Preparation and Characterization Schiff Base Derivatives with some Transition Metal Complexes

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II-Preparation and characterization Schiff base Derivatives with some transition metal complexes

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Abstract:

This research consists of the synthesis of some Schiff bases as ligands, the following type of ligands:

(2-hydroxy-benzylidene)- thiourea = (L_1)
(2-hydroxy-benzylidene)- urea = (L_2)

The complexation of these ligands with some transition metal ions (Zn^{+2}, Cd^{+2}, Hg^{+2}) was prepared. The Schiff bases with their corresponding prepared transition metal complexes have been characterized on the bases of their (C.H.N) elemental analysis, IR, UV-VIS, atomic absorption, the molar conductivity measurement and melting point.
The structural geometries of complexes were suggested in solid state.

INTRODUCTION:

The chemistry of urea and thiourea and their derivatives has attracted considerable attention of coordination chemists by virtue of their applicability as potential ligands for a large number of metal ions (1). In view of antituberculosis and other pharmacological activities(2) of metal Schiff bases in biological system, the physiochemical studies of the metal complexes are well known for their pharmacological importance(3). Extensive studies on urea and thiourea derivatives metal ion complexes have been reported (4).

The complexes have been characterized and their structures have been established with a view to add some thing new to the medicinal science which will show on test , whether these have actually got any anti disease activity . Schiff bases have been reported to possess significant biological activity (1). Many urea and thiourea derivative have been known to possess fungicidal and posticidal action (5, 6) and several (Schiff base) have been reported to exhibit anti tubercular, anti fungal, insecticidal, acaracidal activity and bactericidal properties (7-10). The preparation of N, S, O donor ligand adducts with metal like (Cu, Ag, Au, Zn, Hg, Cd, Pd) is described then characterized by physical spectroscopic techniques and studied as antitumer (11-13).

The present paper describes the preparation of two type Schiff base ligands derived from (urea and thiourea) and their complexes. Schiff base ligands are very diverse and usually contain N, S and O donor atoms, although purely N donors are known (14), but others ligand N, and S donors (15) Schiff base also can be act as mono,di, tri dentite ligand or more with various donor atom combinations .

The presence of nitrogen, sulpher and oxygen atoms in the structure of an organic chelating agent has led to

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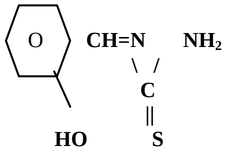
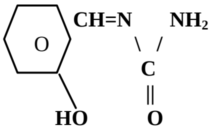
interesting results in the studies of coordination compounds (16).

We have, therefore, undertaken a synthetic and structural study of above new type of complexes as a bidentate ligands:

	
(2-Hydroxy- benzylidene) -thiourea	**(2-Hydroxy- benzylidene) -urea**

EXPERMENYAL:

1- INSTRUMENTATION:

A pye – Unicom sp3-100 infrared spectrophotometer was used to recorded the ir spectra with KBr as a disc , UV/VIS spectra were measured by a HITACHI U-2000 spectrophotometer, Metal Analysis were done by atomic absorption AA-680G (Shimadzu). Element analysis was done by (Perkin-Elmar 2400 CHN Elemental analyzer) in (MOUATA University – JORDAN). Electrical conductance was measured on conductivity CDC304 (Jenway4070) Melting points determined by an electric heated block apparatus (Gallen Kamp), and were uncorrected.

2-MATERIALS:

Metals dichlorides with Tow hydrated (MCl2.2H2O) (M= Zn,Cd,Hg)

Were supplied by BDH chemicals, Ethanol Absolute, diethylether, dimethyl sulphoxide, Urea,thiourea supplied by Aldrich .

A- Preparation of Ligands: were prepared according to the literature [17] The full name of the Schiff base will be replaced by a number (L_1,L_2) respectively as in shown in table (1), and physical properties of these compounds are listed in table (1). The characters ir bands and uv/vis spectrum in DMSO can be shown in table (2) and (3).

B-General procedure for the preparation of complexes :

To a hot solution of ligands (L_1 or L_2) (2 m mole) in absolute ethanol (5 ml) was added to a hot solution of metal chloride (1 m mole) in absolute ethanol (5 ml), the mixture was stirred and refluxed for 2 hours, the color of the solution changed immediately, then the mixture was cooled, and the solution was evaporated in vacuum, or lifted over night at room temperature, after this time a precipitate formed, this was collected by filtration in vacuum, washed and recrystallized from absolute ethanol/ether.

The physical properties of the 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 ligand (1 m mole) in absolute ethanol to a hot solution of metal chloride (1 m mole) in the same solvent .The molar ratio of these complexes was determined according to the methods [18].

RESULTS AND DISCUSSION:

The structures of shiff base complexes were confirmed by spectroscopic techniques like ir and uv /visible. The infrared spectra of the two ligands show the usual broad bands in the region around (3360-3475 cm-1) due to the ν(NH2)stretching frequency (14) the frequencies of this band was no shifting after complexation, precludes the possibility of complexation with this group (19).

The band at 1620 and 1615 cm-1 in the spectrum of (L1) & (L2) respectively due to ν(C=N) stretching which shifted to the lower frequencies in the complexes (20) (table 4).

The red shift generally in ν(C=N) further suggested the coordination to metal ions through nitrogen atom of ν(-C=N-) Schiff's base (21) of the ligand and on complexation indicates involvement of azomethine nitrogen (13, 14, 20) with metal ions.

The band at 1240 cm-1 in the spectrum due to ν(C=S) stretching vibrations in (L1). In the metal complexes this band become weakened and shifted to lower frequency (14) (table 4). The observations indicate the coordination of the ligand (L1) through sulpher atom.

The carbonyl stretching frequency in (L2) decreases to (1635-1655) cm-1 compared to the free ligand at 1680 cm-1, due to coordinate between oxygen of the carbonyl group with the metal (22).

The red shift in metal complexes is found in 1265 cm-1 for ν(C-O) which is very characteristic and show broad band (23) in 3450 cm-1 indicate to presence of O-H in the crystal lattice (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).

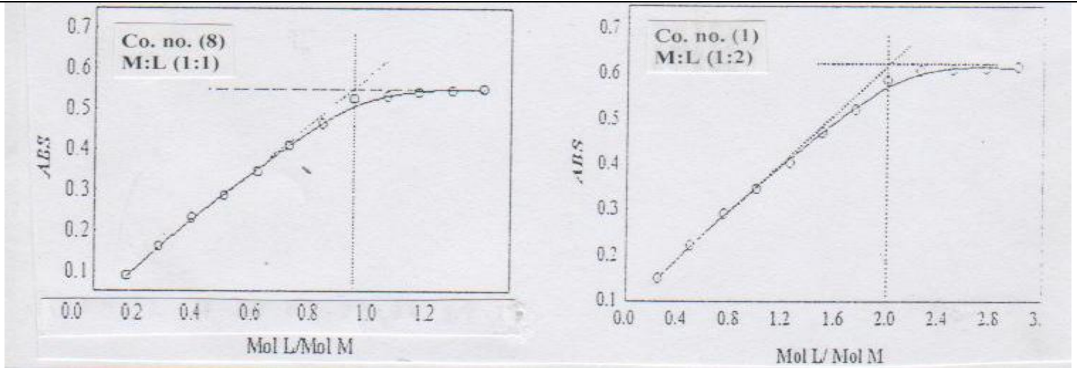
The complexes give different colour from the transition metal salts and the ligands, then this was important indication to coordinate occurrence (24), therefore these colourly complexes show different characteristic absorption band in position, intensity or together when compared with the bands of free ligand and this was another indication for the coordination occurrence (25,26).

The uv/visible spectra of the two prepared ligands (L1, L2) at (10-3M) in ethanol were showed three absorption bands (27). The first band between (380-385) nm represented (n- π*) while the second band (300-305) nm represented (π- π*) (imino) and the third band (265-270) nm is called (B-band) for phenyl group (28).

Generally in the new prepared complexes these bands are shifted to red shift compared with free ligands and high intensity of the bands is indicating for complexes formation (26, 27).

The measurements of the molar electrical conductivity of the complexes at (25Cº) in DMSO are presented in table (4). These results show the high values of the molar conductivity for (1-6) complexes, that's mean these complexes are electrolyte, and low values refer to the complexes (7-12) are non-electrolyte. These results are in agreement with the proposed structures of the complexes.

The mole ratio method are employed in this work. Molar ratio (1:2) metal to ligand (M: L) for (1-6) complexes and (1:1) metal to ligand (M: L) for (7-12) complexes as shown in fig. below (table 4).



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

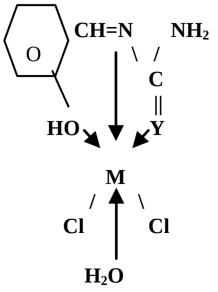
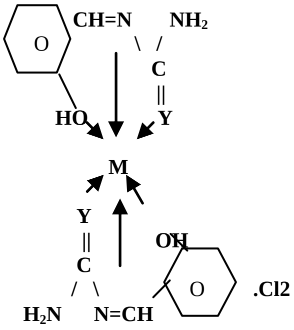
	
Y:[(L_1)=S, (L_2)=O] **Complex no. (7-12)** **M=Zn^{+2},Cd^{+2},Hg^{+2}**	**Y:[(L_1)=S, (L_2)=O]** **Complex no. (1-6)** **M=Zn^{+2},Cd^{+2},Hg^{+2}**

Table (1): physical properties of the shiff 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 (15.64)	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 shiff base ligand

No.	O-H phenol Str. cm^{-1}	C-H Aromatic Str. cm^{-1}	C=O Str. cm^{-1}	C=N Imine Str. cm^{-1}	C=C Aromatic Str. cm^{-1}	C=S Str. 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 ligands

Comp.No.	Bands (nm)	Comp.No.	Bands (nm)	Assignment
L1	380	L2	385	n- π *
	300		305	π- π * (imino)
	266		270	π- π * (aromatic)

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

No.	complexes	Colour	ΔM	M.P C°	UV/VIS nm	Metal Analysis		IR SPECTRA cm^{-1}							
						(% found) % cal	O-H Str.	C=O Str.	C=N Str.	C=S Str.	C-O Str. phenol	M-N Str.	M-S Str. M-O Str.	M-X Str.	
						M%	Cl%								
1	[Zn(L1)2]Cl_2	p.y	65	196-198	276,310,390	13.10 (13.08)	14.34(14.33)	3400b	−	1600	1210	1250	475	380	-
2	[Cd(L1)2]Cl_2	p.y	75	191-193	278,312,395	20.26(20.23)	13.07(13.04)	3400b	-	1590	1215	1255	450	390	-
3	[Hg(L1)2]Cl_2	p.y	85	195-197	280,315,393	31.80(31.76)	11.23(11.19)	3400b	-	1595	1205	1260	455	385	-
4	[Zn(L2)2]Cl_2	p.y	60	169-171	280,315,395	14.00(13.98)	15.30(15.27)	3400b	1645	1595	-	1245	460	405	-
5	[Cd(L2)2]Cl_2	p.y	90	175-177	283,320,398	21.91(21.89)	13.89(13.87)	3400b	1650	1585	-	1265	465	415	-
6	[Hg(L2)2]Cl_2	p.y	70	170-172	285,318,393	33.5(33.48)	11.83(11.80)	3400b	1655	1590	-	1255	463	410	-
7	[Zn(L1) Cl_2. H_2O]	p.y	10	199-201	275,315,392	19.46(19.44)	21.25(21.21)	3400b	-	1585	1220	1250	458	375	280
8	[Cd(L1) Cl_2. H_2O]	p.y	17	213-205	280,314,398	29.54(29.53)	18.66(18.64)	3400b	-	1595	1210	1258	470	370	310
9	[Hg(L1) Cl_2. H_2O]	p.y	19	205-207	285,315,390	42.76(42.75)	15.10(15.07)	3400b	-	1600	1215	1262	472	395	265
10	[Zn(L2) Cl_2. H_2O]	p.y	11	185-187	285,310,395	20.44(20.42)	22.32(22.28)	3400b	1640	1593	-	1248	469	412	315
11	[Cd(L2) Cl_2. H_2O]	p.y	13	190-192	279,316,400	30.68(30.65)	19.45(19.41)	3400b	1635	1587	-	1255	453	408	275
12	[Hg(L2) Cl_2. H_2O]	p.y	18	195-197	287,319,398	44.27(44.24)	15.63(15.59)	3400b	1650	1597	-	1250	465	402	295

(p.y = pale yellow), ΔM in (DMSO) solvent

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II– تحضير ودراسة معقدات بعض العناصر الانتقالية لبعض مشتقات قواعد شف

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الخلاصة:

يتضمن البحث تحضير معقدات لبعض مشتقات قواعد شف(كليكندات) ذات التراكيب التالية :
(2-هيدروكسي– بنزيليدين) – ثايويوريا=(L_1)
(2-هيدروكسي– بنزيليدين) – يوريا =(L_2)

تم تحضير معقدات لهذه الليكندات مع بعض املاح العناصر الانتقالية التي تشمل (Zn^{+2},Cd^{+2},Hg^{+2}) وقد تم تشخيص ودراسة تراكيب الليكندات والمعقدات المحضرة باستخدام تقنية التحليل الدقيق للعناصر (C.H.N) ومطيافية الاشعة تحت الحمراء والاشعة فوق البنفسجية وتقنية الامتصاص الذري اضافة الى قياس الموصلية الكهربائية المولارية ودرجات الانصهار للمعقدات المحضرة وعلى ضوء النتائج تم تعيين التركيب الهندسي لهذه المعقدات.