

## Synthesis and Characterization Complexes Of Ni(II), Co(II) and Mn(II) with Schiff Base Derivatives from (2-hydroxy-benzylidene) and Urea or Thiourea

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### Abstract

Complexes of the Schiff base ligands (2-hydroxy-benzylidene)- thiourea = (L<sub>1</sub>), (2-hydroxy-benzylidene)- urea = (L<sub>2</sub>) of these ligands with some of transition metal ions Mn<sup>+2</sup>, Co<sup>+2</sup> and Ni<sup>+2</sup> have been prepared and characterized by their (C.H.N) elemental analysis, IR, UV-VIS, atomic absorption, Molar conductivity measurements, Magnetic Susceptibility and melting points. From the result probable structures of the prepared complexes were proposed .

### الخلاصة

تم تحضير معقدات قواعد شف (2-هيدروكسي-بنزليدين) - (2-هيدروكسي-بنزليدين) - ثايوريا = (L<sub>1</sub>)، (2-هيدروكسي-بنزليدين) - يوريا = (L<sub>2</sub>) لهذه الليكندات مع بعض املاح العناصر الانتقالية Mn<sup>+2</sup>, Co<sup>+2</sup>, Ni<sup>+2</sup> وقد تم تشخيص ودراسة تراكيب الليكندات والمعقدات المحضرة منها باستخدام تقنية التحليل الدقيق للعناصر (C.H.N) ومطيافية الاشعة تحت الحمراء والاشعة فوق البنفسجية وتقنية الامتصاص الذري فضلا عن قياس الموصلية الكهربائية المولارية ، الحسية المغناطيسية ودرجات الانصهار للمعقدات المحضرة وعلى ضوء النتائج تم استنتاج تراكيب هذه المعقدات.

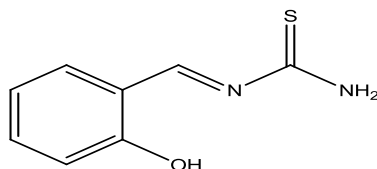
## Introduction

Schiff bases have been widely used as bidentate ligands in the field of coordination chemistry <sup>(1)</sup>. The Schiff base complexes have been used in catalytic reaction <sup>(2)</sup> and as models for biological systems <sup>(3)</sup>. In recent years many copper complexes of Schiff base were prepared <sup>(4)</sup>. It has been reported that the structure of the constituent bonded to the imino nitrogen affects the coordination geometry of the complexes <sup>(5)</sup>. Metal complexes of Schiff bases are extensively studied due to synthetic flexibility, selectivity

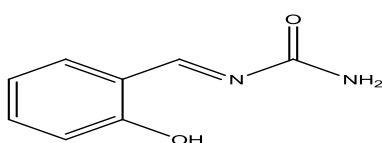
and sensitivity towards a variety of metal atoms <sup>(6)</sup>.

In this work will investigate has been the chemistry of this urea and thiourea compound by preparing its Schiff base with 2-hydroxy-benzylidene, and study of the complexes metal ( $Mn^{2+}$ ,  $Co^{2+}$ , and  $Ni^{2+}$ ); bidentate ligands these:

### (2-Hydroxy-benzylidene) –thiourea (L1)



### (2-Hydroxy-benzylidene) –urea (L2)



## Experimental

### 1- INSTRUMENTATION:

A pye – Unicom sp3-100 infrared spectrophotometer was used to record the IR spectra as KBr and CsI disc ,

UV/VIS spectra were measured by a HITACHI U-2000 spectrophotometer, Elemental Analysis (C.H.N) founded on (Carlo Erloa microanalyzer type 1106),determination of all metals

percentage by atomic absorption spectrophotometry on AA-680G (Shimadzu). Electrical conductance was measured on conductivity CDC304 (Jenway4070) Melting points determined by an electric heated block apparatus (Gallen Kamp), and were uncorrected.

## 2-MATERIALS:

[MnCl<sub>2</sub>.6H<sub>2</sub>O], [CoCl<sub>2</sub>.6H<sub>2</sub>O], [NiCl<sub>2</sub>.6H<sub>2</sub>O] were supplied by BDH, Ethanol Absolute, diethylether, DMSO, Urea, thiourea supplied by Aldrich .

### A- Preparation of the ligand:

Preparation of (L<sub>1</sub>),(L<sub>2</sub>) were prepared according to the literature <sup>(7)</sup> The full name of the Schiff base will be replaced by a number (L<sub>1</sub>,L<sub>2</sub>) respectively as in shown in table (1) for the rest of this paper . The physical properties of these compounds (L<sub>1</sub>, L<sub>2</sub>) are listed in table (1). The characters IR bands and UV/Vis spectrum in DMSO as shown in table (2), (3).

### B-General procedure for preparation of complexes :

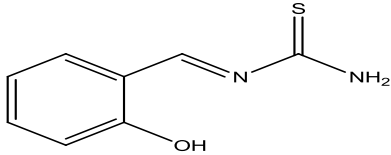
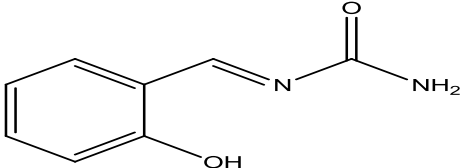
To a hot solution of ligands (L<sub>1</sub> or L<sub>2</sub>) (2 mmole) in absolute ethanol (5 ml), a hot solution of metal chloride (1 mmole) in absolute ethanol (5ml) (dissolved in dilute HCl) <sup>(8)</sup> was added (neutral medium) and the resultant mixture was stirred and refluxed for 2

hours, the color of the solution changed immediately, the reaction mixture was cooled, and the solution was evaporated in vacuum, or lefted over night at room temperature , after this time a precipitate formed . This was collected by filtration in vacuo, washed and recrystallized from absolute ethanol/ether.

The physical properties of prepared complexes are listed in table (4).

The analogous complexes were prepared in a similar manner to that described above by adding a hot solution of ligands (L<sub>1</sub> or L<sub>2</sub>) (1 mmole) in absolute ethanol (5 ml) to a hot solution of metal chloride (1 m mole) in absolute ethanol (5ml).The molar ratio of the complexes was determined according to the methods<sup>(9)</sup>.

**Table(1): physical properties of the Schiff's base ligand**

No.	Name and structure of compound	Yield %	M.P C°	Elemental analysis % found (% cal.)			colour
				C	H	N	
L1	(2-Hydroxy- benzylidene ) -thiourea 	77%	166-168	53.25 (53.31)	4.53 (4.25)	15.36 (15.85)	Yellow
L2	(2-Hydroxy- benzylidene ) -urea 	72%	149-151	58.42 (58.53)	5.00 (4.91)	16.93 (17.06)	white

**Table (2): The characteristic ir bands of the Schiff's base ligand**

No.	$\nu(\text{O-H})$ phenol $\text{cm}^{-1}$	$\nu(\text{C-H})$ Aromatic $\text{cm}^{-1}$	$\nu(\text{C=O})$ $\text{cm}^{-1}$	$\nu(\text{C=N})$ Imine $\text{cm}^{-1}$	$\nu(\text{C=C})$ Aromatic $\text{cm}^{-1}$	$\nu(\text{C=S})$ $\text{cm}^{-1}$
L1	3470	3025	-	1620	1580,1520	1240
L2	3470	3060	1680	1615	1580,1540	-

**Table (3): UV-VISIBAL absorption of the shiff base ligand**

No.	$\pi - \pi^*$
L1	380,300,266
L2	385,305,270

**Table (4): some physical properties of the prepared complexes**

No.	complexes	Color	$\Delta M$ $\mu s$ $mol^{-1}$	M.P C°	UV/VIS nm	Elemental analysis		IR SPECTRA $cm^{-1}$							
						(% found) % cal		$\nu$ (O-H)	$\nu$ (C=O)	$\nu$ (C=N)	$\nu$ (C=S)	$\nu$ (C-O) phenol	$\nu$ (M-N)	$\nu$ (M-S) $\nu$ (M-O)	$\nu$ (M-X)
						M%	Cl%								
1	[Mn(L1)2]Cl2	G.Y	65	186-188	280,320,400	11.13 (11.10)	14.63 (14.61)	3400b	-	1600	1195	1245	450	370	-
2	[Co(L1)2]Cl2	L.B	75	190-192	278,315,410	11.86 (11.83)	14.51 (14.48)	3400b	-	1595	1190	1255	470	375	-
3	[Ni(L1)2]Cl2	L.G	85	193-195	285,325, 415	11.86 (11.84)	14.51 (14.49)	3400b	-	1585	1198	1260	460	395	-
4	[Mn(L2)2]Cl2	G.Y	70	169-171	290,325,405	11.92 (11.89)	15.67 (15.64)	3400b	1655	1593	-	1250	465	410	-
5	[Co(L2)2]Cl2	L.B	80	165-167	295,330,415	12.69 (12.66)	15.53 (15.51)	3400b	1650	1595	-	1240	455	415	-
6	[Ni(L2)2]Cl2	L.G	75	170-172	285,320,400	12.69 (12.67)	15.53 (15.51)	3400b	1660	1580	-	1252	475	405	-
7	[Mn(L1) Cl2.H2O]	G.Y	15	195-197	275,310,410	16.67 (16.65)	21.98 (21.96)	3400b	-	1591	1185	1260	453	390	290
8	[Co(L1) Cl2.H2O]	G.Y	18	185-187	283,325,420	17.73 (17.71)	21.71 (21.69)	3400b	-	1589	1180	1235	463	385	275
9	[Ni(L1) Cl2.H2O]	L.B	20	189-191	290,305,409	17.73 (17.69)	22.71 (22.69)	3400b	-	1587	1200	1230	475	380	285
10	[Mn(L2) Cl2.H2O]	L.G	10	175-177	280,315,405	15.07 (15.04)	15.10 (15.08)	3400b	1645	1605	-	1250	455	405	300
11	[Co(L2) Cl2.H2O]	L.B	12	178-280	285,320,422	14.94 (14.92)	19.45 (19.43)	3400b	1640	1580	-	1240	450	408	305
12	[Ni(L2) Cl2.H2O]	L.G	16	183-185	290,325,410	14.94 (14.91)	15.63 (15.60)	3400b	1635	1590	-	1253	461	412	295

G.Y = green yellowish, L.B = Light Brown, L.G = Light Green

## Results and Discussion

The structures of schiff base complexes were confirmed by spectroscopic techniques ir and uv/visible. Infrared spectra of the two ligands ( $L_1$ ), ( $L_2$ ) show the usual broad bands in the region around (3360-3475  $\text{cm}^{-1}$ ) due to the  $\text{NH}_2$  stretching frequency<sup>(10)</sup> of the amide group of the ligands ; No effect on these frequencies after complexation precludes the possibility of complexation at this group<sup>(11)</sup>.

The band at 1620 and 1615  $\text{cm}^{-1}$  in the spectrum of ( $L_1$ )&( $L_2$ ) respectively due to  $\nu(\text{C}=\text{N})$  stretching shifted to the lower frequencies in the complexes<sup>(12)</sup>(table 4).

The negative shift generally in  $\nu(\text{C}=\text{N})$  suggested coordination to metal ions through nitrogen atom of (-C=N-) Schiff's base<sup>(13)</sup> of the ligand and on complexation indicates involvement of azomethine nitrogen<sup>(7,10)</sup> with metal ions.

The band at 1240  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{S})$  stretching vibrations in ( $L_1$ ), in the metal complexes this band is weakened and lowered<sup>(15)</sup> (table 4). The observations indicate the coordination of the ligand ( $L_1$ ) through sulphur atom.

The carbonyl stretching frequency in ( $L_2$ ) decreases to (1630-1650)  $\text{cm}^{-1}$  compared to the free ligand at 1680  $\text{cm}^{-1}$ , due to the charge transfer from the ligand to the metal<sup>(9)</sup>,

In metal complexes a new peak is found 1265  $\text{cm}^{-1}$  for  $\nu(\text{C}-\text{O})$  which is very characteristic and  $\nu(\text{O}-\text{H})$  was broad<sup>(11,12)</sup> (table 4).

New bands which appeared at low frequencies in the spectra of the prepared complexes were probably due to (metal- nitrogen), (metal- sulphur), and (metal- chloride), bond vibration frequencies (table 4).

The complexes give different colour from the transition metal salts and the ligands, then this was

important indication to coordinate occurrence<sup>(13)</sup>, therefore these colourly complexes show different characteristic absorption band in position, intensity or together when compared with the bands of ligand and this was another indication for the coordination occurrence<sup>(14,15)</sup>.

The uv/visible spectra of the two prepared ligands ( $L_1$ ,  $L_2$ ) at ( $10^{-3}\text{M}$ ) in ethanol were showed three absorption bands<sup>(15)</sup>. The first band between (380-385) nm represented ( $\pi-\pi^*$ ) while the second band (300-305) nm represented ( $\pi-\pi^*$ ) and the third band (265-270) nm is called (B-band) for phenyl group<sup>(16,17)</sup>.

Electronic spectra of Co(II) complexes showed one band at approximately 410 nm assigned for the  ${}^4\text{T}_{2g} \rightarrow {}^4\text{T}_{2g}$  transition of  ${}^9\text{F}_4$  term of  $d^7$  system. this may indicate an octahedral geometry for Co complexes.

The electronic spectra of the Ni(II) complexes, exhibit four bands in the range 10390, 18620, 27900 and 36200  $\text{cm}^{-1}$ . An examination of these bands indicates that the complexes have an octahedral geometry<sup>(18)</sup>. Thus, these bands may be assigned to the three spin allowed transitions  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ ,  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{P})$  respectively.

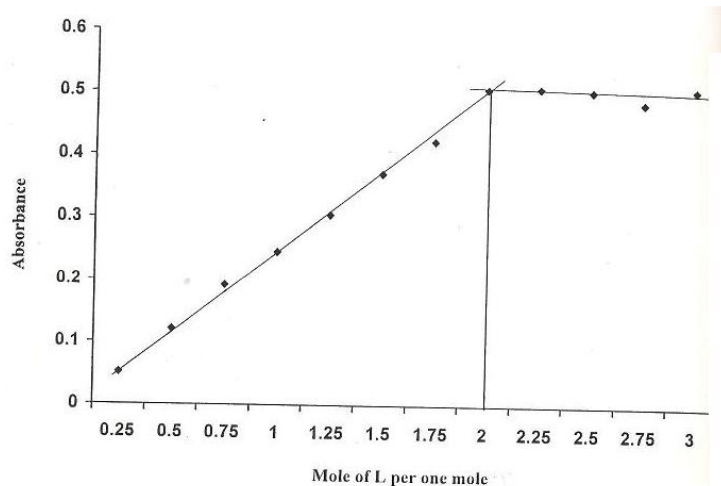
The Mn(II), Co(II) and Ni(II) complexes had normal values of the magnetic moments, i.e. 2.10, 3.50 and 4.70 B.M respectively, indicating their mono nuclear. Based on the experimental evidence obtained the complexes were characterized as six coordinates with octahedral structures<sup>(19)</sup>.

The measurements of the molar electrical conductivity of the complexes at ( $25\text{C}^\circ$ ) in DMSO are presented in table (4). These results show the molar conductivity are relatively high values, these complexes are electrolyte and low values refer to the complexes are non-

electrolyte, are in agreement with the proposed structures of the complexes.

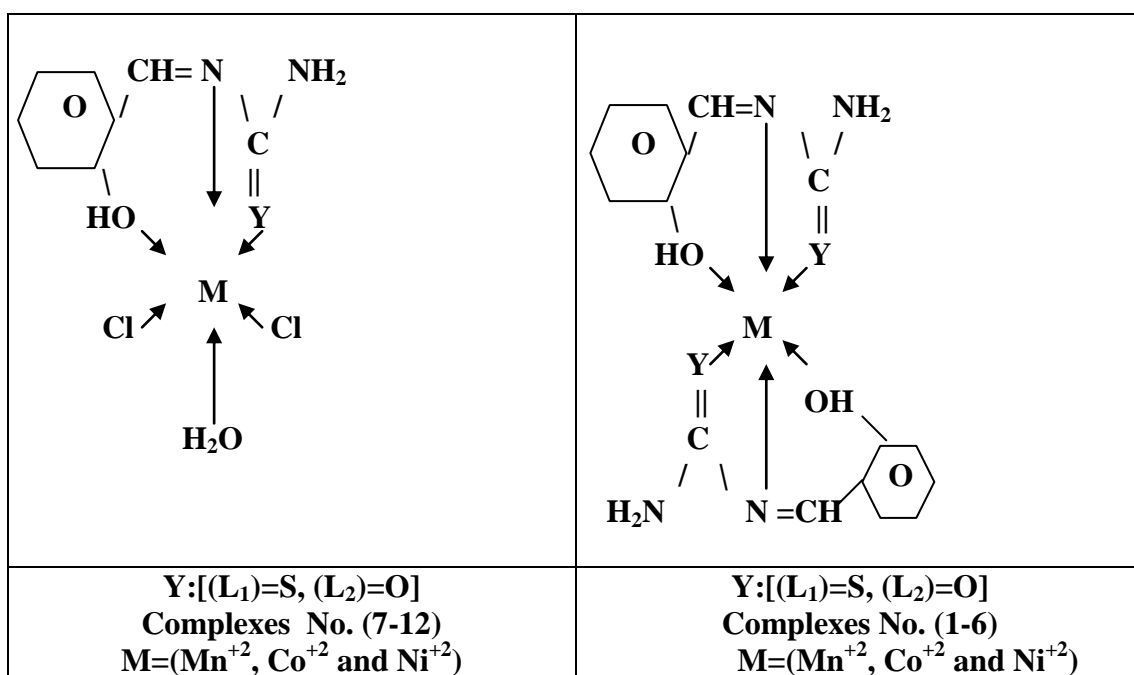
The method of continuous variation mole ratio method are

employed in this work molar ratio(1:1) metal to ligand for(7-12) complexes and (1:2) metal to ligand for (1-6) complexes as shown below:



According to the results obtained from ir, uv/vis, molar ratio, molar conductivity and atomic absorption measurements for the

prepared complexes, the proposed molecular structure of the complexes has an octahedral structure as shown below:



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