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_1), (2-hydroxy-benzylidene)- urea = (L_2)of these ligands with some of transition metal ions Mn^{+2}, Co^{+2} and Ni^{+2} 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 .

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Mn^{+2},Co^{+2},Ni^{+2} (L_2)=   - (

(C.H.N)

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Introduction

Schiff bases have been widely used as bidentate ligands in the field of coordination chemistry [1] . the Schiff base complexes have been used in catalytic reaction [2] and as models for biological systems [3] . In recent years many copper complexes of Schiff base were prepared[4] . It has been reported that the structure of the constituent bonded to the imino nitrogen affects the coordination geometry of the complexes [5] . Metal complexes of Schiff bases are extensively studied due to synthetic flexibility, selectivity and sensitivity towareds avariety of metal atoms [6] .
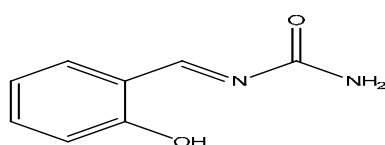
In this work will investigate has been the chemistry of this urea and thiourea compound by preparing its Schiff base with 2-hydroxy-benzylidene , and study of the complexes metal (Mn^{2+} , Co^{2+}, and Ni^{2+}); bidentate ligands these:

(2-Hydroxy- benzylidene) –thiourea (L1)
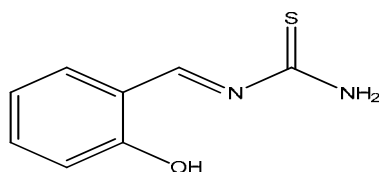
(2-Hydroxy- benzylidene) –urea (L2)

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 microanalyizer 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:

$[MnCl_2.6H_2O]$, $[CoCl_2.6H_2O]$, $[NiCl_2.6H_2O]$ were supplied by BDH, Ethanol Absolute, diethylether, DMSO, Urea, thiourea supplied by Aldrich .

A- Preparation of the ligand:

Preparation of $(L_1),(L_2)$ were prepared according to the literature [7] The full name of the Schiff base will be replaced by a number (L_1,L_2) respectively as in shown in table (1) for the rest of this paper . The physical properties of these compounds (L_1, L_2) 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 $(L_1$ or $L_2)$ (2 mmole) in absolute ethanol (5 ml), a hot solution of metal chloride (1 mmole) in absolute ethanol (5ml) (dissolved in dilute HCl) [8] 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 $(L_1$ or $L_2)$ (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[9].

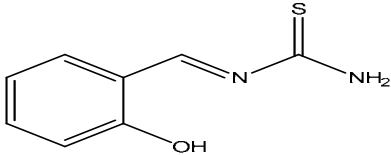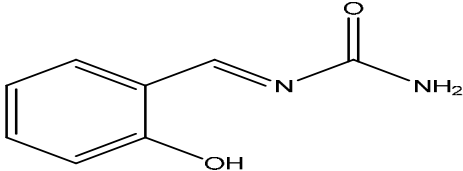**Table(1): physical properties of the Schiff's base ligand**

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.	υ(O-H) phenol cm^{-1}	υ (C-H) Aromatic cm^{-1}	υ (C=O) cm^{-1}	υ (C=N) Imine cm^{-1}	υ (C=C) Aromatic cm^{-1}	υ (C=S) 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	Colour	ΔM μs mol^{-1}	M.P C°	UV/VIS nm	Elemental analysis (% found) % cal		IR SPECTRA cm^{-1}							
						M%	Cl%	υ (O-H)	υ (C=O)	υ (C=N)	υ (C=S)	υ (C-O) phenol	υ (M-N)	υ (M-S) υ (M-O)	υ (M-X)
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.H$_2$O]	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.H$_2$O]	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.H$_2$O]	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.H$_2$O]	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.H$_2$O]	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.H$_2$O]	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 cm^{-1}) due to the NH_2 stretching frequency [10] of the amide group of the ligands ; No effect on these frequencies after complexation precludes the possibility of complexation at this group [11].

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

The negative shift generally in $\upsilon(C=N)$ suggested coordination to metal ions through nitrogen atom of (-C=N-) Schiff's base [13] of the ligand and on complexation indicates involvement of azomethine nitrogen [7,10] with metal ions.

The band at 1240 cm^{-1} due to $\upsilon(C=S)$ stretching vibrations in (L_1),in the metal complexes this band is weakened and lowered [15] (table 4). The observations indicate the coordination of the ligand (L_1) through sulpher atom.

The carbonyl stretching frequency in (L_2) decreases to (1630-1650) cm^{-1} compared to the free ligand at 1680 cm^{-1} , due to the charge transfer from the ligand to the metal [9],

In metal complexes a new peak is found 1265 cm^{-1} for $\upsilon(C-O)$ which is very characteristic and $\upsilon(O-H)$ was broad [11,12] (table 4).

New bands which appeared at low frequencies in the spectra of the prepared complexes were probably due to (metal- nitrogen), (metal- sulpher), 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 [13], 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 [14,15].

The uv/visible spectra of the two prepared ligands (L_1, L_2) at $(10^{-3}M)$ in ethanol were showed three absorption bands [15]. 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 [16, 17].

Electronc spectra of Co(II) complexes showed one band at approximately 410 nm assigned for the $^4T_2g \rightarrow ^4T_2g$ transition of $^9F_4$ 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 cm^{-1} . An examination of these bands indicates that the complexes have an octahedral geometry [18]. Thus, these bands may be assigned to the three spin allowed transitions $^3A_2g(F) \rightarrow ^3T_2g(F)$, $^3A_2g(F) \rightarrow ^3T_1g(F)$ and $^3A_2g(F) \rightarrow ^3T_2g(P)$ 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 [19].

The measurements of the molar electrical conductivity of the complexes at $(25C°)$ 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-

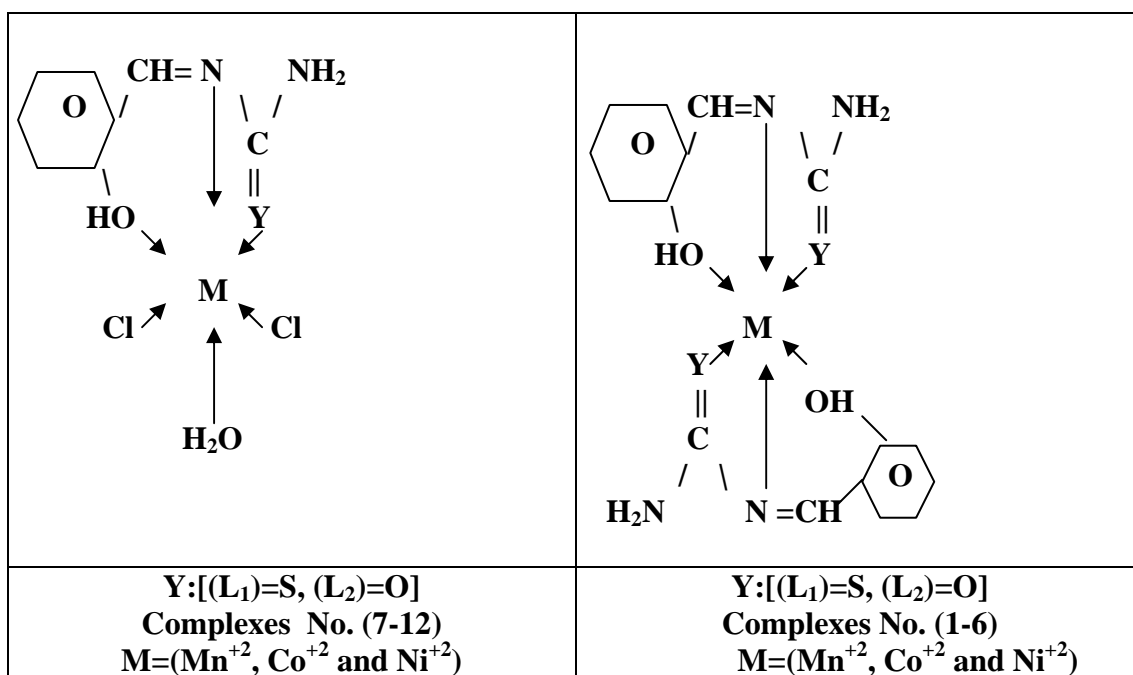electrolyte, are in agreement with the proposed structures of the complexes.

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:
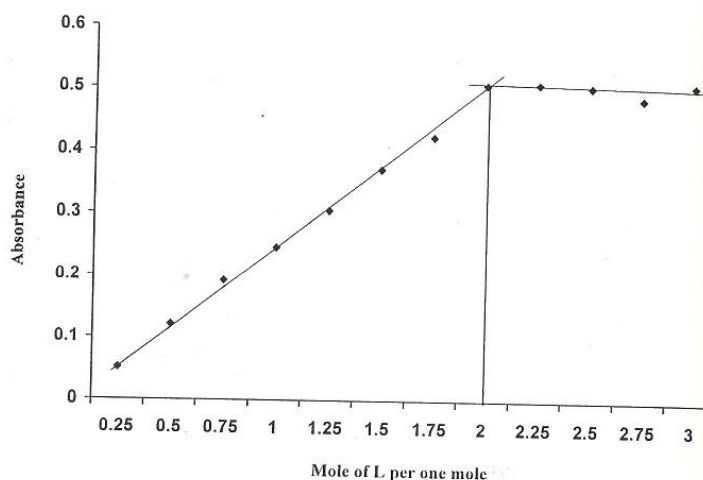
According to the results obtained from ir, uv/vis, molar ratio, molar conductivity and atomic absorption measurements for the prepared complexes, the proposed molecular structure of the complexes has an octahedral structure as shown below:

Y:[(L₁)=S, (L₂)=O] $Y:[(L_1)=S, (L_2)=O]$ **Complexes No. (7-12)** **M=(Mn^{+2}, Co^{+2} and Ni^{+2})**	**Y:[(L₁)=S, (L₂)=O]** $Y:[(L_1)=S, (L_2)=O]$ **Complexes No. (1-6)** **M=(Mn^{+2}, Co^{+2} and Ni^{+2})**

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