

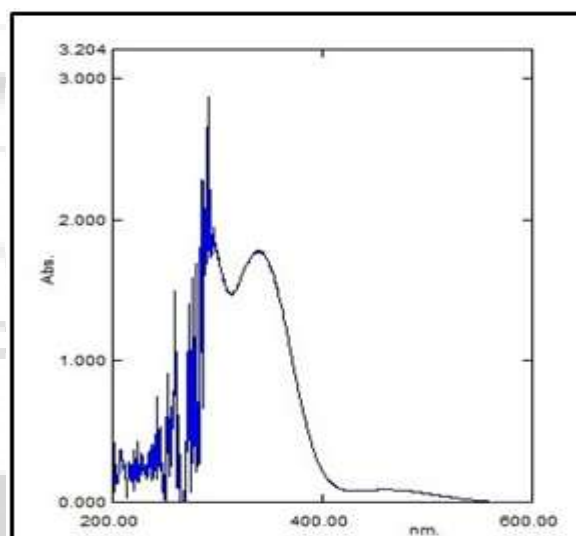


Figure 12: UV -Visible Spectrum of the ligand L₂

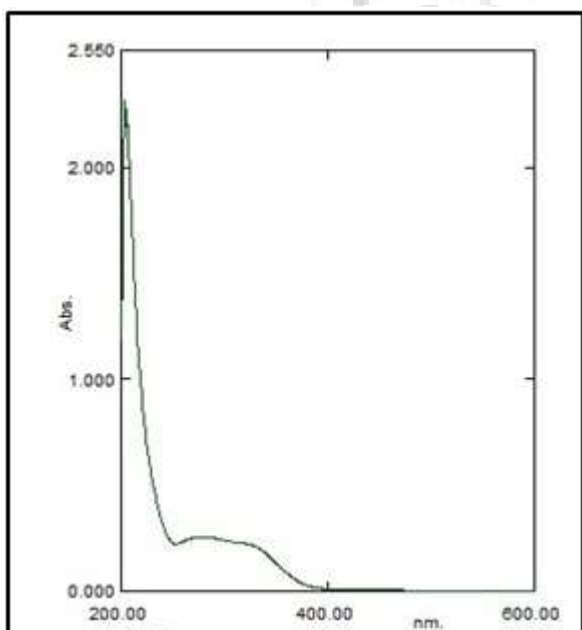


Figure 10: UV -Visible Spectrum of the complex L₁C₁

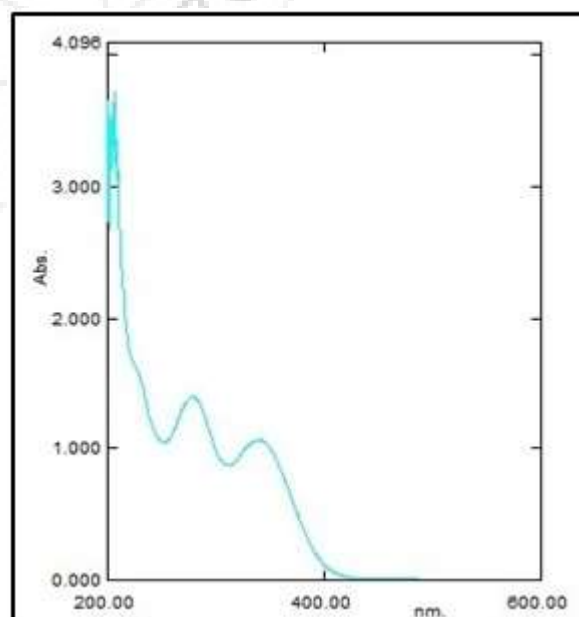


Figure 13: UV -Visible Spectrum of the complex L₂C₁

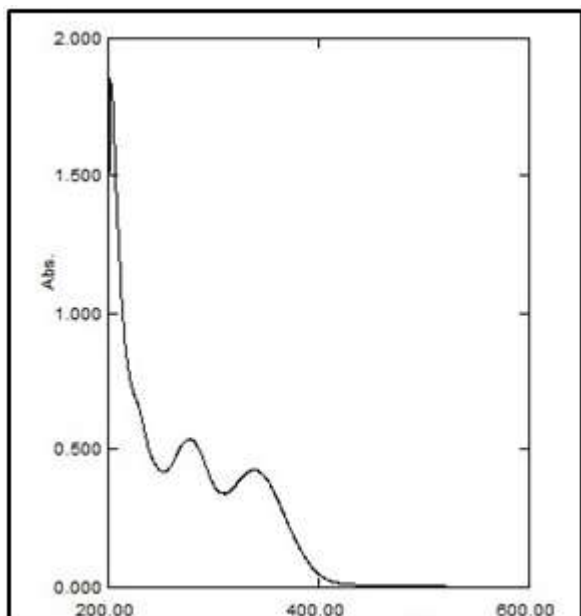


Figure 14: UV -Visible Spectrum of the complex L_2C_2

Table 6: 1H NMR data of the ligands

Ligand	Chemical Shift δ (ppm)
L_1	8.8, 8.9 (2H, HC=N), 7.7-8.4 (11H, Ar-H).
L_2	8.4, 8.5 (2H, HC=N), 6.8-8.4 (11H, Ar-H), 8.5 (1H, OH).

Table 7: ^{13}C NMR data of the ligands

Ligand	Chemical Shift δ (ppm)	
	C=N Azomethine	Aromatic Carbon
L_1	194.9, 177.7	117.5 - 151.8
L_2	177.7, 168.2	116.3 - 161.2

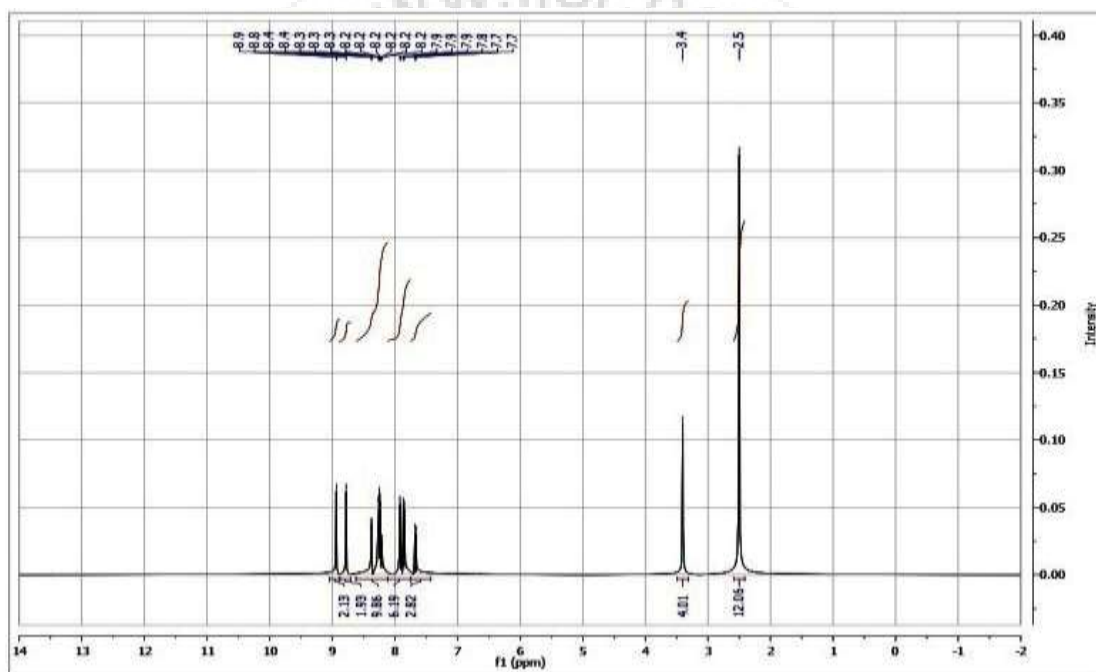


Figure 15: 1H NMR Spectrum of the ligand L_1

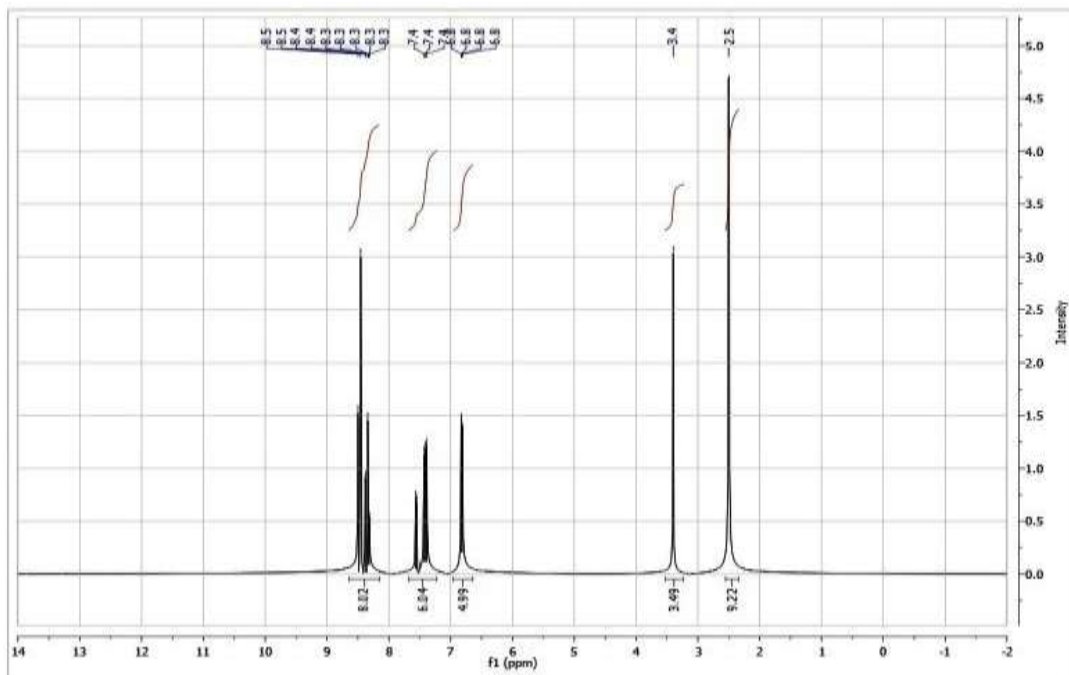


Figure 16: ¹H NMR Spectrum of the ligand L₂

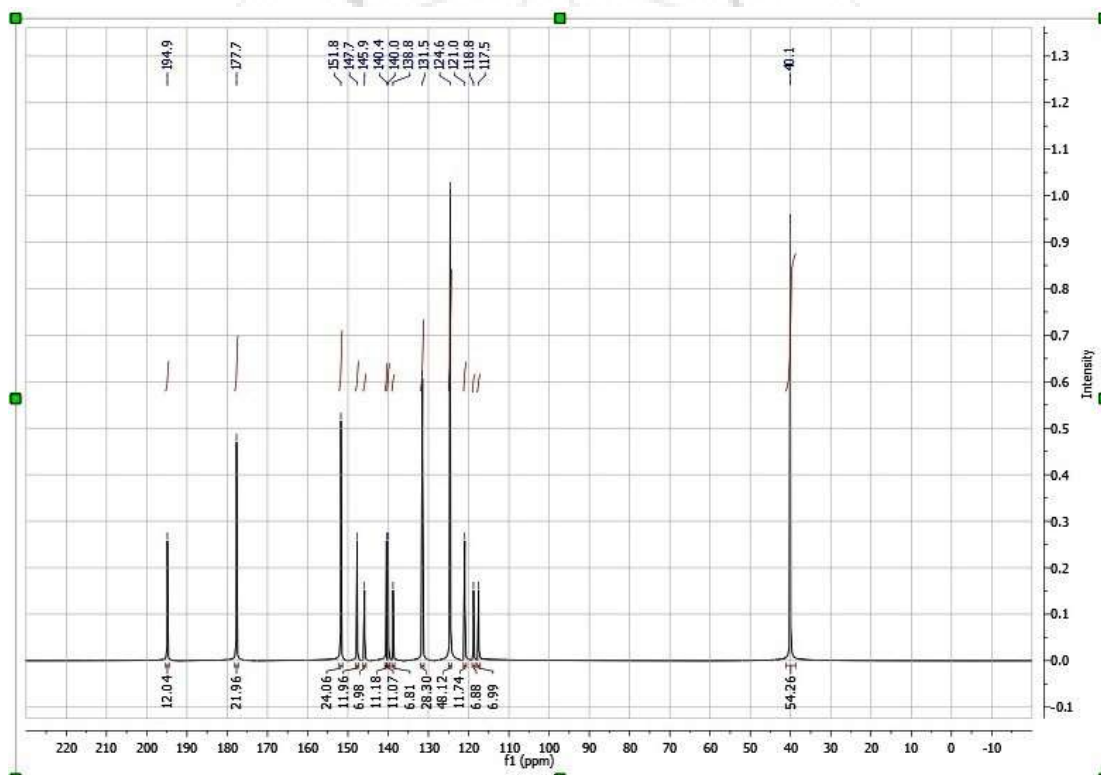


Figure 17: ¹³C NMR Spectrum of the ligand L₁

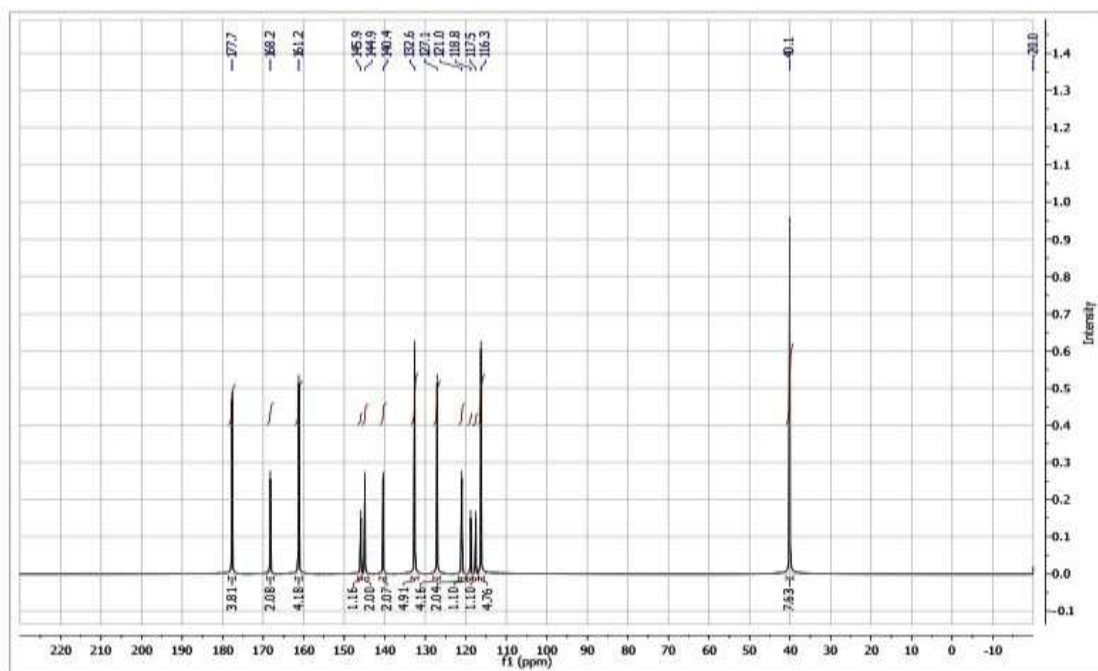
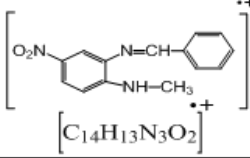
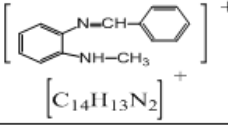
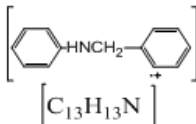
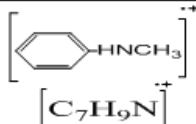
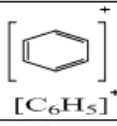


Figure 18: ¹³CNMR Spectrum of the ligand L₂

Table 8: Mass spectra data of the ligands

Sym.	Exact mass m/z	Relative Abundance%	Fragments
L ₁	419.2	15.5	 [C ₂₀ H ₁₃ N ₅ O ₆] ⁺
	279.1	13.3	 [C ₂₀ H ₁₂ N ₂] ⁺
	149	100	 [C ₇ H ₅ N ₂ O ₂] ⁺
	104	11.11	 [C ₇ H ₆ N] ⁺
	163	33.3	 [C ₈ H ₅ N ₃ O ₂] ⁺
	57	37.75	 [CH ₂ -CH ₂ -CH ₂ -CH ₃] ⁺ [C ₄ H ₉] ⁺
L ₂	361.1	12.28	 [C ₂₀ H ₁₅ N ₃ O ₄] ⁺

L ₂	255	100	 $[C_{14}H_{13}N_3O_2]^{++}$
	209	28.07	 $[C_{14}H_{13}N_2]^+$
	183	26.53	 $[C_{13}H_{13}N]^+$
	107	26.31	 $[C_7H_9N]^{++}$
	77	38.59	 $[C_6H_5]^+$

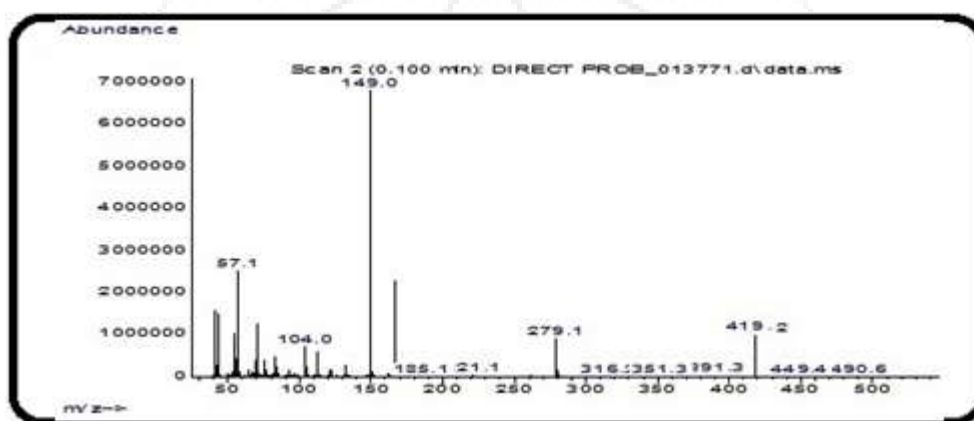


Figure 19: Mass spectrum of the ligand L₁

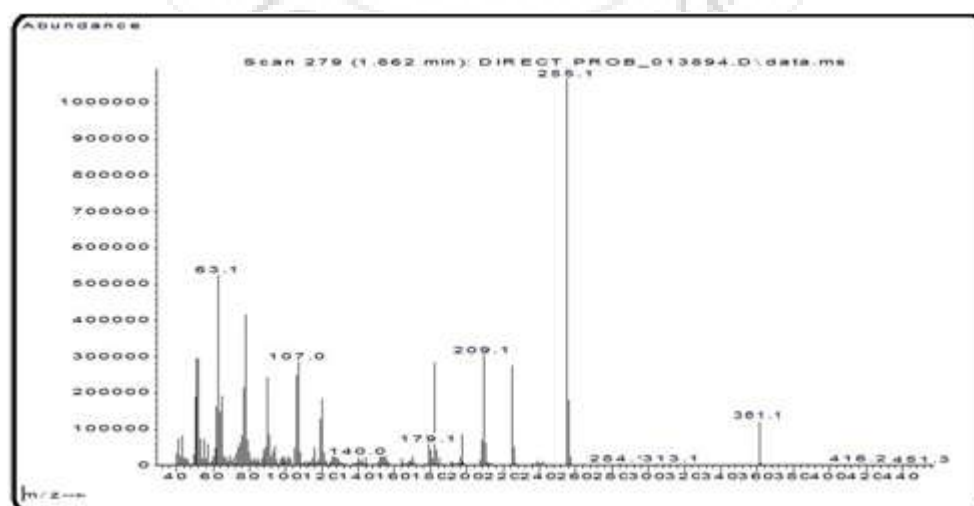


Figure 19: Mass spectrum of the ligand L₂

Table 9: Some structural properties of the synthesized complexes

Sym.	M.wt (gm/ mol)	Molar conductivity Ohm ⁻¹ .Cm ⁻¹ / mol	Type of metal MM ⁻	Concentration from AAS (ppm)	Metal %		Metal to Ligand ratio
					Found	Calculation	
L ₁ C ₁	823.01	19.0	Co	1.5982	7.99	7.16	1:1
			Cd	2.7956	13.97	13.65	1:1
L ₁ C ₂	822.77	16.9	Ni	1.4026	7.01	7.13	1:1
			Cd	2.7044	13.52	13.66	1:1
L ₂ C ₁	765.01	17.0	Co	1.5900	7.95	7.71	1:1
			Cd	2.8308	14.15	14.69	1:1
L ₂ C ₂	764.78	20.0	Ni	1.3444	6.72	7.27	1:1
			Cd	2.8889	14.44	14.69	1:1

Table 10: Some magnetic properties of the synthesized complexes

Sym.	Formula of complex	Correc. Factor D.10 ⁻⁶	Mass magnetic susceptibility X _g .10 ⁻⁶	Molar magnetic susceptibility X _m .10 ⁻⁶	Atomic magnetic susceptibility X _A .10 ⁻⁶	Effective magnetic moment μ _{eff}
L ₁ C ₁	CoCd (SCN) ₄ .C ₂₀ H ₁₃ N ₅ O ₆	-528.7	9.25	7612.989	8141.689	4.405
L ₁ C ₂	NiCd (SCN) ₄ .C ₂₀ H ₁₃ N ₅ O ₆	-528.7	0	0	528.700	1.123
L ₂ C ₁	CoCd (SCN) ₄ .C ₂₀ H ₁₅ N ₃ O ₆	-515.2	9.64	7374.878	7890.078	4.336
L ₂ C ₂	NiCd (SCN) ₄ .C ₂₀ H ₁₅ N ₃ O ₆	-515.2	0	0	515.200	1.108

Table 11: Antimicrobial activity results of the ligands and their complexes at 1000 ppm

Compound	Diameter of inhibition zone (mm)	
	Bacteria (S.aureus)	Fungi (Alternaria)
L ₁	28	29
L ₂	37	55
L ₁ C ₁	29	31
L ₁ C ₂	21	31
L ₂ C ₁	39	31
L ₂ C ₂	37	55
Ciprofloxacin	16	-
Amoxicillin	43	-

4. Conclusion

Schiff base ligands derived from 4- nitro benzene diamine with 4- nitro benzaldehyde or 4- hydroxyl benzaldehyde were synthesized. Also Schiff base complexes of MM-(SCN)₄[M = Co(II), Ni(II) ; M- = Cd (II)] were synthesized. These compounds were identified by analytical and spectral techniques. It was observed that these ligands were bidentate while complexes had coordination number equal four. Moreover all ligands and complexes had good antibacterial and antifungal activity.

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