

## Polyether Hexadentate Schiff Base Ligand with Trivalent Chromium, Iron, Cobalt Ions

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### Abstract

Williamson etherification method used to prepared ether compound from salicylaldehyde with 1,3-dibromopropane and potassium carbonate as base, this compound used with 2-amino-4-chlorophenol to prepare polyether hexadentate Schiff base ligand (HSL) by the 1:2 molar condensations. Cr<sup>3+</sup>, Fe<sup>3+</sup>, Co<sup>3+</sup> ions were reacted with HSL and characterized by <sup>1</sup>H NMR and <sup>13</sup>CNMR technique, infrared, electronic spectra, elemental analysis, thermal analysis, conductivity and magnetic susceptibility measurements, from results the metal ion was bonded to the HSL through the phenol oxygen, imine nitrogen and ether oxygen atoms to suggest octahedral configurations. The biological activity of HSL with its complexes have been studied.

[DOI: [10.22401/JUNS.20.4.01](https://doi.org/10.22401/JUNS.20.4.01)]

Keywords: Hexadentate ligand, Schiff base, Williamson etherification, metal ion complexes.

### 1. Introduction

The Williamson ether synthesis is a method of preparation of ethers using a base, it is a nucleophilic substitution(SN<sub>2</sub>) reaction starting from aromatic aldehydes with bromoalkanes [1]. Schiff bases which have hetero donor atoms used in different fields such as analytical chemistry, coordination chemistry, organic synthesis, industrial and biological and known as heteropolydentate ligands [2-8], these ligands combine with polyether ligands contain ethylene bridge, separated by oxygen atom have received wide attention because of show ability to form stable complexes with transition metal ions [9-14]. A hexadentate dibasic N<sub>2</sub>S<sub>2</sub>O<sub>2</sub> Schiff base derivates from 3-formylsalicylic acid was prepared by the condensation reaction and then reacted with metal (II, III) salts to form different metal complex configurations [15]. Hexadentate Schiff base of 2-hydroxybenzaldehyde with transition ions were prepared and investigated, these transition complexes used as catalysts in the allylic and benzylic reaction and showed great catalytic activity [16]. A novel Ln(III) polyether hexadentate di-Schiff base complexes (N<sub>4</sub>O<sub>2</sub>) were characterized by spectroscopic and thermogravimetric techniques [17]. A hexadentate Schiff base ligand have ether oxygens were coordinate to the Fe(III), Co(III) and Ni(II) ions and characterized by analytical, spectral and

magnetic methods [18]. New polyether ligands with Schiff base were synthesized and characterized by nuclear magnetic resonance, infrared and electronic analysis, the thermo gravimetric decomposition was shown stable polyether ligands with Schiff base against thermooxidative analyses [19].

In this work polyether hexadentate Schiff base ligand with trivalent transition metal ions are synthesized and characterized by different spectral technique to suggest the octahedral structure, the antibacterial activity of HSL with CrHSL, FeHSL, CoHSL complexes are measured.

### 2. Experimental Work

#### 2.1. Instrumentation

Infrared spectra were measured using FTIR 8300 Shimadzu. The UV-Visible spectra were measured by Shimadzu UV-Vis 160A spectrophotometer. The metal ion percent of the prepared complexes were measured by Shimadzu 680 cc-flame. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectra were recorded on a jeol 400 MHz spectrometer in DMSO-d<sub>6</sub> as a solvent and tetramethylsilane (TMS) as internal reference. CHNS-O analysis was carried out on EURO EA elemental analyzer. Thermal analyses (TG-DTG) were gained on a LINSEIS (STA PT-1000). Magnetic susceptibility of the complexes were obtained using magnetic susceptibility balance Johnson Matthey catalytic system at room temperature

and molar conductivity measurements were carried out at room temperature using corning conductivity meter 220. Melting points of ligand and their complexes were measured by Gallenkamp M.F.B. 600.01 apparatus.

### 2.2. Preparation of polyether compound:

1,3-dibromopropane (2.02g, 1mol) was added to salicylaldehyde (2.44g, 2mol) and  $K_2CO_3$  (2.76g, 2mol) in ethanol (25ml) as a solvent then the mixture was refluxed for 48 h and left to cool at room temperature, filtered off, diluted with water (25ml) and extracted by ether (2x20ml), the combined organic layers were washed with 5% NaOH (20ml), 5% HCl (20ml), water (20ml) after that dried with anhydrous  $Na_2SO_4$ , filtered, left to dryness to give ether compound (2.1g) [20].

### 2.3. Preparation of polyether hexadentate Schiff base ligand (HSL):

Absolute ethanol solution (10ml) of 2-amino-4-chlorophenol (2.87g, 2mol) was mixed with absolute ethanol solution (10ml) of ether compound (2.84g, 1 mol). The resulting mixture was refluxed on a water bath for 8h, then left to cool to room temperature; yellow product was precipitated and speared by filtration, then washed with cold ethanol, dried in an oven at  $50^\circ C$  (4.8g).

### 2.4. Preparation of the trivalent metal complexes:

The complexes were prepared by mixing hot ethanolic solution of metal salts ( $CrCl_3 \cdot 6H_2O$ ,  $CoCl_3 \cdot 6H_2O$ ,  $FeCl_3 \cdot 9H_2O$ ) with hot ethanolic solution of HSL 1:1 (metal: ligand) mole ratio and refluxed for 6 hours. A colored precipitate was formed, filtered and washed with hot ethanol then dried in oven at  $50^\circ C$ .

### 3. Results and Discussion

Characterization results of HSL with its complexes set out at Table (1).

**Table (1)**  
*Some characterization data of HSL and metal complexes.*

Compound	Conductivity, DMF solvent $\mu S/cm$	Melting Point, $^\circ C$ colour	Found% (Calculate)%					Suggested formula
			C	H	O	N	Metal	
HSL	-	244-246 Yellow	65.55 (65.06)	4.22 (4.49)	11.11 (11.96)	2.20 (5.23)	-	$C_{29}H_{24}N_2O_4Cl_2$
CrHSL	69.4	250-252 Dark green	54.10 (54.52)	3.55 (3.76)	12.15 (12.53)	4.33 (4.39)	8.19 (8.14)	$[Cr C_{29}H_{22}N_2O_4Cl_2]Cl \cdot H_2O$
FeHSL	75.5	255 -257 Pale yellow	54.11 (54.19)	3.45 (3.74)	12.99 (12.46)	4.55 (4.36)	8.88 (8.69)	$[Fe C_{29}H_{22}N_2O_4Cl_2]Cl \cdot H_2O$
CoHSL	85.7.	280-282 Brown	53.00 (53.93)	3.91 (3.72)	12.45 (12.39)	4.35 (4.34)	9.10 (9.13)	$[Co C_{29}H_{22}N_2O_4Cl_2]Cl \cdot H_2O$

### 3.1. Thermal analysis of metal complexes

The mass lose results that calculated and observed of complexes in the temperature ranges (30-900  $^\circ C$ ) using helium as inert gas were listed in Table (2), The first step of lose confirm the  $H_2O$  molecule in the outer of coordination sphere was presence, the final step of mass lose gave oxide of metal after another steps of thermal decomposition [21].

**Table (2)**  
**Thermal decomposition of HSL complexes.**

Complex formula	Temperature range, °C	Weight loss%		Decomposition complex	Liberate moiety
		Calculate	Found		
Cr [C <sub>29</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub> Cl <sub>3</sub> ]	100-150	25.67	24.3	Cr[C <sub>23</sub> H <sub>19</sub> N <sub>2</sub> O <sub>4</sub> Cl]	-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> -H <sub>2</sub> O
	150-288	11.75	10.6	Cr[C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> Cl]	-C <sub>6</sub> H <sub>3</sub>
	288-400	10.68	10.7	Cr [C <sub>15</sub> O <sub>4</sub> Cl]	-2(CNH) -14H
	400-800	22.45	21.19	Cr [C <sub>6</sub> O <sub>4</sub> ]	-3C -Cl -6C
Fe[C <sub>29</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub> Cl <sub>3</sub> ]	120-190	22.02	22.8	Fe[C <sub>23</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub> Cl <sub>2</sub> ]	-Cl -C <sub>6</sub> H <sub>16</sub> -H <sub>2</sub> O
	233-300	6.45	6.20	Fe[C <sub>23</sub> N <sub>2</sub> O <sub>4</sub> Cl]	-Cl -6H
	315-500	36.04	35.90	Fe[C <sub>9</sub> O <sub>4</sub> ]	-C <sub>7</sub> NCl -C <sub>7</sub> N
	533-700	16.81	15.8	Fe[O <sub>4</sub> ]	-3C -6C
Co[C <sub>29</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub> Cl <sub>3</sub> ]	100-160	19.9	17.79	Co[C <sub>23</sub> H <sub>19</sub> N <sub>2</sub> O <sub>4</sub> Cl <sub>2</sub> ]	-C <sub>6</sub> H <sub>3</sub> Cl -H <sub>2</sub> O
	160-280	6.51	6.00	Co[C <sub>20</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> Cl <sub>2</sub> ]	-3(CH <sub>2</sub> )
	280-410	37.28	34.79	Co[C <sub>6</sub> H <sub>4</sub> O <sub>4</sub> Cl]	-C <sub>6</sub> H <sub>3</sub> Cl -2(CHN) -C <sub>6</sub> H <sub>4</sub>
	410-800	17.27	17.50	Co[O <sub>4</sub> ]	-C <sub>6</sub> H <sub>4</sub> -Cl

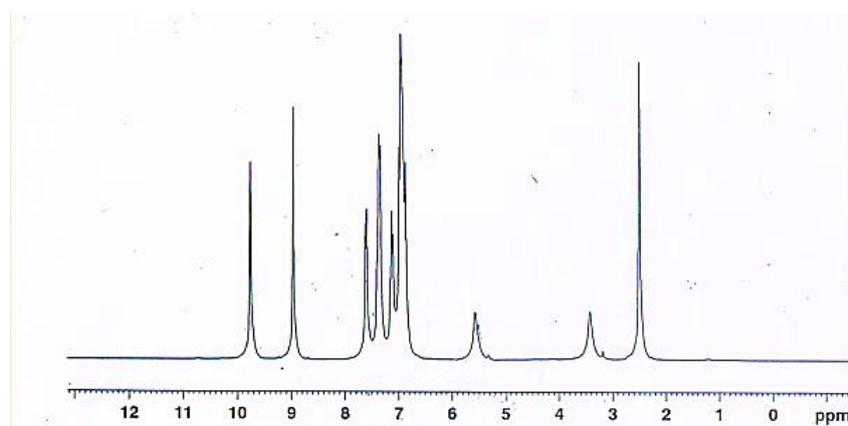
### 3.2. IR and NMR spectrum

Infrared spectrum of the HSL displays band at  $1636\text{cm}^{-1}$  indicating to  $\nu\text{C}=\text{N}$ , this band shift to lower wave number suggested the coordinating of carbon nitrogen double bond to the metal ion in the infrared spectra of the complexes [14].  $\nu(\text{C}-\text{O}-\text{C})$  appear around  $1210\text{cm}^{-1}$  in a HSL, in the spectra of the complexes these stretching frequencies were observed around  $(1120-1151)\text{cm}^{-1}$  indicating to coordination of ether oxygen atom.  $\nu\text{O}-\text{H}$  band appear at  $3500\text{cm}^{-1}$  in the HSL, the disappearance of absorption bands in the complexes spectra confirms the coordination of phenolic oxygen with trivalent transition ion [21]. New bands in the  $(460-489)\text{cm}^{-1}$  and  $(525-569)\text{cm}^{-1}$  regions, supports the bond of  $\nu\text{M}-\text{O}$  and  $\nu\text{M}-\text{N}$ , respectively, these frequencies shown in Table (3).

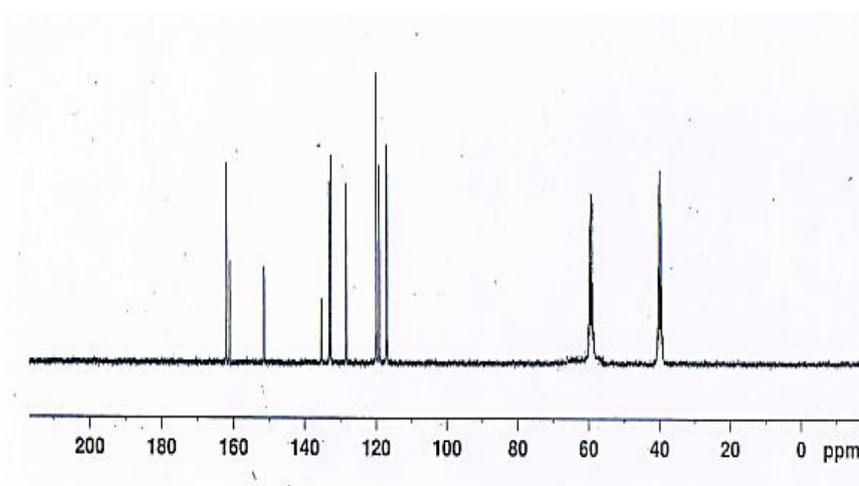
$^1\text{H}$ NMR spectral study for HSL, Fig.(1):  $\delta$  (2.5, 3.4) ppm for methyl protons in different positions  $\text{CH}_2-\text{CH}_2$  and  $\text{CH}_2-\text{O}$ ,  $\delta$  5.46 ppm (broad s, 2H, OH), signals in the region (6.86-7.62) due to aromatic protons, 8.96 characteristic resonance due to imine proton (s,2H,N=CH). The  $^1\text{H}$ NMR of complexes reveals the absence of O-H group due to the coordination. N=CH signals of complexes shift to 9.10 ppm due to the coordination and also  $\text{CH}_2-\text{O}$  signals shift to 3.10 ppm indicating to coordination to metal ions through oxygen ether.  $^{13}\text{C}$  NMR of HSL, Fig.(2): C-OH appear at  $\delta(160.1)\text{ppm}$  shift to  $(161.0)\text{ppm}$  in complexes spectra, signals in the region (115-150) ppm for aromatic carbons rings,  $(162.10)\text{ppm}$  refer to the  $\text{CH}=\text{N}$  shift to  $(162.99)\text{ppm}$  in complexes spectra,  $\text{CH}_2-\text{CH}_2$  (40.45) ppm,  $\text{CH}_2-\text{O}$  (60.56) ppm shift to 61.44 ppm [22].

**Table (3)**  
**Characteristic infrared data of HSL and metal complexes.**

compound	$\nu_{O-H}$ , $cm^{-1}$	$\nu_{C=N}$ , $cm^{-1}$	$\nu_{C-O-C}$ , $cm^{-1}$	$\nu_{C=C}$ , $cm^{-1}$	$\nu_{M-O}$ , $cm^{-1}$	$\nu_{M-N}$ , $cm^{-1}$
HSL	3500	1636	1210	1590- 1543	-	-
CrHSL	-	1610	1150	1533- 1518	460	525
FeHSL	-	1632	1120	1515- 1466	488	569
CoHSL	-	1600	1151	1589- 1530	489	537



**Fig. (1): <sup>1</sup>H NMR for HSL.**



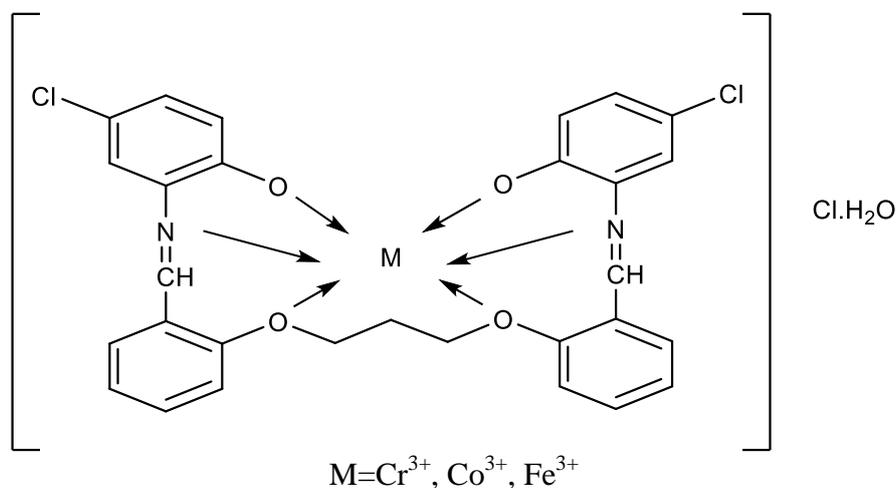
**Fig.(2): <sup>13</sup>C NMR for HSL.**

### 3.3. Ultraviolet-Visible spectroscopy and magnetic susceptibility:

Schiff base spectrum showed two bands at (280,399)nm. First electronic transition was for  $\pi \rightarrow \pi^*$  and the second for  $n \rightarrow \pi^*$  transition. Absorption bands were appeared at 582 nm  ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$ , 430 nm  ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)(\nu_2)$  and 358 nm  $n \rightarrow \pi^*$  (P)( $\nu_3$ ) for octahedral CrHSL geometry, the magnetic

moment of Cr ( $d^3$ ) 3.7 B.M. The pale color of  $Fe^{3+}$  ( $d^5$ ) configuration reflecting a weak spin forbidden bands depend on the ground term  ${}^2T_{2g}(t_{2g}^5)$ , the moment is around 2.2 B.M. as expected for the low spin octahedral geometry. Spin allowed d-d transitions for  $Co^{3+}$ , two bands in the 620-422 nm regions attributed to  ${}^1A_{1g} \rightarrow {}^1T_{1g}(\nu_1)$ ,  ${}^1A_{1g} \rightarrow {}^1T_{2g}(\nu_2)$  and the other band at 350 nm for  $n \rightarrow \pi^*$  transition, the

value of moment is 5.6 B.M. for  $\text{Co}^{3+}$  indicating a low spin octahedral structure[18], these all data suggest the structure of complexes shown in Fig.(3).



**Fig.(3): Suggest conformation of HSL complexes.**

#### 4. Biological importance of HSL complexes

Metal complexes of hexadentate Schiff base showed a good antibacterial activity against *Staphylococcus aureus* and *Pseudomonas aeruginosa* was measured by the disc diffusion technique. The HSL and complexes were dissolved in DMSO control standard (concentrations of  $50\mu\text{g}/0.01\text{cm}^3$ ). Filter paper was put in the solution of compounds in DMSO, after drying it was placed in nutrient agar plates. After 48 h inhibition area was observed at  $37^\circ\text{C}$ , inhibition zone were measured in diameter (mm) for HSL (10,7)mm and the complexes CrHSL (23,29)mm, FeHSL(20,22), CoHSL(29,20) mm for *Staphylococcus aureus* and *Pseudomonas aeruginosa*, respectively.

#### 5. Conclusion

Cr, Fe, Co trivalent ions with polyether hexadentate ligand are suggested to be octahedral complexes through  $\text{N}_2\text{O}_4$  donor atoms. Anti-bacterial activity of HSL and their metal complexes were measured and gave good results.

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