

## **Preparation, identification and antimicrobial studies of some bimetallic bridged thiocyanates complexes containing N,N'-bis (4-isopropyl benzylidene) 4-methyl benzene -1,2-diamine Schiff base ligand**

**Mouayed Yousif Kadhum and Basheer Jawad Al-musawi**

*Department of Chemistry, College of Education for Pure Science, University of Basrah, Basrah, Iraq*

### **ABSTRACT**

New Schiff base ligand (L) was prepared from reaction of 4-isopropyl benzaldehyde with 4-methyl benzene -1,2-diamine. This ligand was treated with tetrathiocyanate complexes of  $MM'(SCN)_4$  [ $M = Co(II)$ ,  $Ni(II)$ ,  $Hg(II)$ ;  $M' = Cd(II)$ ] to form three new complexes. These compounds have been characterized by different analytical and spectral techniques like elemental analysis, infrared, ultraviolet-visible,  $^1H$ ,  $^{13}C$ -NMR, mass spectra, molar conductance, atomic absorption and magnetic susceptibility studies. All the complexes are binuclear mixed metal monomeric bridged of the type  $LM(NCS)_2M'(SCN)_2$ , non electrolytes and have coordination number equal four. Some thermal parameters of the prepared complexes was studied by thermogravimetric analysis (TGA). It was observed that these complexes have a good thermal stability. Antibacterial and antifungal activity of the ligand and its complexes were evaluated. They have significant antimicrobial activity.

**Key words:** Schiff base, Bridged thiocyanates, Bimetallic, Antimicrobial, Preparation

### **INTRODUCTION**

Schiff base are generally bidentate, tridentate, tetradentate or polydentate ligands. These ligands are forming very stable complexes with transition metals. Schiff bases derived from aromatic aldehydes have a wide variety of applications in many fields such as biological, inorganic and analytical chemistry [1]. Schiff base are used in optical and electrochemical sensors as well as in various chromatographic methods to enable detection of enhanced selectivity and sensitivity [2,3]. Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions [4]. In organic synthesis, Schiff base reactions are useful in making carbon-nitrogen bonds. Many biologically important Schiff bases have been reported in literature possessing, antimicrobial, antibacterial, antifungal, anti-inflammatory, anticonvulsant, antitumor and anti-HIV activities [5].

Tetrathiocyanate complexes containing Schiff base ligands of the type  $MM'(SCN)_4 \cdot L$  [ $M' = Zn(II)$ ,  $Cd(II)$ ,  $Hg(II)$ ,  $M = Co(II)$ ,  $Ni(II)$ ,  $Mn(II)$ ] are extensively studied because of the ability of thiocyanate ion to coordinate either through nitrogen or sulfur or both in a bridging fashion [6]. Bimetallic thiocyanates and their derivatives are such potentially useful candidates among the organometallic systems because all of them contain  $-S=C=N-$  bridges, which connect metal atoms, forming infinite two-dimensional or three-dimensional networks. The infinite network confers a relatively large polarization which induces relatively large macroscopic nonlinearities in these materials [7, 8].

In the present work new bidentate Schiff base ligand containing two azomethine groups and its complexes with bimetallic thiocyanates  $MM'(SCN)_4$  are prepared and investigated by different spectral techniques. Molar conductance, magnetic susceptibility, atomic absorption and thermogravimetric analysis have been studied. Antibacterial and antifungal activities of the prepared compounds are evaluated.

## MATERIALS AND METHODS

All reagents and chemicals were of analytical spectroscopic grade and used without further purification. 4-methyl-1,2-diaminebenzen and 4-isopropyl benzaldehyde from Fluka company. Cobalt(II), Cadmium(II), Nickel(II), Mercury(II) nitrates, Potassium thiocyanate, Ethanol, DMSO and methanol from sigma company.

### Physical measurements

Elemental analysis of the prepared compounds was recorded on Euro vector EA 3000 A apparatus. The IR spectra were recorded in the range  $400\text{--}4000\text{cm}^{-1}$  by KBr pellet using FTIR-8400 S-Shimadzu Spectrophotometer. Melting points of the ligand and complexes were determined in electro thermal fisher apparatus.  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR Spectra in DMSO were recorded on NMR spectrophotometer (Varian-500MHZ). The ultraviolet and visible spectra in Ethanol were obtained on SPV-725 spectrophotometer (Germany). Conductance of the complexes was measured in DMF at room temperature using Jenway pcmb conductivity meter. The molar ratio of metal-ligand was determined by atomic absorption apparatus (Analyst 200 Atomic Absorption Spectrometer). Magnetic susceptibility measurements were made at room temperature by Gouy's method.

### Preparation of Schiff base ligand (L)

(N,N' -Bis (4-isopropylbenzylidene ) 4methylbenzene-1, 2-diamine)

A solution of 4-isopropyl benzaldehyde ( 2.964 g, 20 mmol ) in ethanol ( 50ml ) and 4-methyl benzene -1,2-diamine (1.221g ,10mmol) in ethanol (50ml) were placed in around-bottomed flask in the presence of some drops of glacial acetic acid. The solution was stirred for 7 hrs under refluxed. The part of solvent was removed under reduced pressure, then the solution was cooled to leave precipitate. It was filtered, washed with ethanol and dried. The suggested structure for the prepared ligand was given in Figure 1 and some physical properties were listed in Table 1.

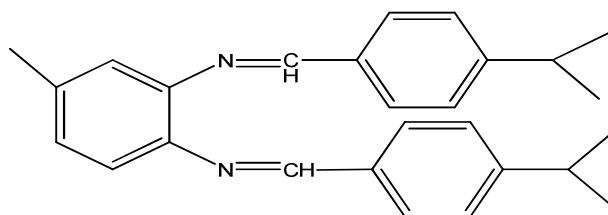


Figure 1 . Proposed structure of the prepared Schiff base ligand

### Preparation of the Complexes

Metal dithiocyanates ( $\text{Co}(\text{SCN})_2$ ,  $\text{Ni}(\text{SCN})_2$ ,  $\text{Cd}(\text{SCN})_2$ ,  $\text{Hg}(\text{SCN})_2$ ) were first prepared by the reaction of these metals nitrates with potassium thiocyanate in methanol. The formed potassium nitrate was removed by filtration and solutions of dithiocyanates were kept for further reaction. For the preparation of  $\text{MM}'(\text{SCN})_4$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Cd}$ ;  $\text{M}' = \text{Cd}, \text{Hg}$ ). Solution of  $\text{M}(\text{SCN})_2$  and  $\text{M}'(\text{SCN})_2$  were mixed in 1:1 molar ratio and stirred for 24 hrs [9]. Solution of these tetrathiocyanates as alone in methanol was mixed with prepared Schiff base in the same solvent in 1:1 molar ratio and stirred for 24 hrs [10]. In each case a solid product formed was filtered off and washed with methanol and water. The suggested structure for the prepared complexes was given in Figure 2 and some physical properties were shown in Table 1.

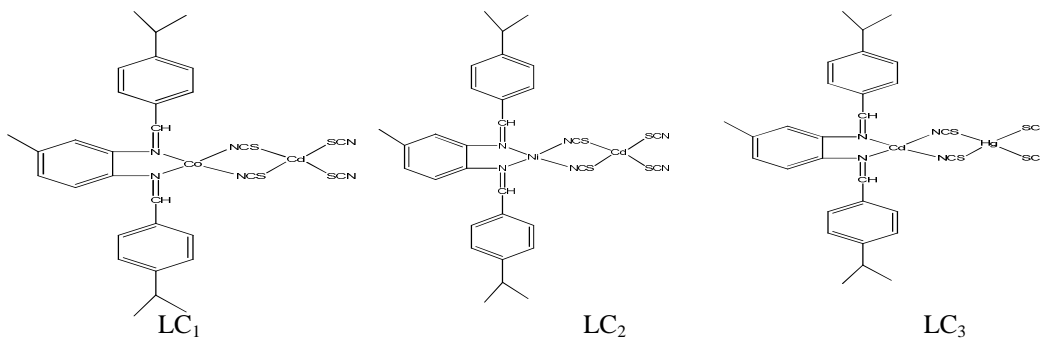


Figure 2. Proposed structure of the prepared complexes

Table 1. Some physical properties of the prepared Schiff base ligand and its complexes

Symb. of Comp	Formula Molecular weigh	Physical state and colour	Time of reaction hrs	Melting point (°C)	Yield (%)
L	C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> 382.54	Light yellow powder	7	145-147	65
LC <sub>1</sub>	CoCd(SCN) <sub>4</sub> C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> 786.21	Blue green powder	10	165 <sup>d</sup>	66
LC <sub>2</sub>	NiCd(SCN) <sub>4</sub> C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> 785.97	Beige powder	11	200 <sup>d</sup>	60
LC <sub>3</sub>	CdHg(SCN) <sub>4</sub> C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> 927.87	Light brown powder	18	161 <sup>d</sup>	55

*d=decomposition*

## RESULTS AND DISCUSSION

### Elemental analysis

The results of elemental analysis for prepared ligand and complexes show that the found percentages of carbon, hydrogen and nitrogen are equivalent to calculated values as show in Table 2. This is evidence that proposed chemical structures of these compounds are true.

Table 2. Elemental analysis data of the ligand and its complexes

Symb. of comp.	Formula of comp.	C%		H%		N%	
		Cal.	Found	Cal.	Found	Cal.	Found
L	C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> 382.54	84.77	84.29	7.90	7.76	7.32	7.34
LC <sub>1</sub>	CoCd(SCN) <sub>4</sub> C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> 786.21	47.36	47.46	3.85	3.81	10.69	10.38
LC <sub>2</sub>	NiCd(SCN) <sub>4</sub> C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> 785.97	47.36	47.32	3.85	3.54	10.69	10.53
LC <sub>3</sub>	CdHg(SCN) <sub>4</sub> C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> 927.87	40.13	39.99	3.26	3.21	9.06	9.34

### Infrared spectra

The important infrared spectral bands of the prepared ligand and complexes are presented in Figures 3-5 and Table 3. The tentative assignments of the observed bands for these compounds were made by comparing the spectra with these reported in the literature on similar systems [11]. The band appearing at 1616 cm<sup>-1</sup> due to azomethine group in the ligand is shifted to lower frequency at 1603, 1614 and 1614 cm<sup>-1</sup> in the complexes LC<sub>1</sub>, LC<sub>2</sub> and LC<sub>3</sub> respectively, indicating the participation of the azomethine nitrogen in interaction with the metal ion [12]. Also the infrared spectra of complexes show the presence of two bands in the region 2058-2139 cm<sup>-1</sup> indicating that both bridging and terminal thiocyanates are present in these complexes [13]. Similarly it is observed bands in the region 737-740 cm<sup>-1</sup> and 808-815 cm<sup>-1</sup> belong to the bonding nature of thiocyanate by sulfur and nitrogen atoms respectively [14].

Table 3. IR data of the ligand and its complexes

Symb. of comp.	$\nu$ C-H Arom. cm <sup>-1</sup>	$\nu$ C-H Aliph. cm <sup>-1</sup>	$\nu$ HC=N cm <sup>-1</sup>	$\nu$ C-N in SCN cm <sup>-1</sup>	$\nu$ C=C cm <sup>-1</sup>	$\nu$ -S-CN cm <sup>-1</sup>	$\nu$ S-CN- cm <sup>-1</sup>
L	3020m	2966s 2924m 2868m	1616w	-----	1514m	-----	-----
LC <sub>1</sub>	3020sh	2960s 2926m 2870m	1614w	2058,2139s	1458m	810m	737m
LC <sub>2</sub>	3030sh	2962s 2924m 2870m	1614w	2063,2106s	1460s	815m	740m
LC <sub>3</sub>	3030sh	2960s 2926m 2870m	1614w	2061,2115	1460s	808m	740m

*s = strong, m = medium, w = weak, sh = shoulder*

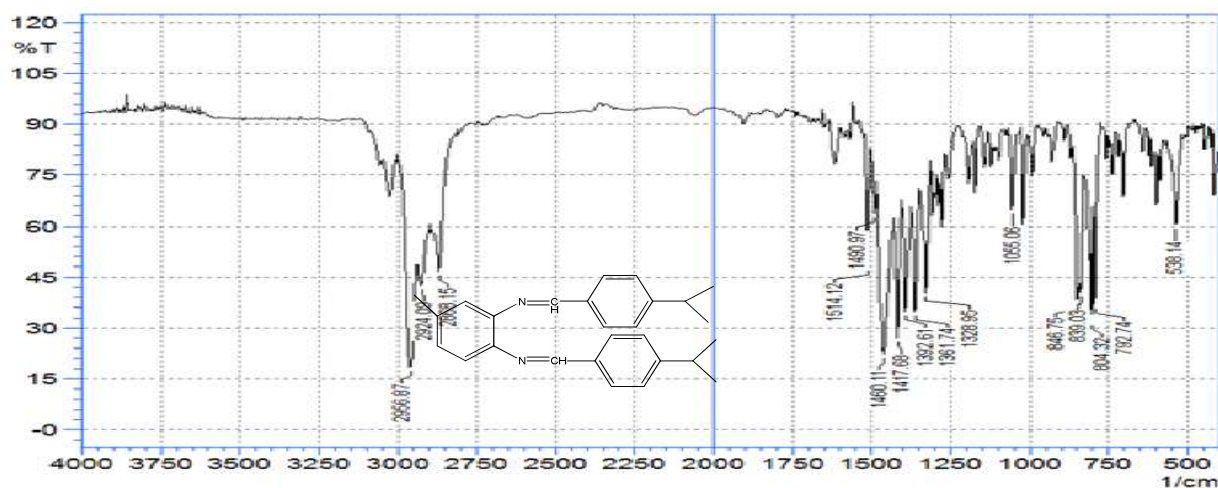
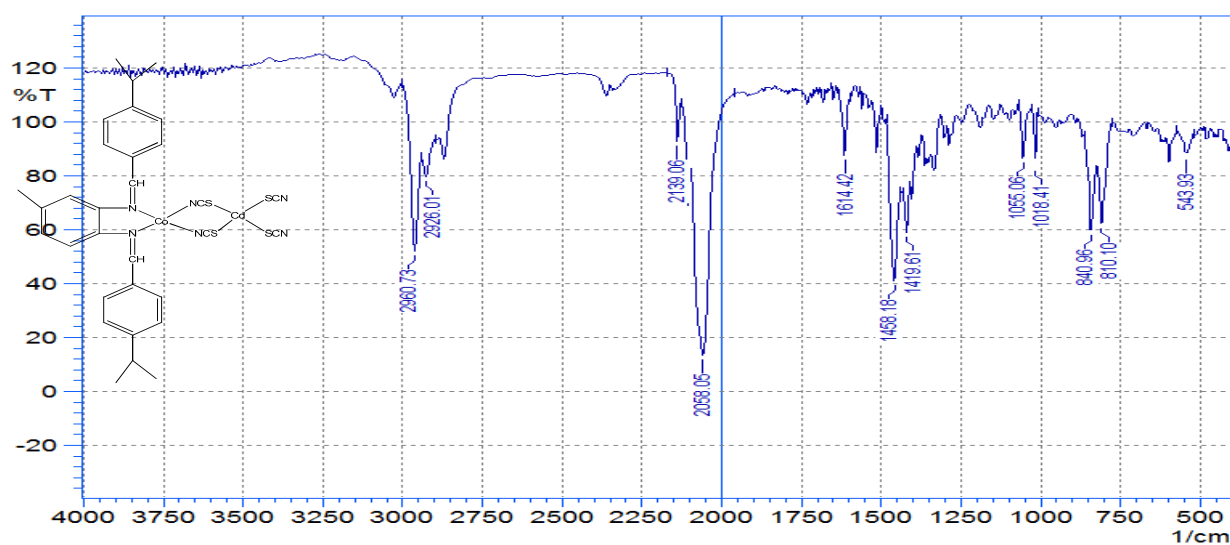
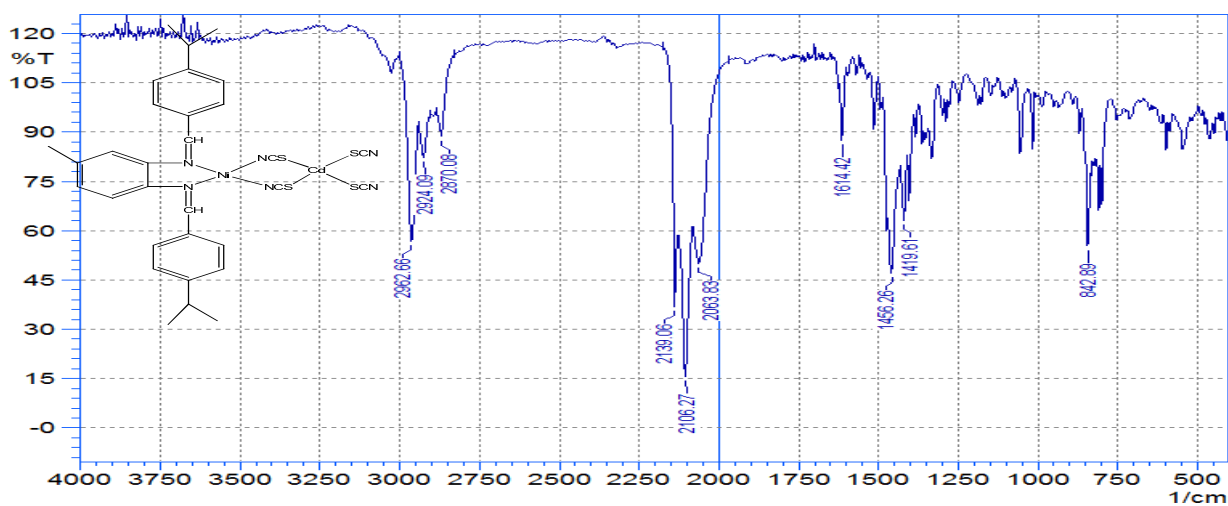
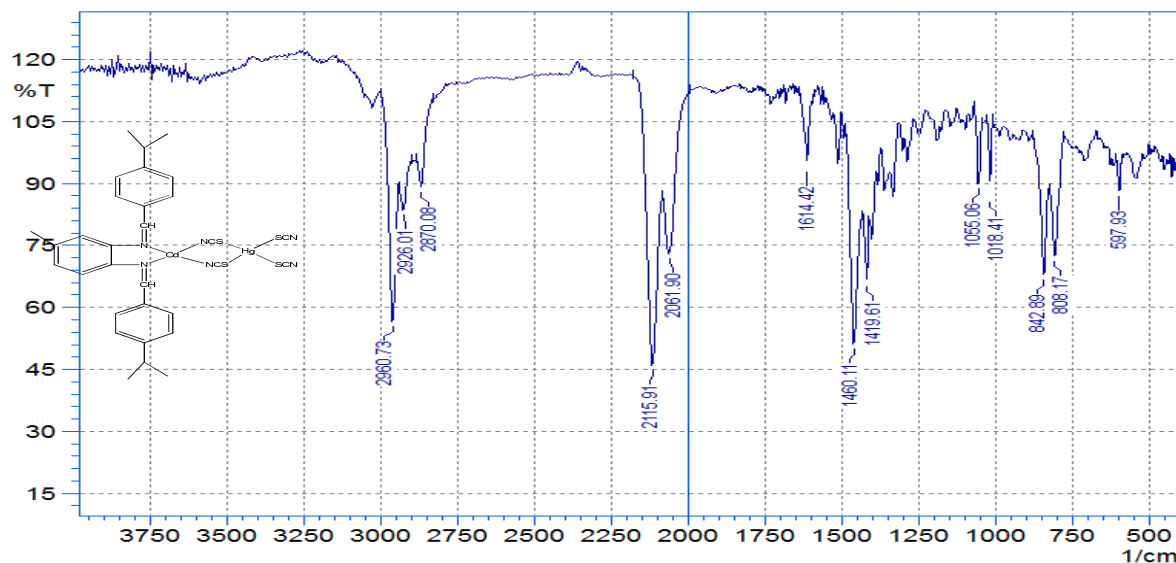


Figure 3 . IR Spectrum of the ligand

Figure 4 . IR Spectrum of the complex LC<sub>1</sub>Figure 5 . IR Spectrum of the complex LC<sub>2</sub>

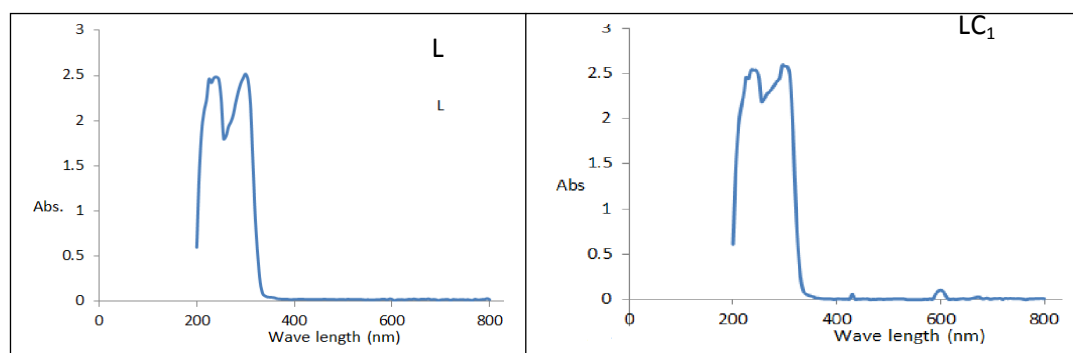
Figure 6 . IR Spectrum of the complex LC<sub>3</sub>

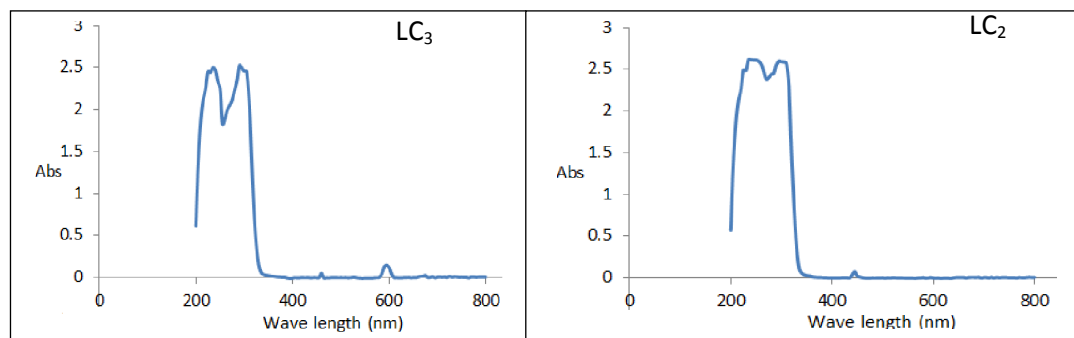
### UV-Visible spectra of the ligands and complexes:

The electronic spectrum data of the Schiff base ligand shown in Table 4 and Figure 7 appear absorption band at 225 nm due to  $\pi-\pi^*$  transition for the benzene ring. That observed at 240 and 300 nm is reasonably assigned to  $\pi-\pi^*$  and  $n-\pi^*$  transitions of azomethine moiety. In the spectra of the complexes shown in Table 4 and Figure 7. The absorption bands belong to azomethine group are shifted to lower wavelengths compared to the ligand indicating that the imine nitrogen is involved in the coordination with metal ion [15]. The spectra of complexes show that the absorptions in the range 430-460 nm and 595-600 nm are due to ligand to metal charge transfer and d-d transition band of the metal in the complex. The d-d transitions of the complexes LC<sub>1</sub> and LC<sub>2</sub> are found at 600 and 595 nm respectively indicating these complexes have coordination number equal to four [16,17].

Table 4 . Electronic data of the ligand and its complexes

Compound	$\lambda$ nm	Transition	Geometry
L	225	$\pi-\pi^*$	
	240	$\pi-\pi^*$	
	300	$n-\pi^*$	
LC <sub>1</sub>	225	$\pi-\pi^*$	Tetrahedral
	235	$\pi-\pi^*$	
	295	$n-\pi^*$	
	430	C.T	
	600	${}^4A_{2(F)} \rightarrow {}^4T_{1(P)}$	
LC <sub>2</sub>	225	$\pi-\pi^*$	Square planar
	235	$\pi-\pi^*$	
	290	$n-\pi^*$	
	460	C.T	
	595	${}^1A_{1(g)} \rightarrow {}^1B_{(g)}$	
LC <sub>3</sub>	225	$\pi-\pi^*$	Tetrahedral
	235	$\pi-\pi^*$	
	295	$n-\pi^*$	
	445	C.T	





### $^1\text{H}$ , $^{13}\text{C}$ -NMR spectra of the ligand

The  $^1\text{H}$ NMR spectra of the ligand L was recorded in DMSO Using 500MHZ and it showed a number of characteristic signal of the ligand as shown in Figure 8 . The two singlet peaks observed in the  $\delta$  8.62,8.75 ppm was assigned to the azomethine protons in the molecule .The signals due to the aromatic protons were observed in the range  $\delta$  7.16-7.61 ppm .The multiplet peaks observed in the range  $\delta$  3.01-3.08 ppm were assigned to the isopropyl protons .The singlet peaks observed in the  $\delta$  2.35 ppm was assigned to the methyl protons bonded with phenyl .The doublet peaks observed in the  $\delta$  1.31-1.32 ppm were assigned to the methyl protons in isopropyl .  $^{13}\text{C}$ NMR data of ligand were correspondent with  $^1\text{H}$ NMR data indicated above as shown in Table 5 and Figure 9 , and that confirm the proposed structure of the ligand .

Table 5 .  $^{13}\text{C}$ NMR data of the ligand

Symbol	Chemical shift $\delta$ (ppm)	Assignment
C <sub>1</sub>	177.68-176.78	2C,-N=C-
C <sub>2</sub>	153.26-120.58	18C,Ar
C <sub>3</sub>	34.19	2C,CH
C <sub>4</sub>	23.37	1C,CH <sub>3</sub> -Ar
C <sub>5</sub>	21.20	4C,CH <sub>3</sub>

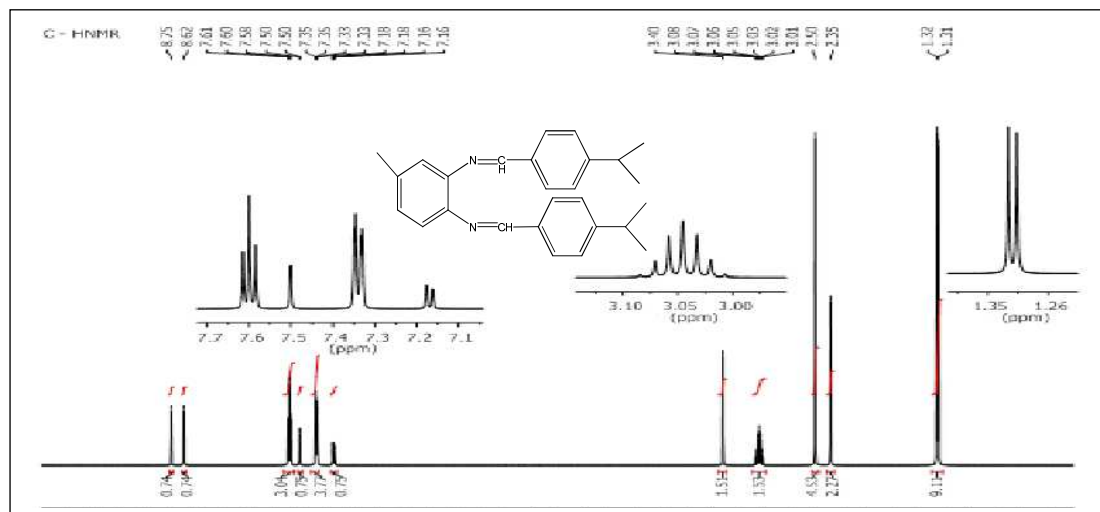


Figure 8 .  $^1\text{H}$ NMR spectrum of the ligand

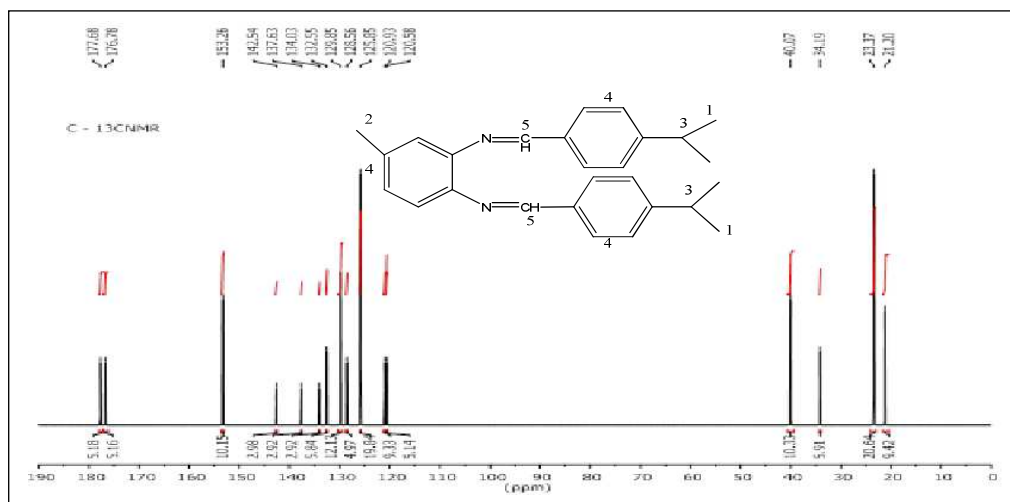
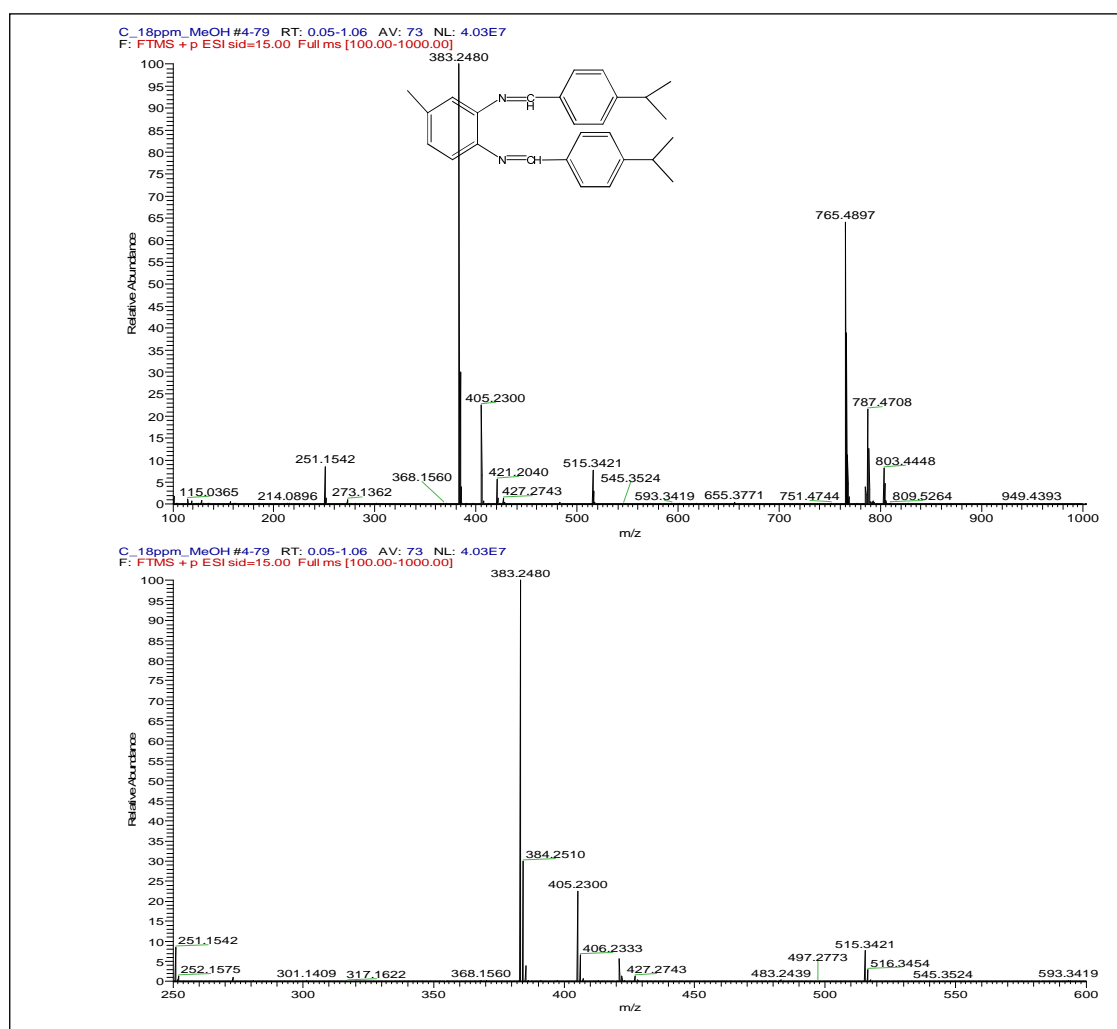
Figure 9 .  $^{13}\text{C}$ NMR spectrum of ligand

Figure 10 . Mass spectrum of the Schiff base ligand

### Mass spectra of the ligand

The mass spectrum of the Schiff base ligand (Figure 10) show a well-defined peaks at  $m/z=383$  and  $405$  which coincides with formula weight of the Schiff base of  $[\text{M}+\text{H}]^+$  and  $[\text{M}+\text{Na}]^+$  respectively. The peak at  $m/z=765$  and

787 can be attributed to dimeric structure of the ligand  $[2M+H]^+$  and  $[2M+Na]^+$ . In addition, the spectrum of the ligand show another peaks corresponding to its various fragments.

### Thermal analysis

Thermogravimetric (TG)/ differential thermogravimetric (DTG) analysis of complexes  $LC_1$ ,  $LC_2$  and  $LC_3$  under  $N_2$  was examined ( Figure11 ).The decomposition of the complexes take place in two stages. In the first stage ,the complex  $LC_1$  shows a weight loss of 22.2% (calc.21.6%) in the temperature range 225-420 °C ( $DTG_{max} = 384.64$  °C) ,corresponding to removal of  $C_{13}H_{22}$ . The second decomposition stag shows a weight loss of 6.5% (calc.6.6%) in the temperature range 530-620 °C ( $DTG_{max} = 572.02$  °C), corresponding to the removal of 2HCN. It was observed presence of rapprochement in the stages of decomposition for other prepared complexes. Some properties of thermal stability calculated from TGA and DTG curves for these complexes were shown in Table 6 .

Table 6 . Some thermal stability properties of the prepared complexes

Comp.	Decom.Temp°C			Temp of 50% Wt. loss (°C )	Rat of decom %/min	Char Content at 700 (°C)	Activation Energy KJ/mol	Temp. Rang (°C)	Assignment
	1 <sup>st</sup> DT		2 <sup>nd</sup> DT						
	T <sub>i</sub>	T <sub>op</sub>							
$LC_1$	225	384.64	420	-----	1.117	71%	64.528	310-385	$C_{13}H_{22}$
	530	572.04	620		0.315		65.6866		
$LC_2$	240	369.28	400	-----	1.143	75%	72.6477	310-360	$C_{12}H_{20}$
	450	557.71	630		0.333		78.289		
$LC_3$	220	366.21	420	680	1.066	50%	55.696	270-383	$C_{25}H_{28}$
	550	628.37	680		0.565		61.19		

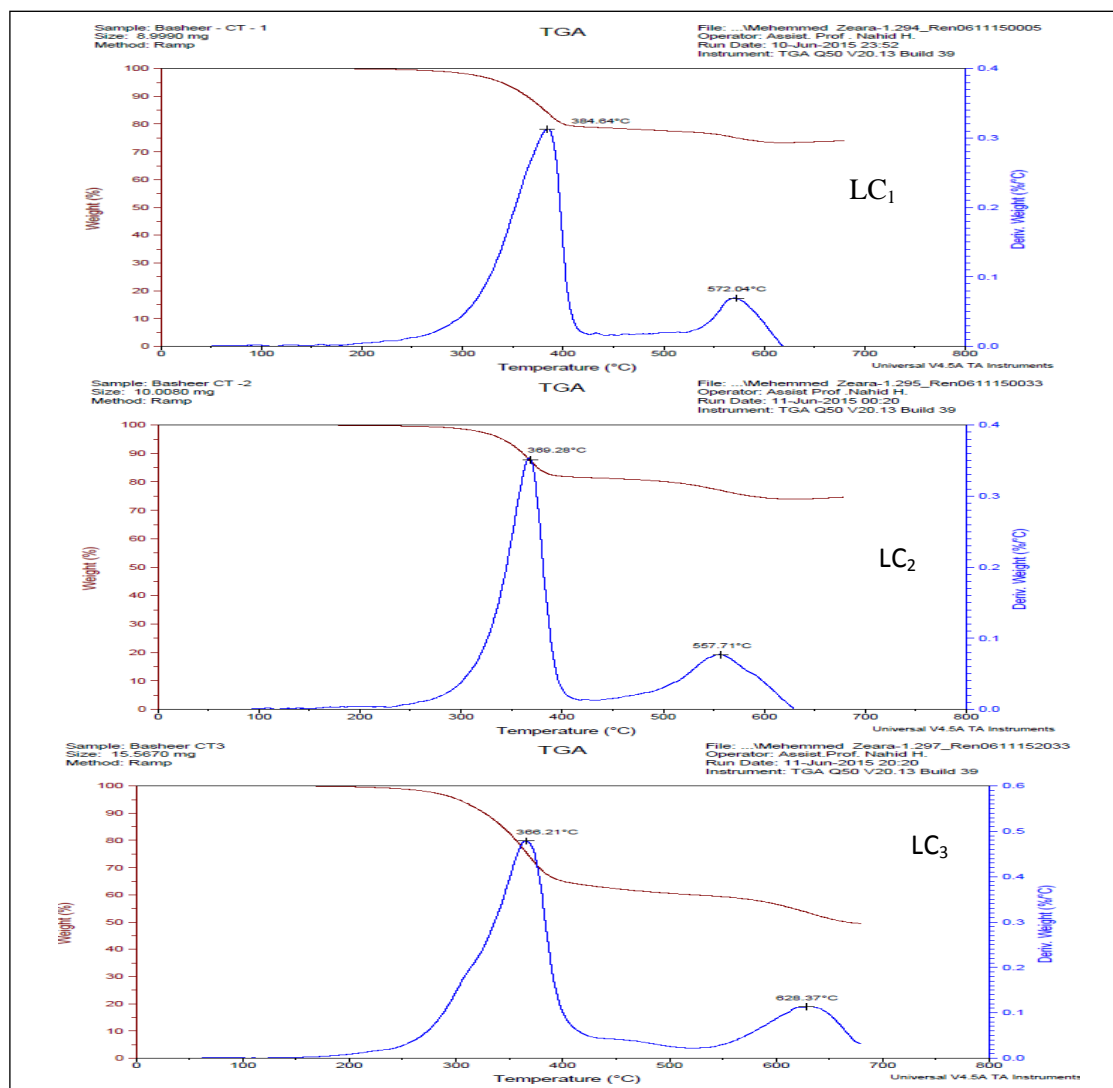


Figure 11 . Thermogravimetric analysis of the prepared complexes



### Structural characterization of the complexes

The atomic absorption data, molar conductivities and magnetic susceptibilities data are listed in Table 7. The reaction of the ligand with all the metals was 1:1 molar ratio for and the percentage of the metals in the complexes was in good agreement with the theoretical values as evidenced by atomic absorption measurements. The molar conductance values of the complexes were low indicating that all the complexes were non electrolytes. Magnetic moment  $\mu_{\text{eff}}$  of the complexes was measured by Faraday method at room temperature. The  $\mu_{\text{eff}}$  values for the complex LC<sub>1</sub> was 4.45 BM indicating that complexes LC<sub>1</sub>, LC<sub>3</sub> are tetrahedral while LC<sub>2</sub> is square planar geometry.

Table 7. Some structural properties of the prepared complexes

Symb.	Formula M.wt	Molar conductivity Ohm <sup>-1</sup> cm <sup>-1</sup> /mol	Metal Co/Ni		Metal Cd		$\mu_{\text{eff}}$ B.M
			found	Calcul.	found	Calcul.	
LC <sub>1</sub>	CoCd(SCN) <sub>4</sub> .C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> 786.21	11	6.08	7.50	13.68	14.30	4.45
LC <sub>2</sub>	NiCd(SCN) <sub>4</sub> .C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> 785.97	16.5	6.14	7.47	13.75	14.30	D
LC <sub>3</sub>	CdHg(SCN) <sub>4</sub> .C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> 927.87	17.6	-----	-----	11.49	12.11	D

D = Diamagnetic

### Antimicrobial activity

The antibacterial and antifungal activities of the Schiff base ligand and its complexes have screened for their in vitro antibacterial activity against *staphylococcus*, *Escherichia coli*, *Aspergillus niger* and *A.flavus*. The zones of inhibition produced by the test compounds are presented in table (8). It is observed that the metal complexes possess higher growth inhibition potential compared to that of the ligand. It is suggested that the complexes having antibacterial and antifungal activities inhibit multiplication process of the microbe by blocking their active sites.

Table 8. Antimicrobial activity results of the Schiff base ligand and its complexes

Compound	Diameter of inhibition zone (mm)			
	Fungi species		Bacteria species	
	<i>A.niger</i>	<i>A.flavus</i>	<i>S. aureus</i>	<i>E.coli</i>
L	29	17	21	19
LC <sub>1</sub>	35	21	31	27
LC <sub>2</sub>	37	33	23	47
LC <sub>3</sub>	45	47	42	37
Ceftazidime	17	15	3	17
Ampicillin	12	10	18	7

### CONCLUSION

Schiff base ligand derived from 4-methyl-1,2-diaminobenzen and 4-isopropyl benzaldehyde and its complexes with MM'(SCN)<sub>4</sub> [M = Co, Ni, Cd. M' = Cd, Hg] were prepared. The ligand and its complexes were identified by the analytical and spectral techniques. It was observed that these complexes have coordination number equal four and have a good thermal stability. Both the Schiff base ligand as well as its complexes possess significant antibacterial and antifungal activity.

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