

## **Preparation and Characterization of Some Transition Metal Complexes with Schiff base of thiosemicarbazone**

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### **Abstract**

A series of new metal chelates of Ni(II), Zn(II), Cd(II) and Hg(II) with Schiff base [ *p*-hydroxy acetophenone thiosemicarbazone]. The ligand was prepared by condensation reaction between *p*- hydroxy acetophenone with thiosemicarbazide. The chelate complexes of Ni(II), Zn(II), Cd(II) and Hg(II) have been prepared and identified by elemental analysis, molar conductance measurement, magnetic susceptibility measurement at room temperature, infrared and electronic spectra.

**Key words** : Schiff base, Metal chelat complexes, Characterization.

### **الخلاصة**

تضمن البحث تحضير سلسلة جديدة من المعقدات الكلايية لكل من ايونات النيكل (II) والخاصين (II) والكادميوم (II) والزنابق (II) مع قاعدة شف المحضرة من تفاعل تكثيف بار- هيدروكسي اسيتوفينون مع الثاوسيميكاربازايد. شخصت المعقدات الكلاييه المحضره بوساطة التحليل الدقيق للعناصر والتوصلية المولارية والحساسية المغناطيسية والاشعة تحت الحمراء والاطياف الالكترونية.

### **Introduction**

Compounds containing an azo methane group (-CH=N) are known as Schiff bases <sup>(1)</sup>. This class of organic compound are important materials due to their sythetic flexibility, structural similarities with natural biological substances and also due to presence of imine group which imports in elucidating the mechanisim of transformation and rasemination reaction in biological system <sup>(2-4)</sup>. In addition of their selectivity and sensitivity to wards the central metal atoms <sup>(5)</sup>. Thiosemicarbazone derivatives of Schiff base compounds containing N,S donor chromophores metal complexes, bonding through the sulfur and hydrazine nitrogen atoms <sup>(6-8)</sup>.

The aim of the present work is to synthesize thiosemicarbazone ligand and to study its to coordination behavior with Ni(II), Zn(II), Cd(II) and Hg(II).

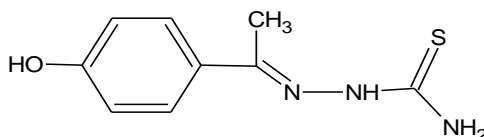
### **Experimental**

#### **Materials and measurements**

All chemicals used in this work were of highest purity and used as supplied by the manufactures. The melting points of ligand and its metal complexes were determined with Electrothermal melting point apparatus. Elemental analysis was performed by Micro analytical unit of EA 300 A C.H.N Elemental analyzer, Al-Albat university Jordan. IR spectra ( KBr pellets ) were recorded using a Testscan Shimadzu FTIR 8000 series. Electronic spectra were recorded using Shimadzu Uv-Vis 1700 spectrophotometer. Electrical conductivity was measured by Digital Conductivity Meter Alpha-800 with solute concentration ( $10^{-3}$ M) in DMF. The magnetic susceptibility were measured on powder samples using Faraday method for this purpose, Balance Magnetic (MSB-MKI) had been employed.

### **Preparation of ligand**

The ligand was prepared as reported in the literature<sup>(9)</sup>. The mixing equimolar amounts of *p*-hydroxy acetophenone (1.36 g, 0.01 mol ) in (50 ml) ethanol, with an ethanolic solution (50 ml) of thiosemicarbazide (0.91 g, 0.01 mol ) containing 3 drops of glacial acetic acid was heated under reflux for 3 hours. The precipitate formed was separated out, filtered off, recrystallized from hot ethanol and dried over CaCl<sub>2</sub>.



**Fig. 1: The proposed structural formula of ligand**

### **Synthesis of complexes**

All complexes were prepared by adding (4.18 g, 0.02 mol ) of ligand dissolved in ethanol (20 ml ) to a solution of metal chloride (0.01 ml ) dissolved in the same solvent (20 ml ). After the mixture was refluxed for one hour, the solution was evaporated to dryness. The dried product was recrystallized from hot ethanol and dried over anhydrous CaCl<sub>2</sub>.

### **Results and Discussion**

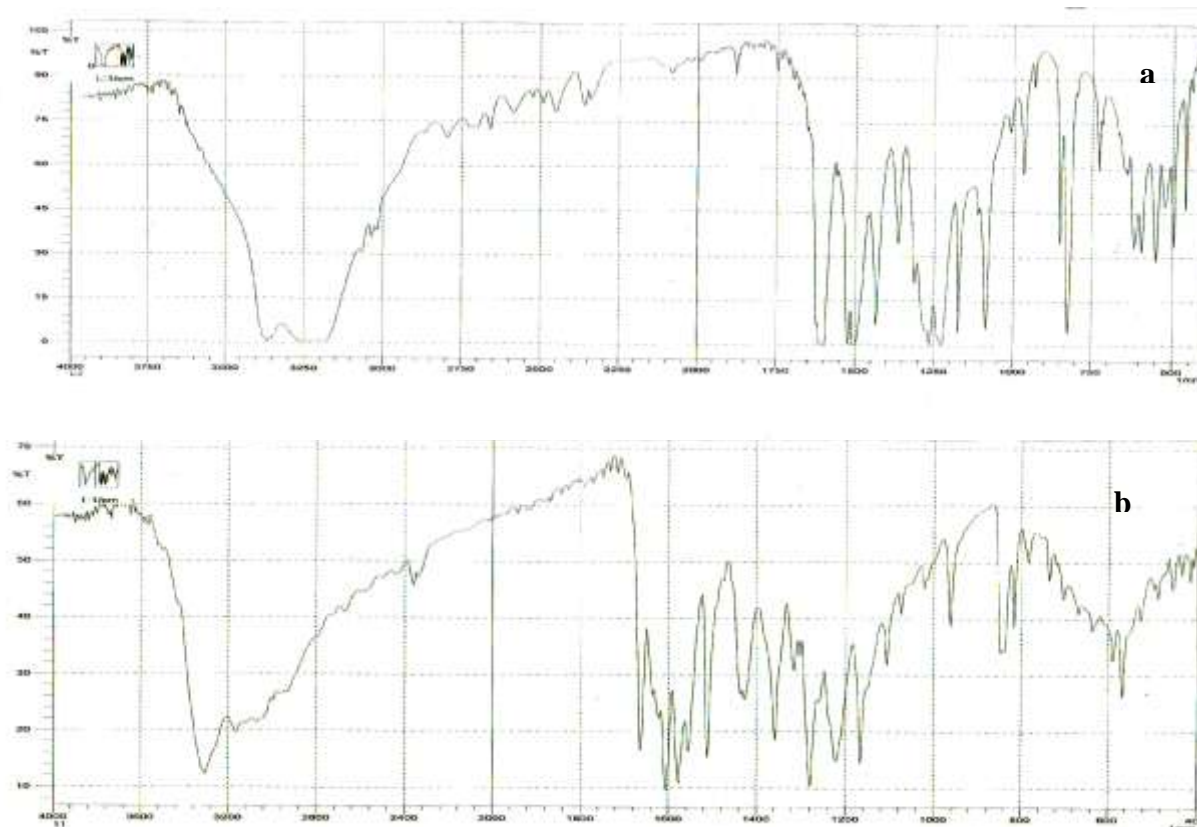
#### **General**

The ligand is pale yellow crystal which is soluble in most organic solvents. The chelate complexes of this ligand vary in color crystals. All complexes were found stable at room temperature and were soluble in common organic solvents, but insoluble in water. Some physical and chemical properties for ligand and its complexes are listed in table.1. The elemental analysis and metal contents data are shown in table.1.

#### **Infrared Spectra**

The most important infrared spectral bands that provide conclusive structural evidence for the coordination of the ligand to the central metal ions are given in table.2. The IR spectra of the free ligand show two bands at 3330, 3185 cm<sup>-1</sup> may be attributed to the (NH<sub>2</sub>, NH) respectively<sup>(10,11)</sup>. This band remains in the same region in all complexes spectra. The absorption band at 3430 cm<sup>-1</sup> in the spectrum of free ligand may be attributed to the  $\nu(\text{OH})$  of hydroxyl group<sup>(12)</sup>. The spectrum of ligand shows absorption band at 1615 cm<sup>-1</sup> due to  $\nu(\text{C}=\text{N})$  of azomethine group<sup>(13-15)</sup>. This band shifts to lower frequency 1615-1600 cm<sup>-1</sup> with little change in shape in the spectra of the chelate complexes<sup>(16)</sup>, indicating its involvement in coordination of the ligand metal ions<sup>(17)</sup>. Another band appeared 1120 cm<sup>-1</sup> in the spectrum of Schiff base ligand due to  $\nu(\text{C}=\text{S})$  this band was shifting to lower frequency 1110-1105 cm<sup>-1</sup> in chelate complexes, this is support of coordination of S-donor centers to metal ions<sup>(18,19)</sup>.

New weak bands in the region 600-400 cm<sup>-1</sup> occurring in the spectra of complexes. These bands did not present in the spectrum of ligand may be attributed to  $\nu(\text{M}-\text{N})$ <sup>(20)</sup>, and  $\nu(\text{M}-\text{S}=\text{C})$ <sup>(21,22)</sup>. Based on the results presented above lead to suggest that the ligand behaves as nature bidentate<sup>(23)</sup> chelating agents, coordinating with the metal ions by nitrogen of azomethane group and sulphur atoms of thione group. Representative example for their spectra is given in Fig .2.



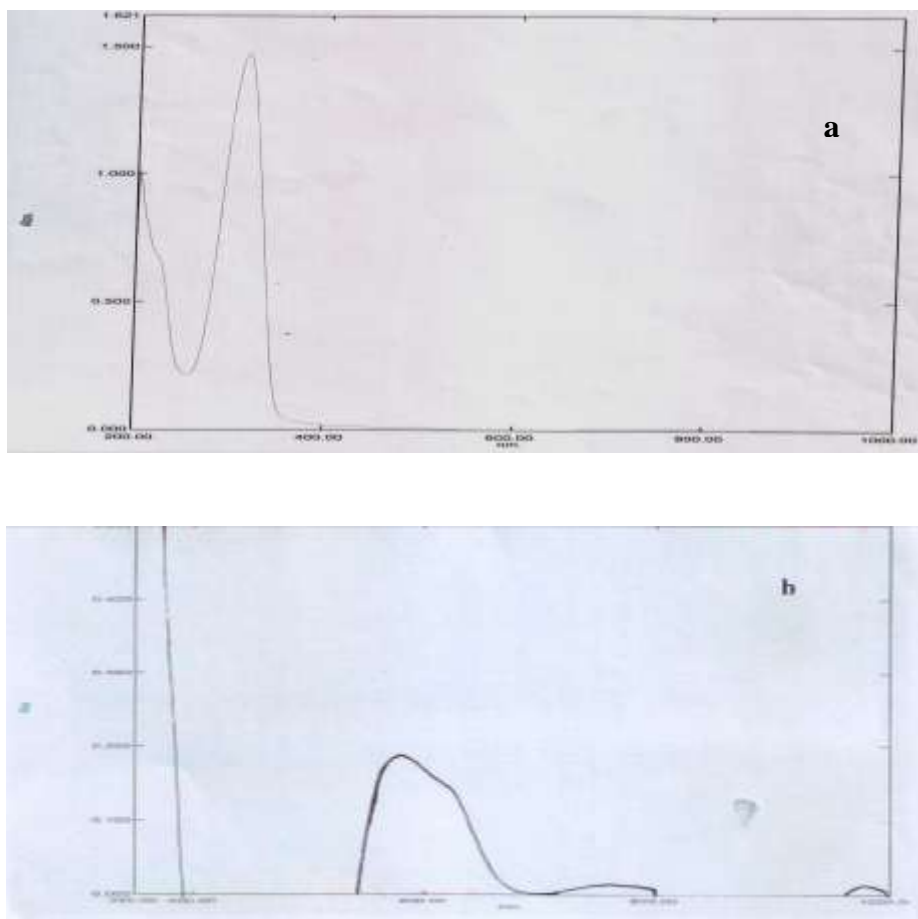
**Fig.(2)**  
**IR spectra of : (a) the ligand & (b) [ NiL<sub>2</sub>Cl<sub>2</sub>]**

**Magnetic measurement and electronic spectra**

The data obtained from the measurements of electronic spectra and magnetic susceptibility are given in table 3.

The electronic spectrum of Ni(II) complex exhibit three bands at 10225 cm<sup>-1</sup>, 13192 cm<sup>-1</sup> and 17271 cm<sup>-1</sup> corresponding to <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub>(F), <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub>(F) and <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub>(P) transitions respectively Fig.(3) . The magnetic moment value of the Ni(II) complex (μ<sub>eff</sub>=3.18 B.M) which may suggest octahedral structure<sup>(24)</sup>. The complexes of Zn(II), Cd(II) and Hg(II) do not show any d-d transition bands, its diamagnetic moment<sup>(25)</sup>.

According to these results the following structure formule of these chelate complexes may be proposed in Fig 4.



**Fig . (3) U.V Spectrem of : (a) ligand & (b) [ NiL<sub>2</sub>Cl<sub>2</sub>]**

**Table. 1: Physical properties and analytical data of the ligand (L) and its complexes.**

No.	Compound	Colour	M.P °C	Formula	Found (cacl)%			
					C	H	N	M
1	HL	Pale Yellow	215	[C <sub>9</sub> H <sub>11</sub> N <sub>3</sub> SO]	51.02 (51.67)	5.53 (5.26)	20.75 (20.09)	(----) (----)
2	[NiL <sub>2</sub> Cl <sub>2</sub> ]	Green	199	[C <sub>18</sub> H <sub>22</sub> N <sub>6</sub> S <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub> Ni]	41.71 (41.56)	4.16 (4.23)	16.45 (16.16)	11.56 (11.29)
3	[ZnL <sub>2</sub> Cl <sub>2</sub> ]	White	244	[C <sub>18</sub> H <sub>22</sub> N <sub>6</sub> S <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub> Zn]	40.87 (41.03)	4.49 (4.17)	15.67 (15.95)	12.79 (12.42)
4	[CdL <sub>2</sub> Cl <sub>2</sub> ]	White	245	[C <sub>18</sub> H <sub>22</sub> N <sub>6</sub> S <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub> Cd]	38.05 (37.69)	4.12 (3.83)	14.20 (14.65)	19.96 (19.54)
5	[HgL <sub>2</sub> Cl <sub>2</sub> ]	White	236	[C <sub>18</sub> H <sub>22</sub> N <sub>6</sub> S <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub> Hg]	32.23 (32.67)	3.12 (3.32)	13.06 (12.70)	29.94 (30.25)

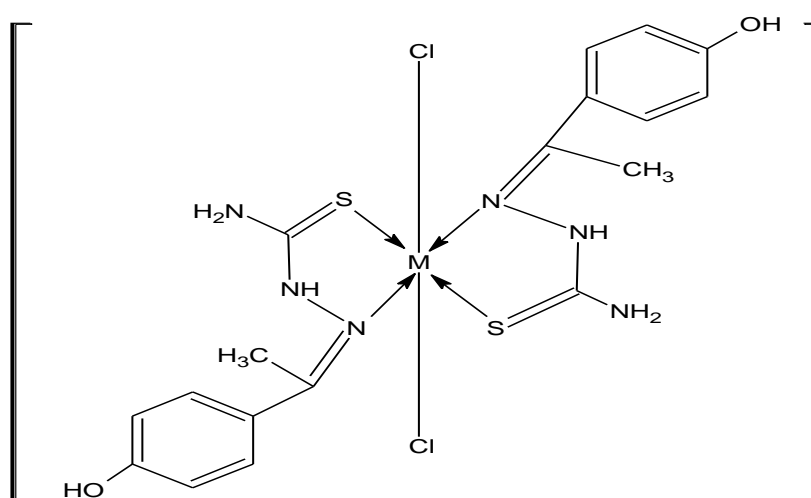
**Table. 2: Characteristic IR absorption bands of the ligand and its complexes in  $\text{cm}^{-1}$  units.**

Compound	$\nu(\text{NH}_2)$	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{S})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{N})$
HL	3330 w	3185 w	1615 s	1120 s	----	----
$[\text{NiL}_2\text{Cl}_2]$	3340 w	3165 w	1600m.sh	1105 m	430 w	415 w
$[\text{ZnL}_2\text{Cl}_2]$	3330 w	3160 w	1605 m	1100 m	465 w	425 w
$[\text{CdL}_2\text{Cl}_2]$	3335 w	3170 w	1605 m	1105 m	445 w	475 w
$[\text{HgL}_2\text{Cl}_2]$	3325 w	3175 w	1600m	1110 m	420 w	505 w

HL = Ligand , s = strong , sh =shoulder , m= medium , w= weak

**Table. 3: Electronic spectra and magnetic moment data of the complexes**

Complex	Absorption bands ( $\text{cm}^{-1}$ )	Transition	$\mu_{\text{eff}}$ (B.M)
$[\text{NiL}_2\text{Cl}_2]$	10225	$\nu_1$ ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$	3.18
	13192	$\nu_2$ ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$	
	17271	$\nu_3$ ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$	
$[\text{ZnL}_2\text{Cl}_2]$	----	----	dia
$[\text{CdL}_2\text{Cl}_2]$	----	----	dia
$[\text{HgL}_2\text{Cl}_2]$	----	----	dia



**Fig. 4: The proposed structural formula of prepared chelate complexes**

**M =Ni (II), Zn(II), Cd(II), and Hg(II)**

## Conclusion

This paper report the preparation and identification of bidentate Schiff base and its complexes with Ni(II), Zn(II), Cd(II) and Hg(II) metal ions. The isolation compounds were characterized by available techniques. All the complexes are stable and nonionic nature and the geometry is proposed for all complexes show octahedral stereochemistry .

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