Original Article

Synthesis And Spectral Studies Of Some New Binuclear Thiocyanate Complexes Containing Schiff Base Ligands Derived From 3,4-Diaminotoluene

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Abstract

New Schiff base ligands L_1,L_2 and L_3 were synthesized from the reaction of 3,4- diaminotoluene with indole-3-caboxaldehyde , 4-morpholine carboxaldehyde or 2-naphthaldehyde. Complexes of $CoCd(SCN)_4$ with those ligands have been synthesized and characterized. The characterization of ligands and their complexes was done by elemental analysis, molar conductance, ^1H, ^{13}C-NMR, mass spectra, magnetic susceptibility, infrared, and electronic spectral studies. All the synthesized ligands were bidentate, and The complexes are monomeric binuclear mixed metal bridges of type $LCo(NCS)_2Cd(SCN)_2$ (L= L_1,L_2 or L_3), non-electrolytes and have a four-coordinate number corresponding to tetrahedral geometry.

Key words: Schiff base, Bimetallic, Complex, Bridged thiocyanates

Introduction

Schiff bases can be easily obtained from primary amines condensing with carbonyl compounds, whether they are aldehydes or ketones (1-3). Bidentate Schiff bases containing two nitrogen donor atoms are important in the formation of stable compounds as a result of their coordination with different metal ions, which reflects their importance in biological systems (4,5). There is recognition of the significance of metal complexes of Schiff bases in the disciplines of supramolecular chemistry, material science, medicinal applications, and bioinorganic chemistry (6). Compounds related to organic oxygen carriers, both natural and synthetic, as well as active stereospecific catalysts for reduction, oxidation, hydrolysis, and transformation reactions in inorganic and organic chemistry, are all produced by Schiff base metal complexes (7). Due to their potential for use in numerous chemistry domains, dinuclear metal complexes and the ligands that promote their formation have been thoroughly studied (8-10). For these dimeric complexes to form, the single-coordinated metal ion must be in an unsaturated coordination environment, and there must be bridging atoms or groups, such as thiocyanates (11). In this work, we have studied the synthesis of some Schiff bases as ligands coordinated with complexes of $CoCd(NCS)_4$ to obtain new complexes with the formula $CoCd(NCS)_4$ L (L = Schiff base ligands), and then they were characterized by different spectroscopic and analytical methods.

Materials and reagents

The analytical reagent grade (AR) and highest purity of all compounds utilised were employed. They included 3,4-diaminotoluen (Merck), indole-3-caboxaldehyde (Merck), 4-morpholine carboxaldehyde (Merck), 2-naphthaldehyde (Merck), cobalt (II) nitrate hexahydrated (Sigma), cadmium (II) nitrate tetrahydrated (Sigma), potassium thiocyanate (Sigma), DMSO (Sigma), methanol (Sigma), and ethanol (Sigma).

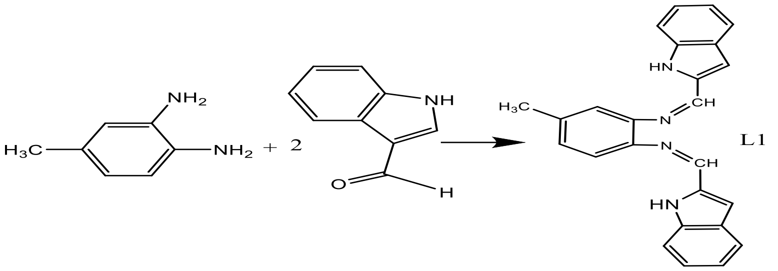
Instruments

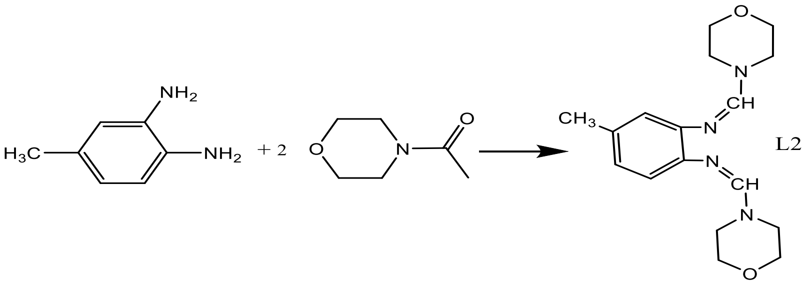
Using the ECS-4010 CHNSO analyzer, microanalyses of carbon, hydrogen, and nitrogen were performed. A phoenix-986 AA spectrophotometer used atomic absorption to determine the metal content of the complexes.

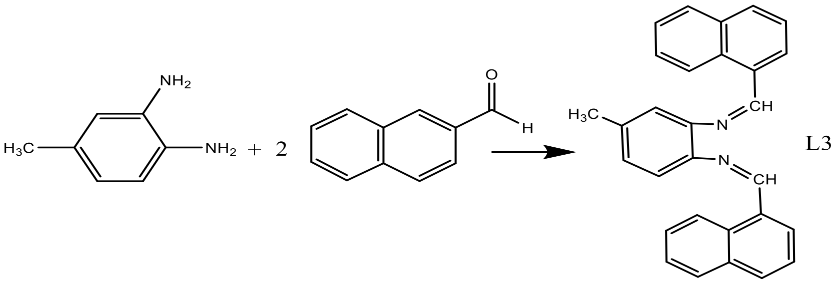
Utilizing electro-thermal fisher apparatus, the melting points of the produced compounds were measured. FT-IR spectra were recorded by the FT-IR 84005 Shimadzu spectrophotometer at room temperature (4000–400 cm^{-1}) in KBr discs. ^{1}H and ^{13}CNMR spectra, as a solution in DMSO-d6, were recorded on a 500 MHz Varian- NMR spectrophotometer at room temperature using TMS as an internal standard. The MS model 5975C VL MSD (EI) 70 eV was used to record mass spectra. The Faraday method was used to evaluate the molar magnetic susceptibility of powdered materials on MSB-MKI at room temperature. By applying Pascal's constant and using $Hg[Co(SCN)_4]$ as a calibrant, the diamagnetic corrections were made. The Jenway pcmb conductivity meter was used to test the molar conductivities of 10^{-3} M solutions of the solid complexes in DMF. The absorption spectra of $1x10^{-4}$ M solutions of the Schiff base ligands and their metal complexes in ethanol were recorded using a Shimadzu UV 1800. The cobalt content in the complexes was estimated by standard methods by atomic absorption using a phoenix-986 AA spectrophotometer.

Synthesis of Schiff base ligands

The Schiff base ligands (L_1, L_2, L_3) were synthesized using a similar procedure (12) by a reaction of 0.01 mole (1.221 gm) 3,4-diaminotoluene with 0.02 mole of indole-3-caboxaldehyde, 4-morpholine carboxaldehyde or 2-naphthaldehyde in an ethanol solvent with a few drops of glacial acetic acid. After being refluxed for a few hours, the reaction mixture was cooled to room temperature. The solid product underwent filtering, washing, and recrystallization before being dried on silica. (L_1, m.p. 172 ºC, yield = 80%), (L_2, m.p. 124 ºC, yield 85%), (L_3, m.p. 165 ºC, yield 78%). The synthesized equations are shown below:



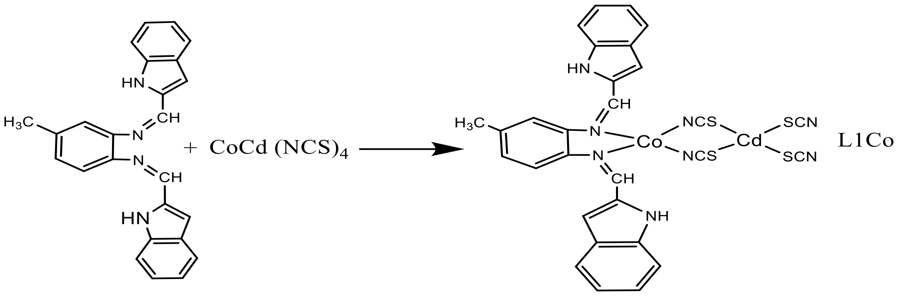


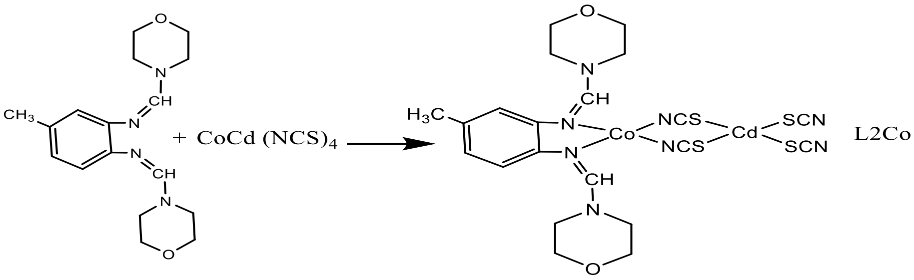


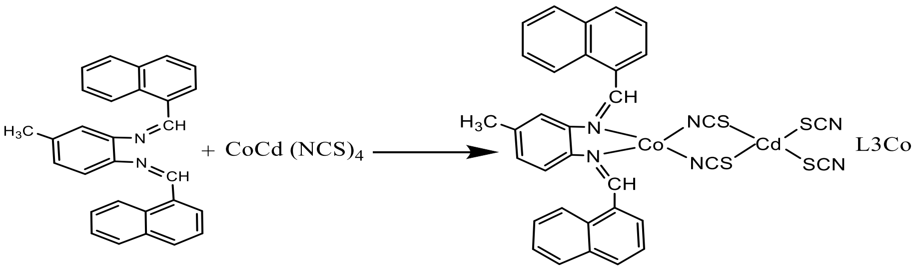
Synthesis of the Complexes

Firstly, the preparation of metal dithiocyanates (metal = Co, Cd) involved a direct reaction between potassium thiocyanate and metal nitrates in methanol. Filtration was used to remove KNO_3, and the dithiocyanate solutions were stored for further reactions. For the synthesis of $CoCd(SCN)_4$, 1:1 molar solutions of $Co(NCS)_2$ and $Cd(NCS)_2$ were mixed and stirred for 36 h (13). In a 1:1 molar ratio, solutions of L_1, L_2, or L_3 in ethanol were added to suspensions or solutions of these $CoCd(SCN)_4$ compounds in the same solvent and stirred under reflux. In each case, a solid was formed which was filtered off, washed with the solvent and dried in a vacuum. (L_1Co, m.p. 210

ºC(dec.), yield 82%), (L_2Co, m.p. 204 ºC (dec.), yield 85%), (L_3Co, m.p. 242 ºC (dec.), yield 87%). The synthesized equations were shown below:







Results and Discussion

For synthesized Schiff base ligands and their complexes, elemental analysis (%C, %H, %N, %Co) reveals that these percentages are identical to calculated values as presented in Table 1. This demonstrates that the suggested chemical structures of these compounds are accurate. The characterized infrared spectral bands of the synthesized ligands and their complexes are represented in Figures 1-6 and Table 2. The potential assignments of the observed bands for these compounds were formed by comparing the spectra with those described in the literature on related systems $^{(14, 15)}$. The appearance of bands at 1635 cm^{-1}, 1618 cm^{-1} and 1691 cm^{-1} due to the azomethine group in the ligands L_1 , L_2 and L_3 respectively, were shifted to lower frequencies at 1631 cm^{-1},1615 cm^{-1} and 1689 cm^{-1} in the complexes L_1Co, L_2Co and L_2Co respectively, demonstrating the azomethine nitrogen's involvement in the interaction with the metal ion. In addition, the existence of two bands in the region 2063-2150 cm^{-1} in the infrared spectra of complexes indicates the presence of both bridging and terminal thiocyanates in these complexes. In a similar manner, it has been noted that bands in the range 424-474 cm^{-1} are related to the bonding nature of thiocyanate by sulfur and nitrogen atoms $^{(16)}$.

The electronic spectra of the ligands and their complexes were summarized in Figures 7-12. The free ligands (L_1, L_2, L_3) were shown in three bands. The π-π transition in the C=C of the phenyl and azomethine groups is responsible for the first and second bands, whereas intra charge transfer is responsible for the third band. These bands were shifted in the complexes to shorter or longer wavelengths $^{(17)}$. Also, the spectra of complexes L_1Co and L_2Co showed new bands that were assigned to d-d transitions found at 761nm and 439 nm, respectively. In addition, the ^{1}HNMR and ^{13}CNMR spectra of the Schiff base ligands, as shown in Figures 13-18, showed all the expected signals as indicated in Table 3. Also, the mass spectra of the ligands (L_1, L_2, L_3) shown in Figures 19-21 indicate the presence of molecular ions at m/z=375 $[C_{25}H_{19}N_4]^{+}$, m/z=316 $[C_{17}H_{24}N_4O_2]^{\cdot +}$ and m/z=398 $[C_{29}H_{22}N_2]^{\cdot +}$ respectively. Also, the spectra showed the presence of a characteristic peak in L_1, L_2 and L_3 at m/z=247 $[C_{16}H_{13}N_3]^{\cdot +}$, m/z=217 $[C_{12}H_{15}N_3O]^{\cdot +}$ and, m/z=258 $[C_{18}H_{14}N_2]^{\cdot +}$ respectively, which belong to base ions. Additionally, another peak corresponding to the ligands various fragments was assigned to their mass spectra. On the other hand, Table 4 included a list of molar conductivities and magnetic susceptibilities. The low molar conductance of the complexes suggests that none of these complexes were electrolytic (18). The μ_{eff} values for the complexes L_1Co, L_2Co, and L_3Co indicated that these complexes have tetrahedral geometry (19).

Table 1: The percentage of elements in the Schiff base ligands and their complexes

Symb. of Compound	**Formula**	**C%**		**H%**		**N%**		**Co%**	
	M.wt (gm/mol)	**found**	**cal.**	**found**	**cal.**	**found**	**cal.**	**found**	**cal.**
L_1	$C_{25}H_{19}N_4$ 375.46	79.87	79.98	5.16	5.10	14.88	14.92	-	-
L_2	$C_{17}H_{24}N_4O_2$ 316.41	64.61	64.53	7.59	7.65	17.75	17.71	-	-
L_3	$C_{29}H_{22}N_2$ 398.51	87.53	87.41	5.52	5.56	7.14	7.03	-	-
L_1Co	$CoCd(SCN)_4C_{25}H_{19}N_4$ 780.12	44.61	44.65	2.61	2.58	14.32	14.36	7.98	7.55
L_2Co	$CoCd(SCN)_4C_{17}H_{24}N_4O_2$ 796.24	39.53	39.22	5.17	5.06	14.23	14.07	7.32	7.40
L_3Co	$CoCd(SCN)_4C_{29}H_{22}N_2$ 877.34	52.09	52.02	4.31	4.25	9.52	9.58	6.91	6.72

Table 2: Important infrared bonds of the ligands and their complexes

Sym. of Comp. cm^{-1}	**C-H Arom. cm^{-1}**	**HC=N cm^{-1}**	**C=C cm^{-1}**	**C-H Azomethine cm^{-1}**	**NH cm^{-1}**	**C-N in M-SCN cm^{-1}**	**S-C in M-SCN cm^{-1}**	**C-N in M-SCN-M cm^{-1}**	**M←N cm^{-1}**	**M-NSC cm^{-1}**	**M-SCN cm^{-1}**
L$_1$	3047 3111	1635	1591	2886	3385	-	-	-	-	-	-
L$_1$Co	3066 3150	1631	1595	2877	3332	2075	744	2140	596	438	426
L$_2$	3160	1618	1588	2860	-	-	-	-	-	-	-
L$_2$Co	3155	1613	1578	2860	-	2075	747	2150	590	472	447
L$_3$	3053	1691	1624	2858	-	-	-	-	-	-	-
L$_3$Co	3053	1689	1627	2858	-	2063	752	2135	597	474	424

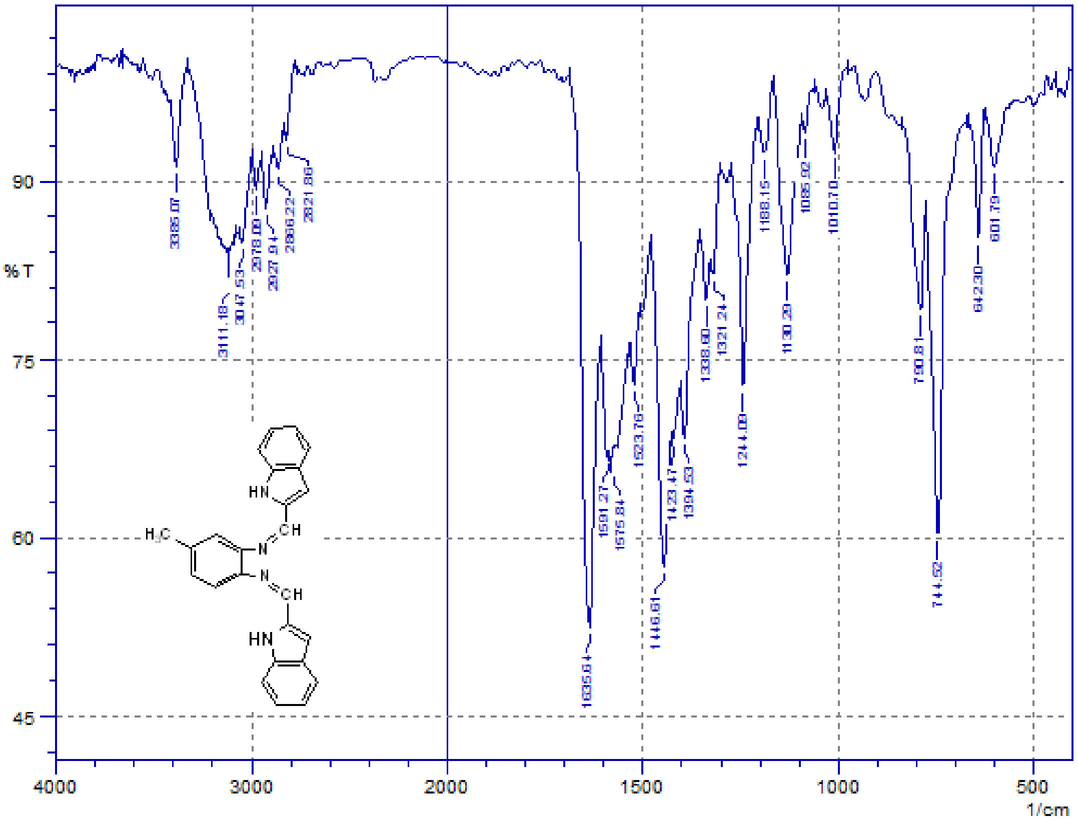


Figure 1: IR Spectrum of the ligand L_1

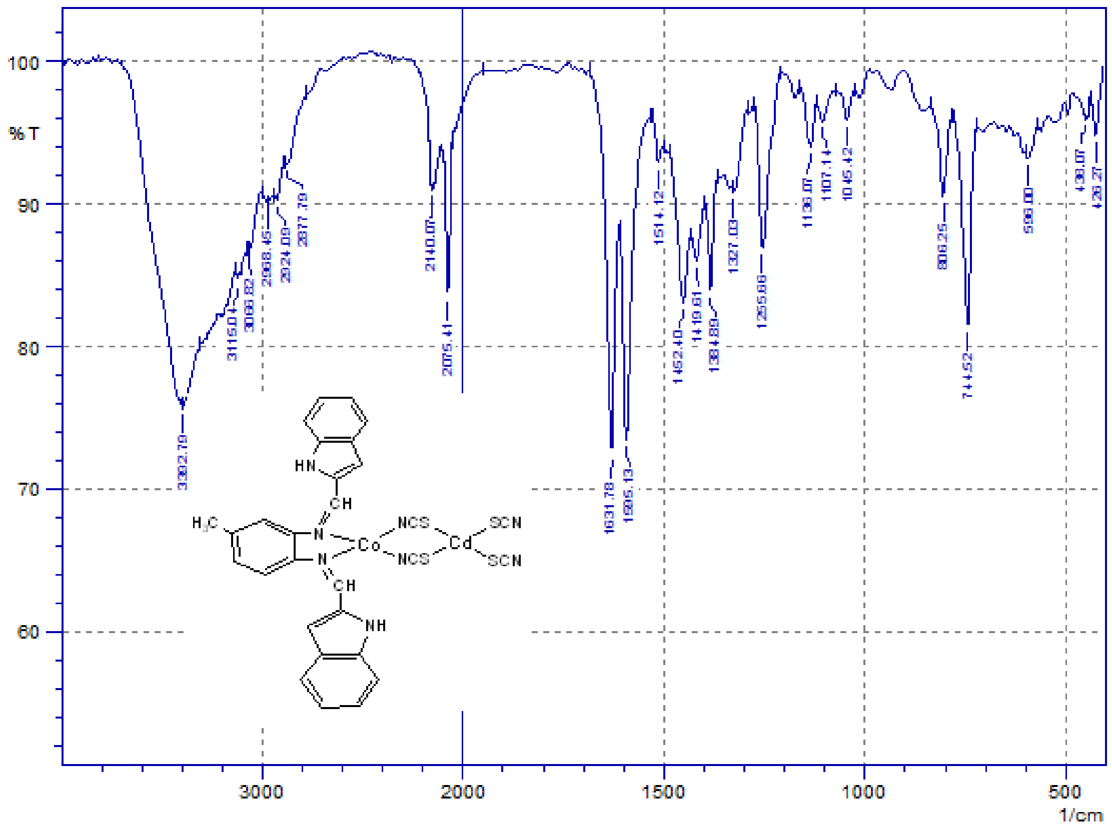


Figure 2 : IR Spectrum of the complex L_1Co

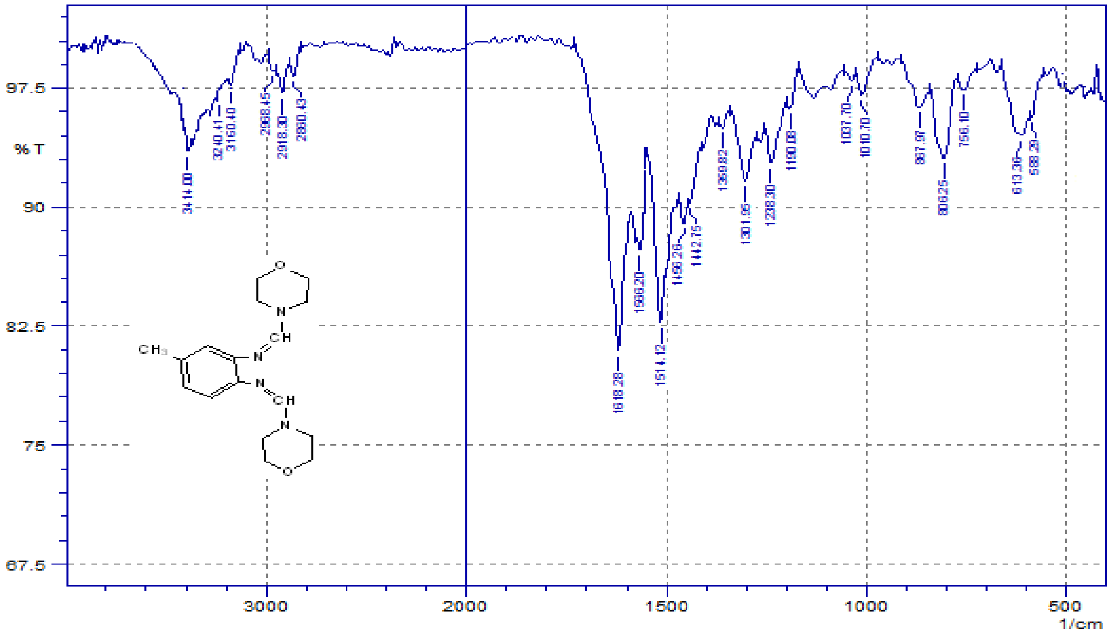


Figure 3 : IR Spectrum of the ligand L_2

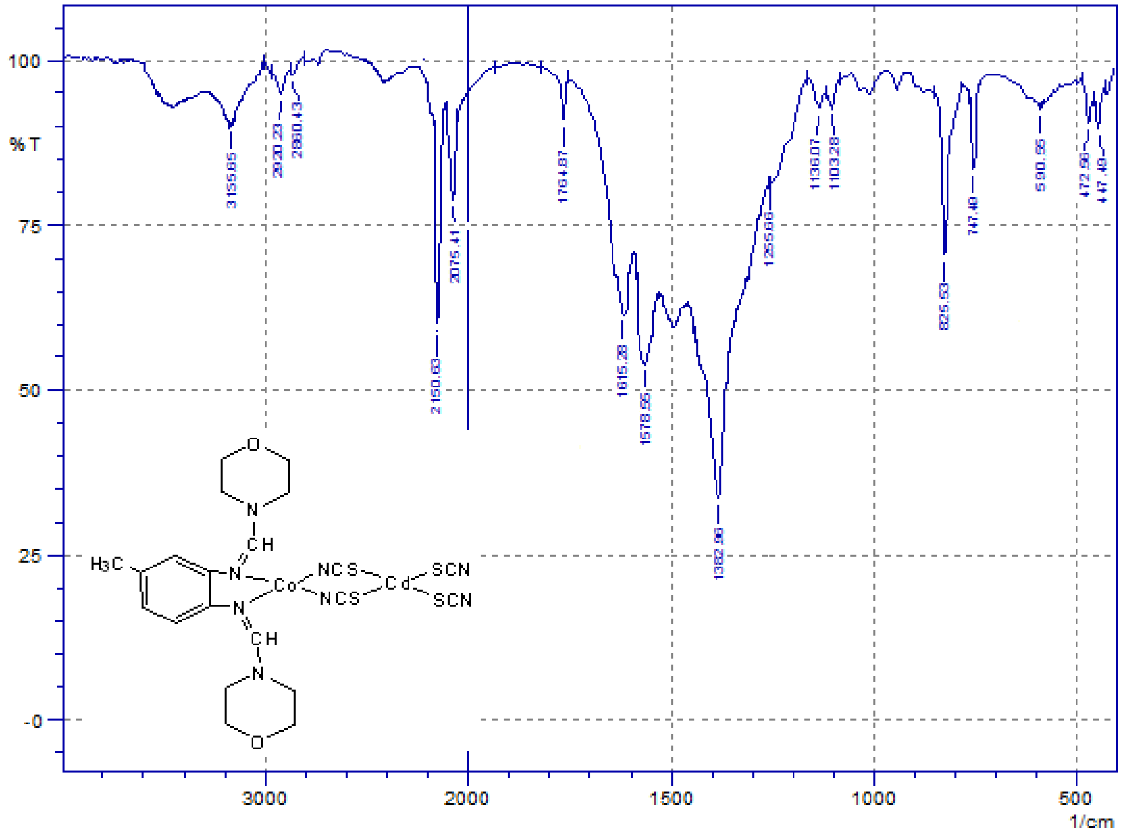


Figure 4: IR Spectrum of the complex L_2Co

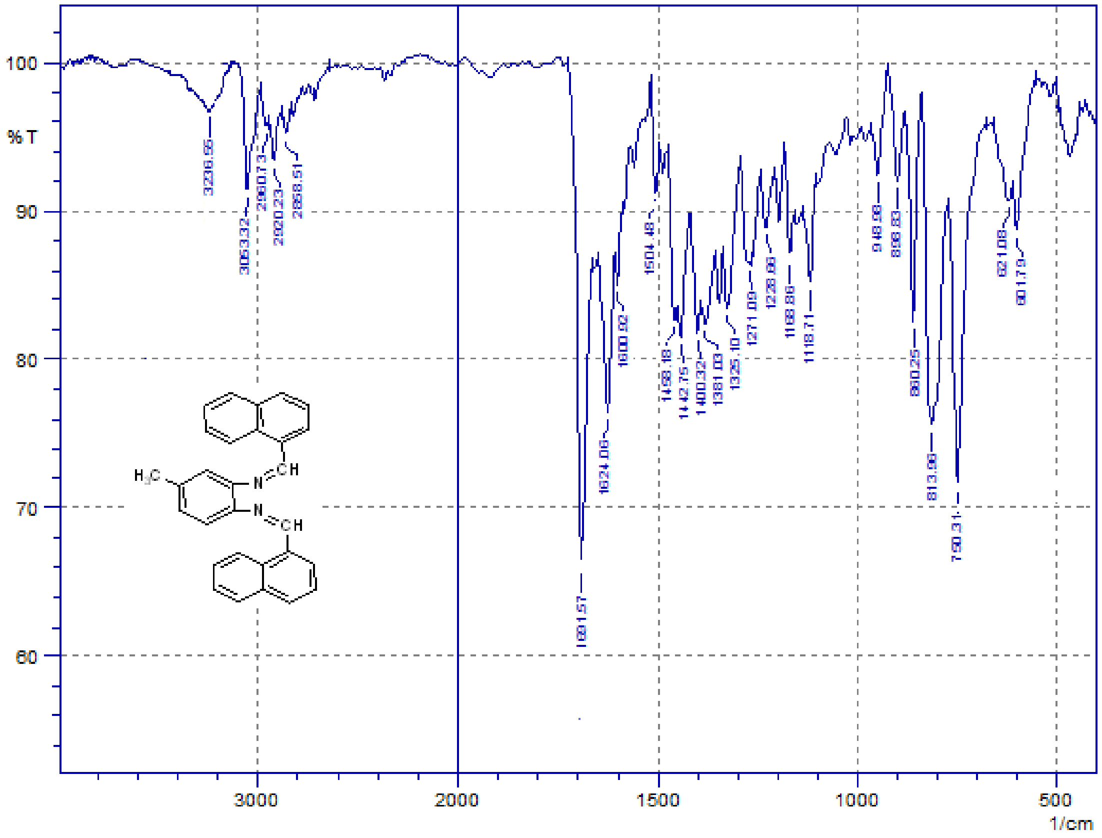


Figure 5 : IR Spectrum of the ligand L_3

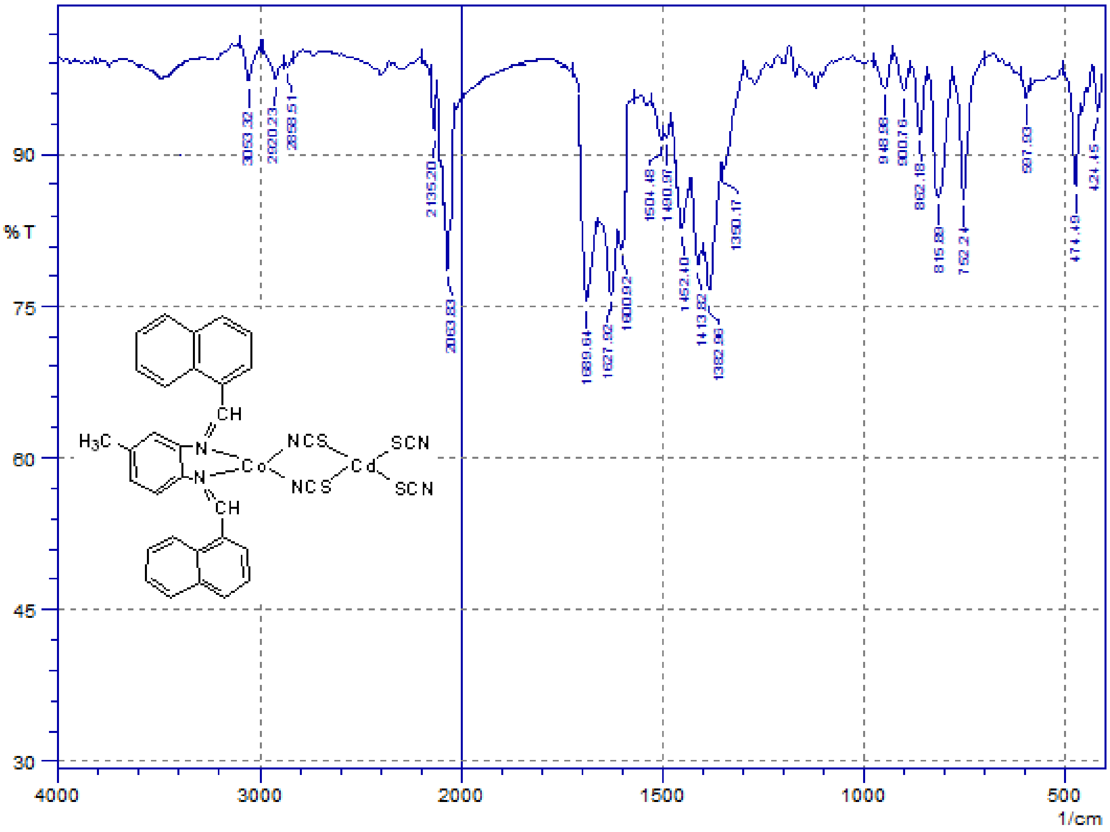
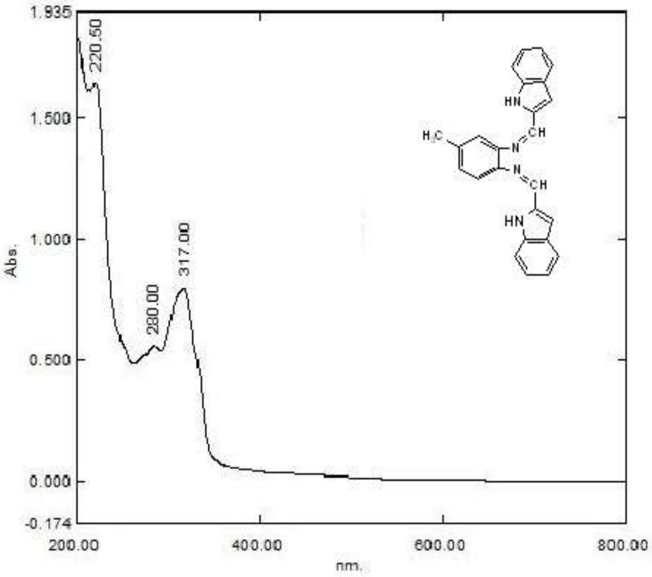


Figure 6: IR Spectrum of the complex L_3Co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1.000
0.500
0.000
-0.174
Abs.
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317.00
200.00
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600.00
800.00
nm.
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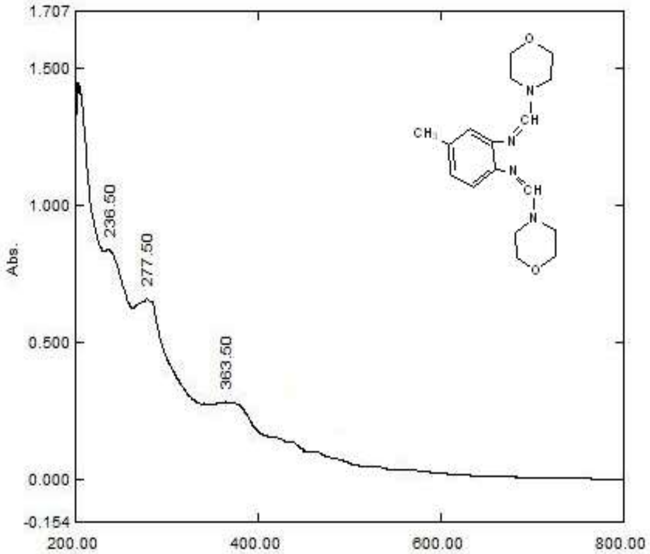
H₃C
N
CH
HN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1.000
0.500
0.000
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200.00
400.00
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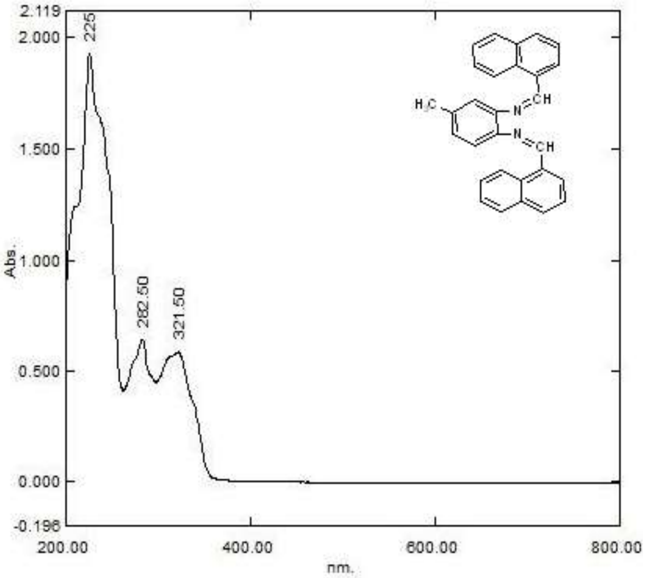
800.00
N
O
CH₃
CH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2.000
1.500
1.000
0.500
0.000
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400.00
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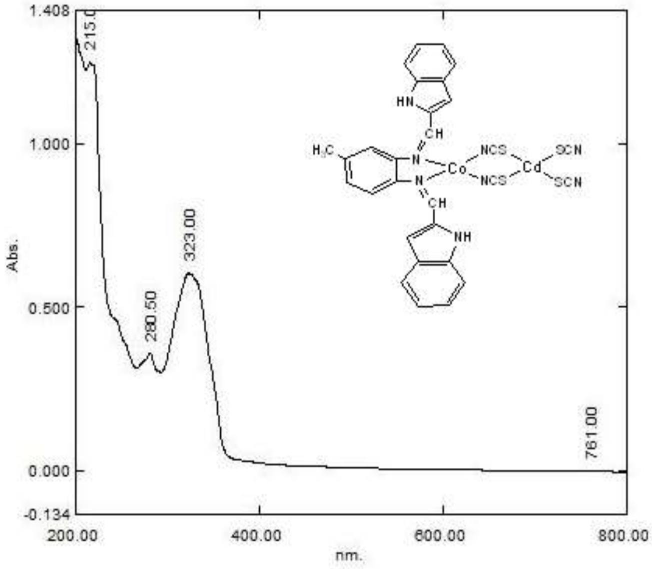
nm.
H₃C
N
CH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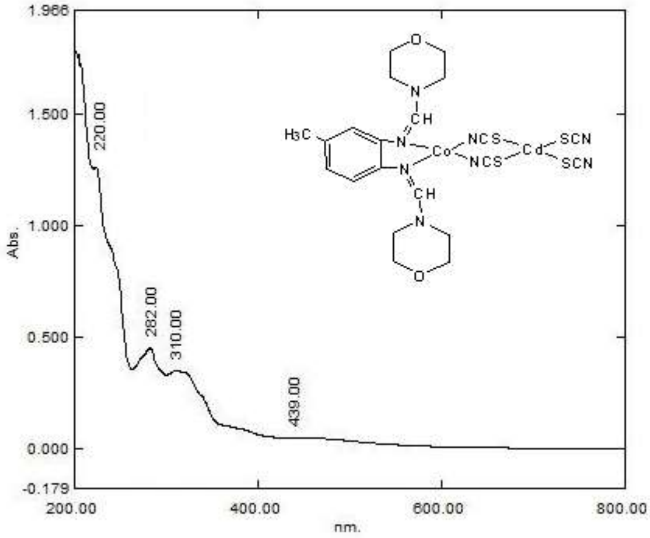
Cd
SCN



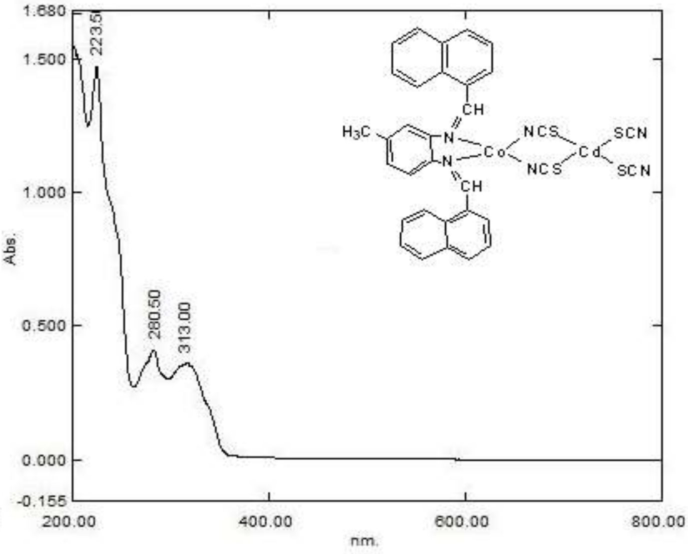


Table 3: Chemical shifts of ^{1}HNMR and ^{13}CNMR for the Schiff base ligands

Ligand	**^{1}HNMR**	**^{13}CNMR**
	Chemical shifts (ppm)	**Chemical shifts (ppm)**
L_1	2.35 (3H,CH_3) , 6.99-7.77 (13H, Ar-H) , 8.64 , 8.79 (2H,CH=N) , 11.63, 11.76 (2H , NH)	C1(134.03), C2(128.56) ,C3(120.59), C4(140.84), C5(146.20) , C6(120.93), C7(21.21), C8(166.86), C9(122), C10(108.78), C11(127.54), C12(121.48), C13(121.79) , C14(120.97), C15(111.99), C16(136.71),C17(166.34), C18(122), C19(108.78), C20(127.54), C21(121.48), C22(121.79), C23(120.97),C24(111.99),C25(136.71)
L_2	2.35 (3H , CH_3) , 3.22- 3.77 (16H,CH_2-cyclic) ,7.18- 7.29 (3H ,Ar-H) , 7.80, 8.07(2H, CH=N)	C1(134.32), C2(127.57), C3(124.19) , C4(144.10) ,C5(143.84), C6(123.70), C7(21.21), C8(153.05), C9(46.99), C10(65.78), C11(65.78), C12(46.99), C13(153.12), C14(46.99), C15(65.78), C16(65.78),C17(46.99)
L_3	2.34(3H, CH_3) , 7.13-8.02(17H, Ar-H) , 8.39, 9.39(2H, CH=N)	C1(134.03), C2(128.56), C3(120.59), C4(140.84), C5(146.20) , C6(120.93), C7(21.21), C8(187.72),C9(130.73), C10(128.32), C11(125.51), C12(133.18), C13(130.25) , C14(129.15),C15(127.54), C16(126.55), C17(124.27), C18(131.27), C19(186.49), C20(130.73), C21(128.32), C22(125.51), C23(133.18), C24(130.25), C25(129.15), C26(127.54), C27(126.55), C28(124.27), C29(131.27)

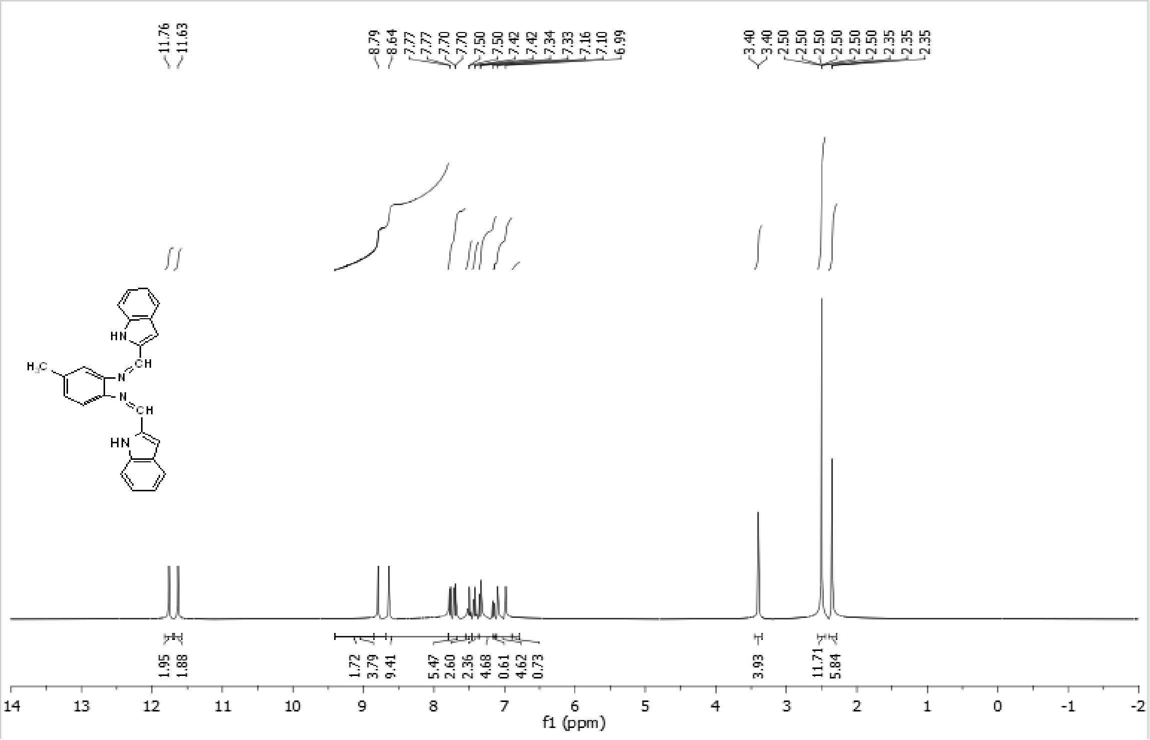


Figure 13 : ^{1}HNMR spectrum of the ligand L_1

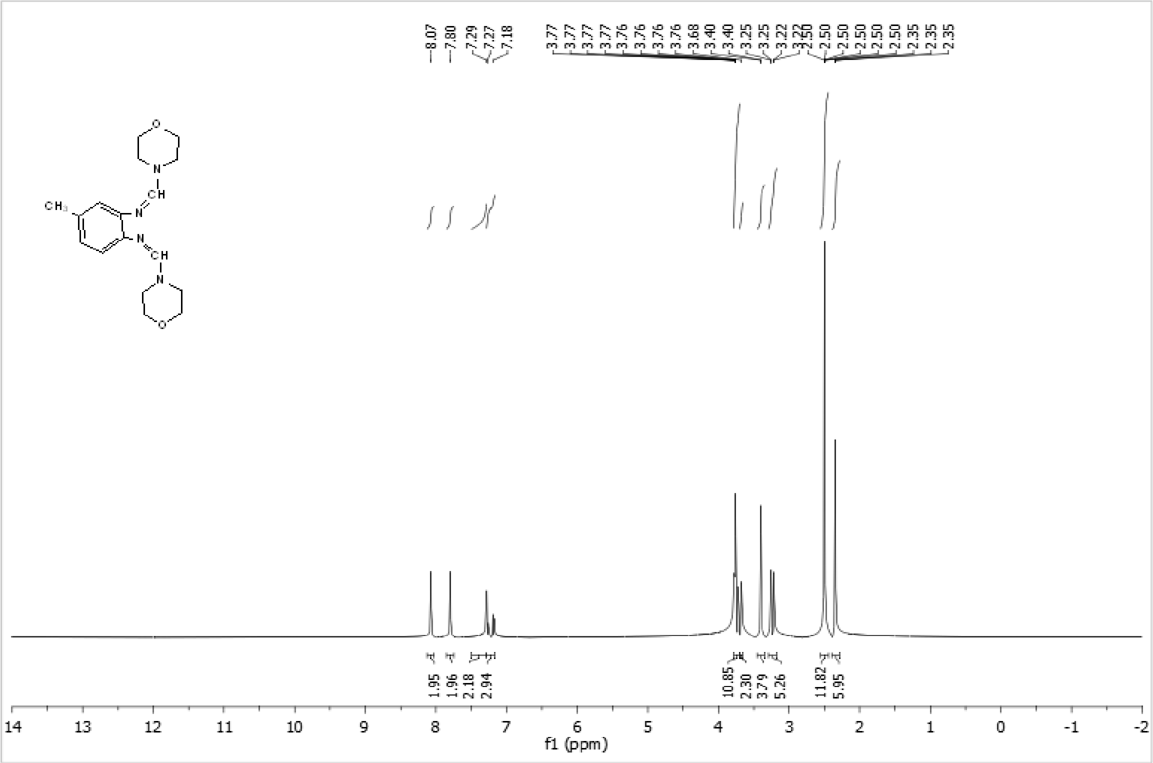


Figure 14: ^{1}HNMR spectrum of the ligand L_2

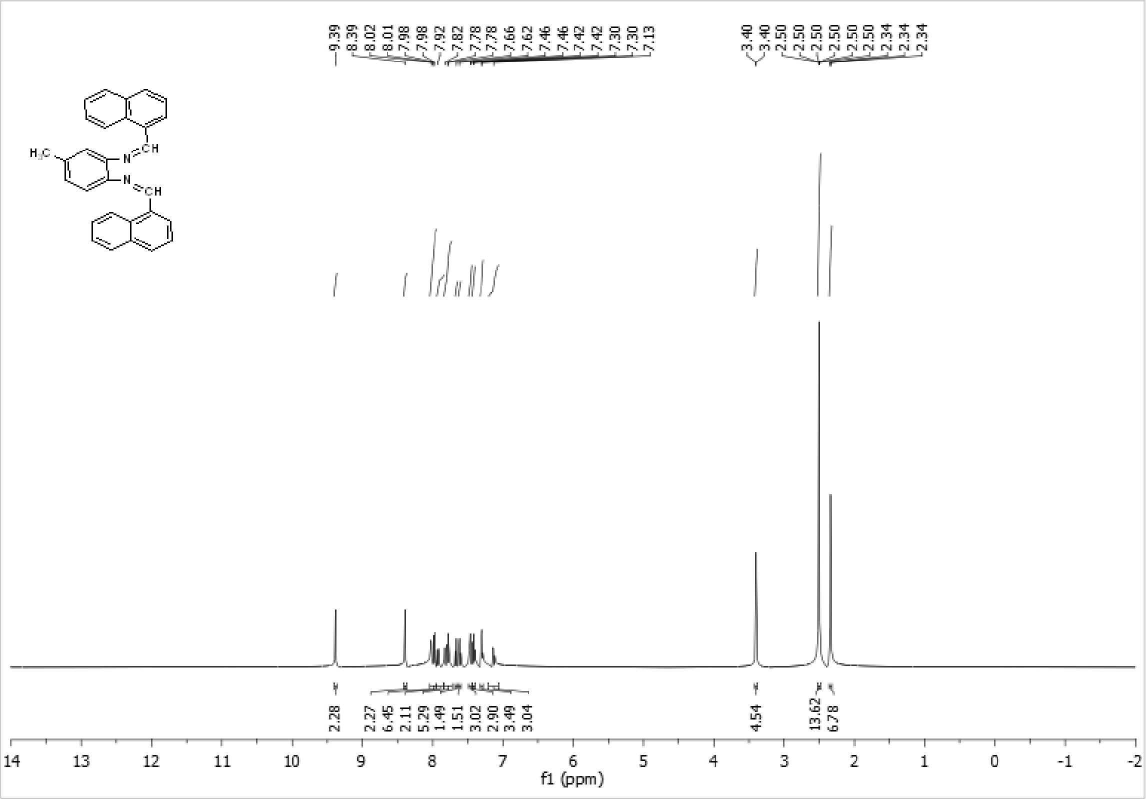


Figure 15 : ^{1}HNMR spectrum of the ligand L_3

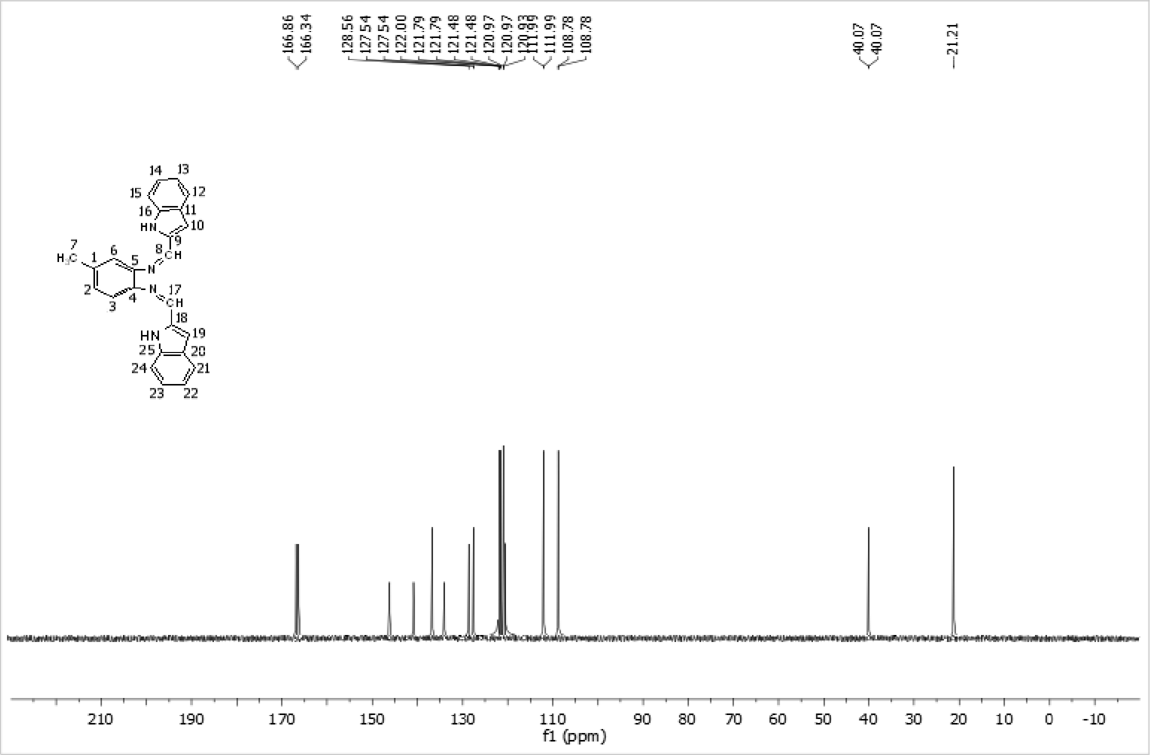


Figure 16 : ^{13}CNMR spectrum of the ligand L$_1$

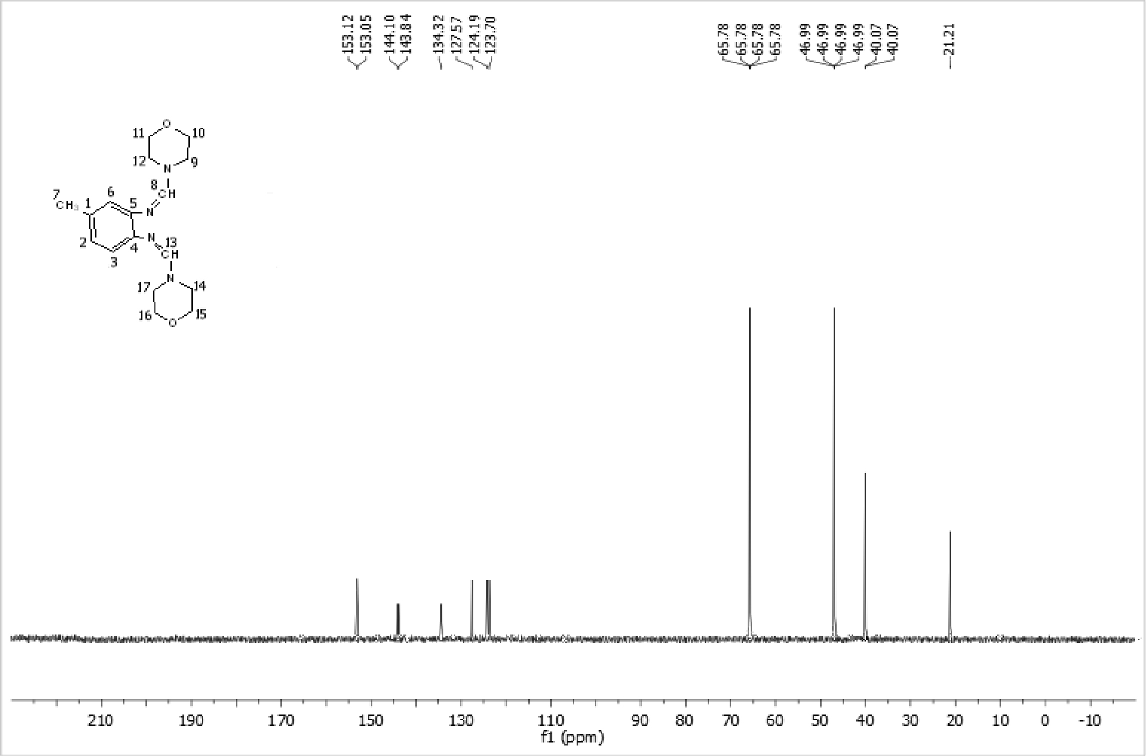


Figure 17: ^{13}CNMR spectrum of the ligand L$_2$

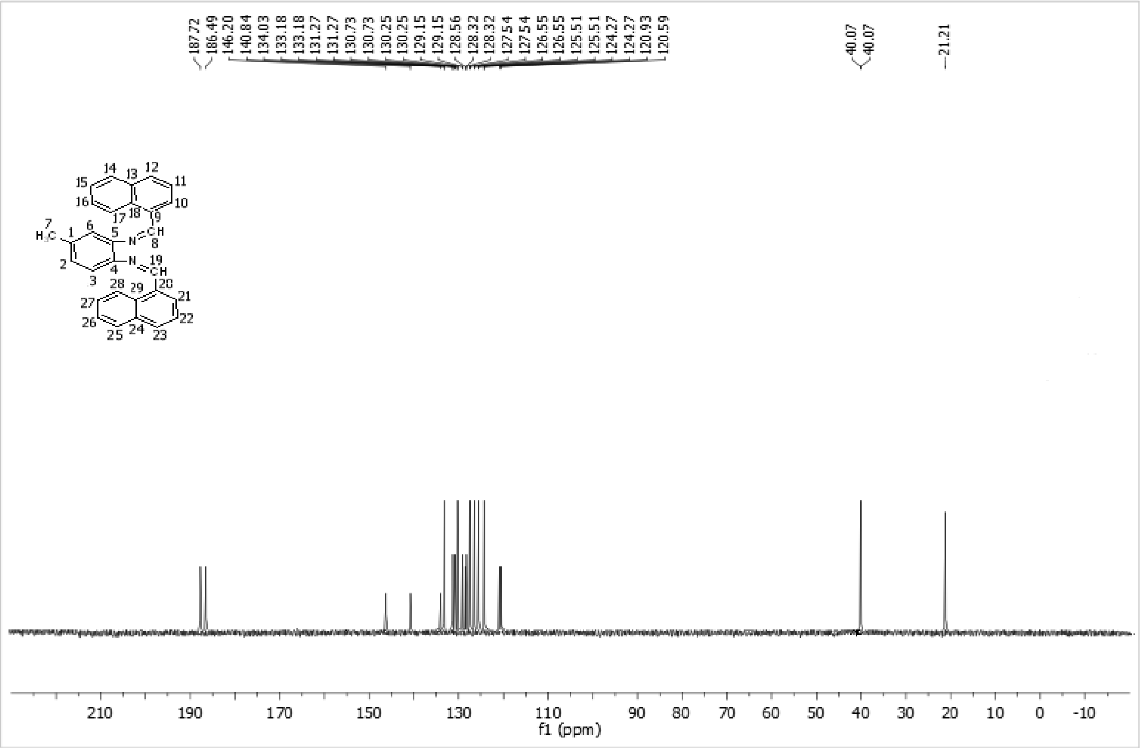


Figure 18: ^{13}CNMR spectrum of the ligand L_3

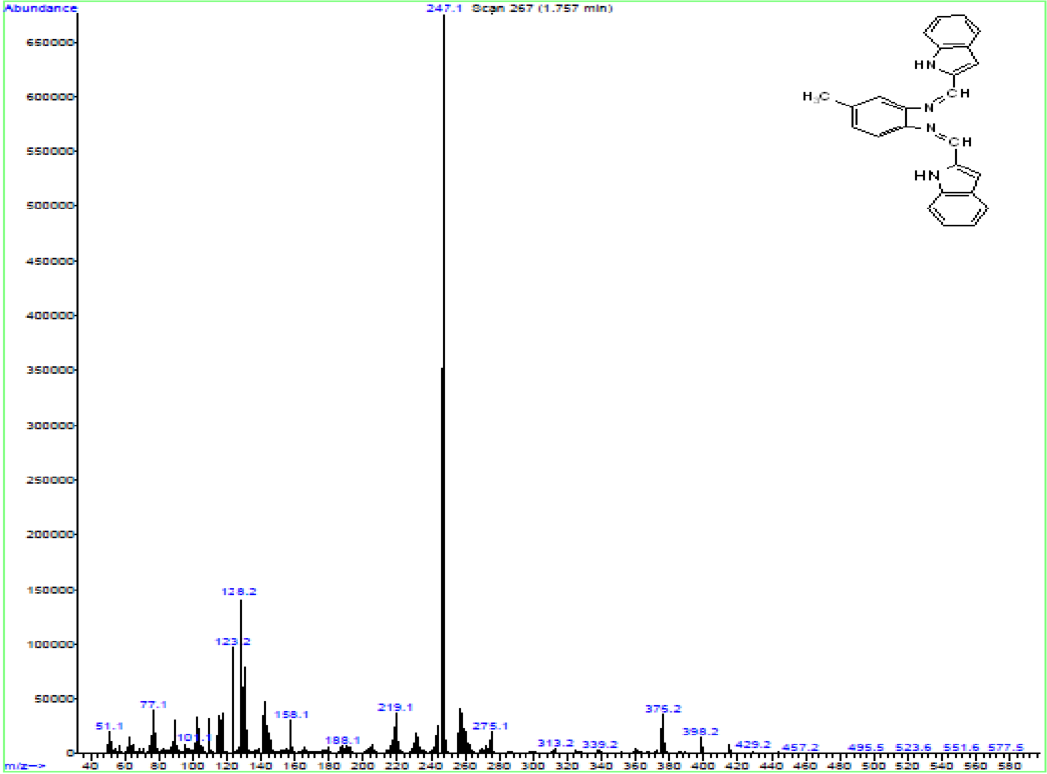


Figure 19: Mass spectrum of the ligand L_1

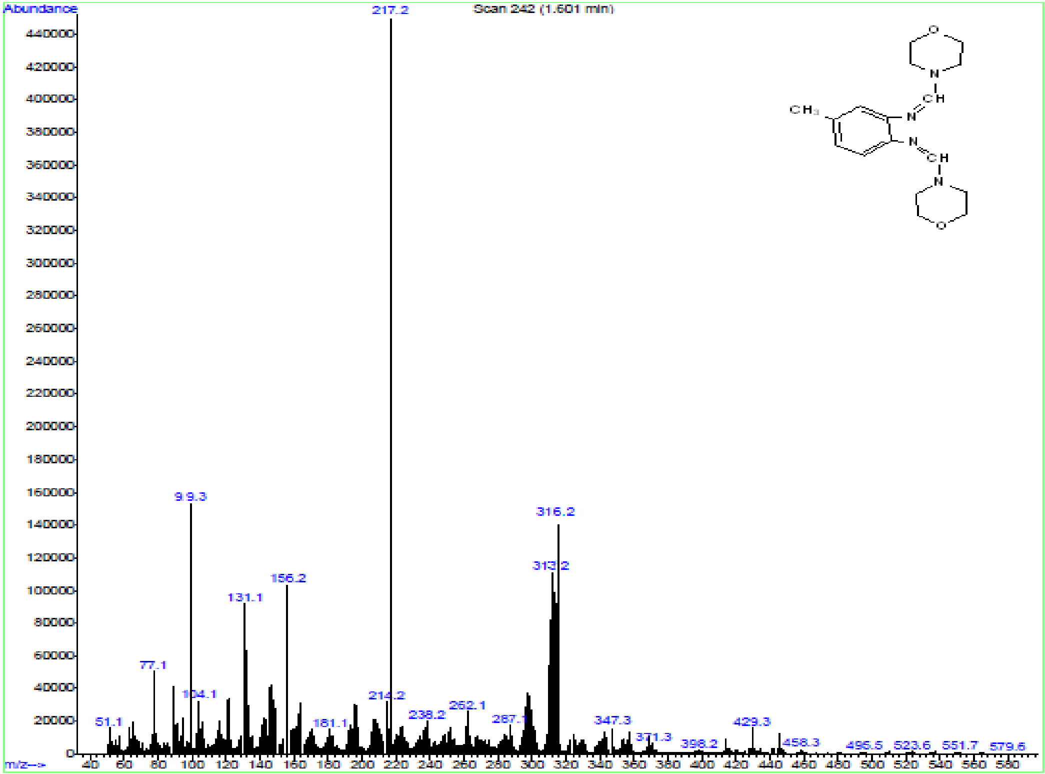


Figure 20: Mass spectrum of the ligand L_2

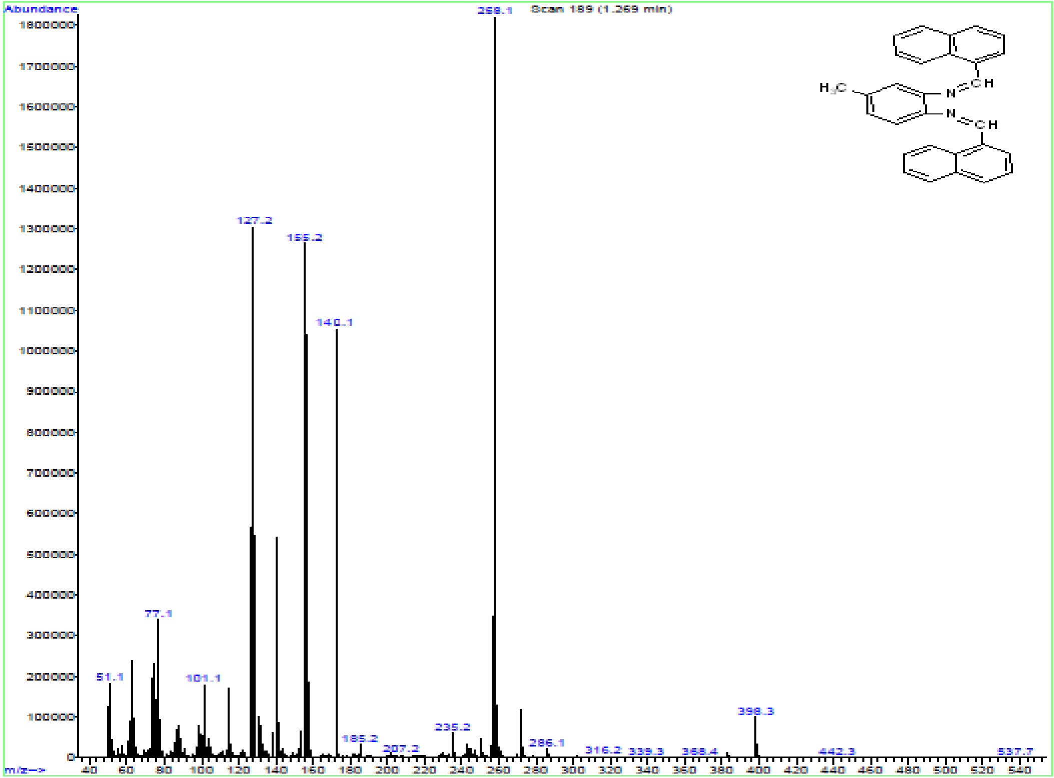


Figure 21: Mass spectrum of the ligand L_3

Table 4: Molar conductivity and magnetic moment of the complexes

Sym. of Complex	Formula of Complex M.wt(gm/mol)	μ_{eff} (B.M)	Molar Conductivity $Ohm^{-1}cm^{1}/mol$	Magnetic Properties	Hybridization and geometry
L_1Co	$CoCd(SCN)_4C_{25}H_{19}N_4$ 780.12	4.267	21	Paramagnetic	sp^3 (tetrahedral)
L_2Co	$CoCd(SCN)_4C_{17}H_{24}N_4O_2$ 796.24	4.105	14	Paramagnetic	sp^3 (tetrahedral)
L_3Co	$CoCd(SCN)_4C_{29}H_{22}N_2$ 877.34	4.286	15	Paramagnetic	sp^3 (tetrahedral)

Conclusions

Schiff base ligands derived from 3,4-diaminotoluene with indole-3-caboxaldehyde, 4-morpholine carboxaldehyde or 2-naphthaldehyde and their complexes with $CoCd(SCN)_4$ were prepared. The ligands and their complexes were characterized by different analytical and spectral methods. The coordination number of these complexes was found to be four, which corresponds to tetrahedral geometry and non-electrolytes.

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