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Synthesis and Characterization Complexes Of Cr(III),Mo(V) and W(VI) with Schiff Base Derivatives from (2-hydroxy-benzylidene) and Urea or Thiourea and Study of its biological activity.

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biological activity.

ABSTRACT

This study included synthesis of Schiff base ligands (2-hydroxy-benzylidene)-thiourea = (L1), (2-hydroxy-benzylidene)- urea = (L2) , the ligands were prepared from reaction (2-hydroxy-benzylidene) with urea or thiourea. Metal complexes of these ligands with some of transition metal ions Cr+3, Mo+5 and W+6 have been prepared and characterized by their (C.H.N) elemental analysis, IR, UV-VIS, atomic absorption, Molar conductivity measurements and melting points. From the result probable structures of the prepared complexes were proposed .Also includes, the study of biological effect for these complexes on four deferent pathogenic species: (Streptococcus paecalies, Staphylococcus aureus),(Escherichia coli, Klebsiella Peneumonia). The first and second species are Gram positive while the other are Gram negative (by using agar well diffusion method). Finally,it was found that compounds show different activity of inhibition on growth of the bacteria.

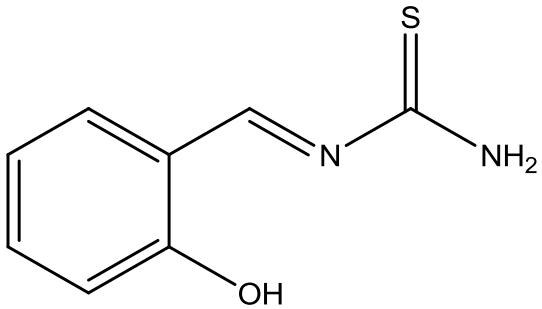
Introduction:

Compound containing an azomethane group (-CH=N-) are known as schiff bases. schiff bases are generally bi- or tri- dentate ligands capable of forming very stable complexes with transition metals. Schiff base metal complexes with different drugs are relatively less studied. The wide use of antibiotics in man and animals and extensive use in areas other than the treatment and prophylaxis of disease have resulted in a serious problem of drug resistance. More bacterial strains have become resistant to the available drugs. Various strategies have been worked out and tried upon to cope with the resistance problem and enhance the activity, or broaden the spectrum of the drug(1). Preparation of different synthetic derivatives of antibiotics based on structure activity relationship has been on one of the best approaches. a relation between the structure of the complexes and their anti-bacterial activity can be observed(2).

In the present work we have attempted to widen the scope of derivatization by providing more flexibility through Schiff base formation with the drug substances containing –NH2 groups and complexation with metal elements.

The Schiff base structure provides for a greater choice and flexibility and complexation with a metal element and stability and versatility of the molecule. Construction of the molecular model indicates that the structure is suitable for chelate formation. In many cases the pharmacological activity of antibiotics after complexation with metals is enhanced as compared to that of the free ligands(1-4).

In this work, we will investigate 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

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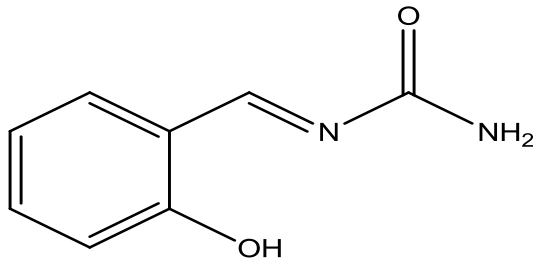


(2-Hydroxy- benzylidene) -urea

Experimental:-

INSTRUMENTATION:

A pye – Unicom sp3-100 infrared spectrophotometer was used to recorded 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.

MATERIALS:

[CrCl3.6H2O], [MoCl5.6H2O], [WCl6.6H2O] were supplied by BD Hchemicals, Ethanol Absolute, diethy lether, DMSO, Urea, thiourea supplied by Aldrich.

A- Preparation of the ligands:

These (L1),(L2) were prepared according to the literature (5) The full name of the Schiff base will be replaced by a number (L1,L2) respectively as in shown in table (1) for the rest of this paper . The physical properties of these compounds (L1, L2) 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 (L1 or L2) (2 m mole) in absolute ethanol (5 ml), a hot solution of metal chloride (1 m mole) in absolute ethanol (5 ml) (dissolved in dilute HCl) (6) was added 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 (L1 or L2) (1 m mole) 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 (7).

C- Study of biological activity for (L) ligand and their metal complexes :

The biological activity of the new ligand and their metal complexes were studied against two selected type of bacteria which included pseudomonas aeugiose as gram negative (-Ve) and Bacillus. Subtilis as gram positive (+Ve) to be cultivated and as control for the disc sensitivity test (8) , this method involves the exposure of the zone of inhibition toward the diffusion of micro–organism on agar pla. The plates were incubated for (24 hours) , at 37C° , the zone of inhibition of bacteria growth around the disc was observed

Results and Discussion:

The structures of schiff base complexes were confirmed by spectroscopic techniques ir and uv /visible. Infrared spectra of the two ligands (L1),(L2) show the usual broad bands in the region around (3360-3475 cm-1) due to the NH2 stretching frequency (9) of the amide group of the ligands ; No effect on these frequencies after complexation precludes the possibility of complexation at this group (10).

The band at 1620 and 1615 cm-1in the spectrum of (L1)&(L2) respectively due to υ(C=N) stretching shifted to the lower frequencies in the complexes (11)(table 4) .

The negative shift generally in υ(C=N) suggested coordination to metal ions through nitrogen atom of (-C=N) Schiff's base (12) of the ligand and on complexation indicates involvement of azomethine nitrogen (5,9) with metal ions.

The band at 1240 cm-1 due to υ(C=S) stretching vibrations in (L1),in the metal complexes this band is weakened and lowered (14) (table 4). The observations indicate the coordination of the ligand (L1) through sulpher atom.

The carbonyl stretching frequency in (L2) 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 (7),

In metal complexes a new peak is found 1265 cm-1

for υ(C-O) which is very characteristic and υ(O-H) was broad (10) (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).

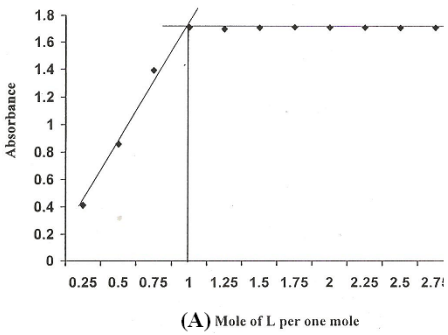
The complexes give different colour from the transition metal salts and the ligands, then this was important indication to coordinate occurrence (11), therefore these colourly complexes show different characteristic absorption band in position, intensity or together when compared with the bands of ligand and this was another indication for the coordination occurrence (12,13).

The uv/visible spectra of the two prepared ligands (L1, L2) at (10-3M) in ethanol were showed three absorption bands (13). The first band between (380-385) nm represented (n - π*) while the second band (300-305) nm represented (π - π*) and the third band (265-270) nm is called (B-band) for phenyl group (13, 14).

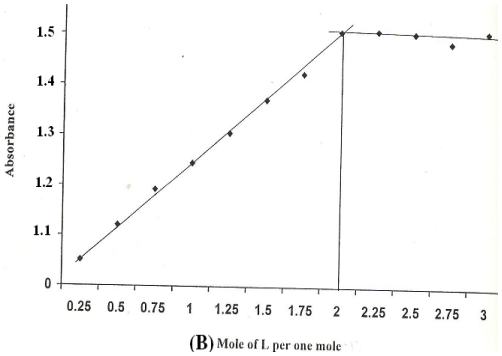
Generally in the new prepared complexes these bands are shifted to short or long wavelength compared with free ligands and high intensity of the bands is indicate for complexes formation (12,15).

The measurements of the molar electrical conductivity of the complexes at (25C°) in DMSO are presented in table (4). These results show the high values of the molar conductivity, 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 fig.(A) and (1:2) metal to ligand for (1-6) complexes fig.(B) as shown below:

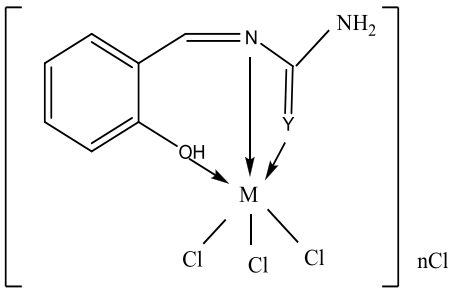


[Cr(L1) Cl3]

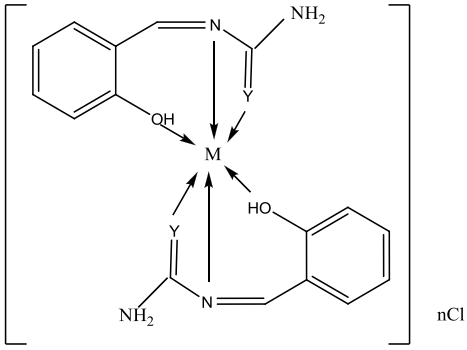


[Cr(L1)2]Cl3

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:[(L_1)=S, (L_2)=O]
Complexes No. (7-12)
(M=Cr^{+3},n=0); (M=Mo^{+5} ,n=2); and
(M=W^{+6},n=3)



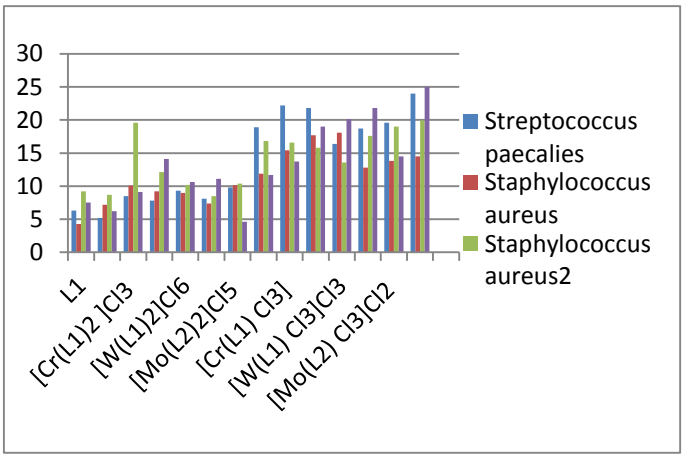
Y:[(L_1)=S, (L_2)=O]
Complexes No. (1-6)
(M=Cr^{+3},n=3); (M=Mo^{+5} ,n=5); and
(M=W^{+6},n=6)

Biological Activity:

As a result from the study of anti microbial of prepared ligands (L_1, L_2) and their metal complex as shown in figure below the following points were concluded:

1- the result of antibacterial activity study for ligands (L_1, L_2) indicates that the new ligands exhibited antibacterial activity against the studied bacteria at low and high concentration [16,17].

2- The prepared ligands and their metal complexes exhibt good activity ,which showed inhibition area for compound and conplexes against different kinds of bacteria.
3- Complexes were more active than the corresponding ligandes.
4- Activity of complexes depends on the type of metal.
5- The result reflected that the metal complexes of W(VI) showed the highest activity at low concentration (20-40ppm) , comp aired to the Cr(III) and Mo(V) complexes which showed the highest activity at >40ppm concentration.
6- Generally , the result of prepared complexes exhibited antibacterial activity toward psedomonans bacteria was more than the complexes inhibition Bacillus bacteria[18].



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

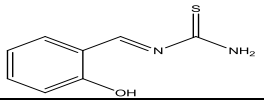
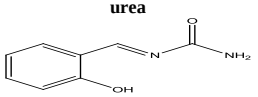
No.	Name and structure of compound	Yield %	M.P C°	Elemental analysis % found (% cal.)			colour
				C	H	N	
L_1	(2-Hydroxy- benzylidene) - thiourea 	77%	166-168	53.25 (53.31)	4.53 (4.25)	15.36 (9.85)	Yellow
L_2	(2-Hydroxy- benzylidene) - urea 	72%	149-151	58.42 (58.53)	5.00 (4.91)	16.93 (17.06)	white

Table (2): The characteristic ir bands of the shiff base ligand

No.	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}
L_1	3470	3025	-	1620	1580,1520	1240
L_2	3470	3060	1680	1615	1580,1540	-

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

No.	n- π * , π- π *
L_1	380,300,266
L_2	385,305,270

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

No.	complexes	Colour	ΔM / S cm^2 mol^{-1}	M.P C°	UV/VIS nm	Elemental analysis (% found) % cal	IR SPECTRA cm^{-1}							
							υ(O-H)	υ(C=O)	υ(C=N)	υ(C=S)	pheno)	υ(M-N)	υ(M-S)	υ(M-X)

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7	9	8	10	11	12
[Cr(L1) Cl3]	[W(L1) Cl3]Cl3	[Mo(L1) Cl3]Cl2	[Cr(L2) Cl3]	[Mo(L2) Cl3]Cl2	[W(L2) Cl3]Cl3
P.B	G	B	P.o	R	P.g
18	125	65	15	75	110
179-181	195-197	187-189	183-185	198-200	205-207
273,310,396,585	295,320,400,545	280,325,398,500	285,325,395,595	290,335,390,495	300,330,385,530
15.29 (15.17)	31.72 (31.66)	21.05 (20.99)	16.04 (15.95)	21.81 (21.75)	32.62 (32.55)
31.76 (31.69)	37.24 (37.18)	39.47 (39.38)	33.33 (33.26)	40.90 (40.85)	38.29 (38.19)
3400b	3400b	3400b	3400b	3400b	3400b
-	-	-	1590	1580	1585
1600	1585	1605	1590	1580	1585
1200	1185	1195	-	-	-
1230	1255	1240	60	1255	1240
475	455	480	480	450	465
365	375	370	410	415	400
260	305	280	265	275	300

p.b= pale brown, b= brown, p.o= pale orange, g=green, (p.g= pale green)

1	2	3	4	5	6		
[Cr(L1)2]Cl3	[Mo(L1)2]Cl5	[W(L1)2]Cl6	[Cr(L2)2]Cl3	[Mo(L2)2]Cl5	[W(L2)2]Cl6		
P.B	B	G	P.o	R	P.g		
120	150	180	115	165	185		
185-187	193-195	204-206	178-180	186-188	191-193		
275,315,395,590	277,320,390,491	280,325, 393,520	283,330,385,58 8	287,325,383,505	290,335,388,540		
10 (9.95)	15.09 (15.0)	24.21 (21.16)	10.65 (10.55)	15.89 (15.79)	25.27 (25.18)	M%	
20.76 (20.68)	28.30 (28.22)	28.42 (28.37)	22.13 (22.08)	29.80 (29.72)	29.67 (29.59)	Cl%	
3400b	3400b	3400b	3400b	3400b	3400b		
-	-	-	1595	1590	1595		
1590	1595	1600	1595	1590	1595		
1190	1180	1195	-	-	-		
1240	1265	1250	1245	1260	1235		
465	470	465	480	455	450		
385	380	390	400	405	410		
-	-	-	-	-	-		

تحضير ودراسة معقدات الكروم(III) , الموليبدينيوم (V) والتنكستن(VI) مع قواعد شف المشتقة من (2-هيدروكسي- بنزيليدين) والثايوريا اواليوريا ودراسة فعاليتها البايولوجية

عمر حمد شهاب

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الخلاصة:

تم تحضير قواعد شف (2-هيدروكسي- بنزيليدين)- ثايويوريا=(L1) ،(2-هيدروكسي- بنزيليدين)- يوريا =(L2) من تفاعل (2-هيدروكسي- بنزيليدين) مع اليوريا او الثايوريا. معقدات هذه الليكندات مع بعض أملاح العناصر الانتقالية Cr+3,Mo+5,W+6 وقد تم تشخيص ودراسة تراكيب الليكندات والمعقدات المحضرة منها باستخدام تقنية التحليل الدقيق للعناصر (C.H.N) ومطيافية الأشعة تحت الحمراء والأشعة فوق البنفسجية وتقنية الامتصاص الذري فضلا عن قياس الموصلية الكهربائية المولارية ودرجات الانصهار للمعقدات المحضرة وعلى ضوء النتائج تم استنتاج تراكيب هذه المعقدات. يتضمن البحث أيضا دراسة بعض جوانب التاثير البايولوجي للمعقدات المحضرة في نمو أربع أجناس بكتيرية مرضية الأولى والثانية منهما موجبة لصبغة الغرام وهما: (Streptococcus paecalies, Staphylococcus aureus), والاثنان الآخران سالبة لصبغة الغرام وهما: (Escherichia coli, Klebsiella Peneumonia) وباستخدام طريقة الحفر بالا كار وجد أن لهذه المركبات فعالية متفاوتة القوة في تثبيط نمو البكتريا المدروسة.