Synthesis ,Characterization and Theoretical Treatment Of Sandwich Schiff Base Complexes Derived from Urea and Thiourea with some Transition Metals and Study of its Biological Activity

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ABSTRACT

This research consists of the synthesis of some Schiff bases as ligands. The ligands are – L1, 1, 3 - Bis - (2-hydroxy-benzylidene) - thiourea and L2, 1, 3 – Bis - (2-hydroxy-benzylidene) – urea,). These ligands are complexed with transition metal ions of Mn^{+2}, Co^{+2}, Ni^{+2}. The prepared transition metal complexes have been characterized by elemental analysis, IR, UV-VIS, and atomic absorption methods. The molar conductivity measurement and melting point of prepared complexes were also measured. From the results obtained by different techniques, it was found that the proposed structures of the prepared complexes have octahedral structure. A theoretical treatment of the formation of complexes was studied. This was done using the HYPERCHEM-6 program for the Molecular mechanics and Semi-empirical calculations. The free ligand and its complexes have been tested for their antibacterial activities against two types of human pathogenic bacteria -Staphylococcus aureus and Escherichia coli. The first groups are Gram positive while the second groups are Gram negative (from diffusion method). Finally, it was found that that compounds show different activity of inhibition on growth of the bacteria.

Keywords: Sandwich Schiff bases, Synthesis, Characterization, Biological activity
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INTRODUCTION

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

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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 derivatives have been known to possess fungicidal[5] and pesticidal[6] action and several others have been reported to exhibit anti tubercular [7], anti-fungal[8], insecticidal, acaracidal activity[9] and bactericidal[10] properties .

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[11-13], but other ligands are N and S donors[14,15]. Schiff base also can act as mono ,di, tri dentate 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 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 as shown in fig .1:
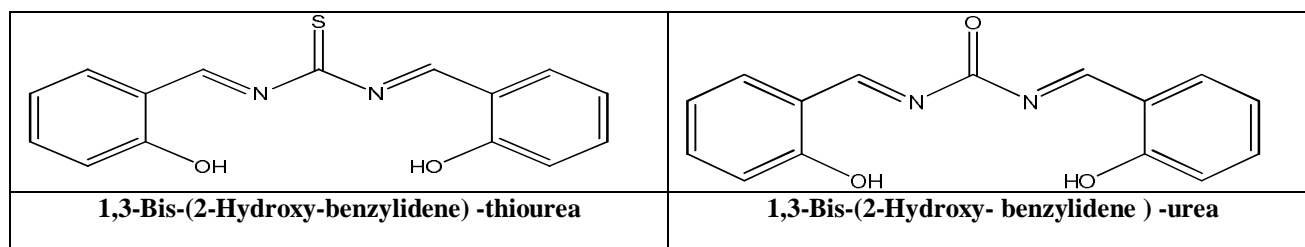

| **1,3-Bis-(2-Hydroxy-benzylidene) -thiourea** | **1,3-Bis-(2-Hydroxy- benzylidene) -urea** |

Fig. 1 :The general structures of ligands.

MATERIALS AND METHODS

Instrumentation: A Pye – Unicom SP3-100 Infrared Spectrophotometer was used to record the IR spectra using KBr disc , UV/VIS spectra were measured by a HITACHI U-2000 spectrophotometer, Elemental Analysis were done by atomic absorption AA-680G (Shimadzu). Electrical conductance was measured on conductivity meter CDC304 (Jenway4070). Melting points were determined by an electric heated block apparatus (Gallen Kamp).

Materials: $MnCl_2.6H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ were supplied by BDH chemicals and Absolute Ethanol, diethyl ether, DMSO, Urea , Thiourea were supplied by Aldrich .

Preparation of the ligands: Ligands L1,L2 were prepared according to the literature[17].

Preparation of complexes : To a 5 ml (2 m mole) hot solution of ligands ,L1 or L2, in absolute ethanol add 5 ml (1 m mole) hot solution of metal chloride dissolved in dilute HCl [18] 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 kept over night at room temperature .The precipitate formed was collected by filtration in vacuo, washed and recrystallized from absolute ethanol/ether.. The analogous complexes were prepared in a similar manner. The molar ratio of the complexes was determined according to the methods[19].

Study of biological activity for ligands and their metal complexes: The biological activity of the ligands and their metal complexes were studied against two selected type of bacteria which included Escherichia coli, as gram negative (-Ve) and Staphylococcus aureus as gram positive (+Ve) to be cultivated and as control

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for the disc sensitivity test [20]. This method involves the exposure of the zone of inhibition toward the diffusion of micro–organism on agar plate. 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 ligands and their complexes were confirmed by spectroscopic techniques like IR and UV /Visible.

IR Spectra: The infrared spectra of the complexes have been recorded. The IR spectra show the band at 1610 cm^{-1} & 1620 cm^{-1} in the spectrum of L1 and L2 respectively due to $\upsilon^{(C=N)}$ stretching which shifted to the lower frequencies in the complexes [20,21] (Table 1).The negative shift generally in $\upsilon^{(C=N)}$ further suggested the coordination to metal ions through nitrogen atom of (-C=N-) Schiff's base [22] of the ligand and on complexation indicates involvement of azomethine nitrogen [13,14,21] with metal ions. The band at 1250 cm^{-1} in the spectrum due to $\upsilon^{(C=S)}$ stretching vibrations in L1. In the metal complexes this band is weakened and lowered [14] (Table 2). The observations indicate the coordination of the ligand L1 through sulpher atom. The carbonyl stretching frequency in L2 decreases to 1605-1620 cm^{-1} compared to the free ligand at 1685 cm^{-1}, due to the charge transfer from the ligand to the metal [23]. In metal complexes a new peak is found at 1265 cm^{-1} for $\upsilon^{(C-O)}$ which is very characteristic and $\upsilon^{(O-H)}$ was broad [24] (Table 2). 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 and $\upsilon^{(M-O)}$, $\upsilon^{(M-S)}$ (bridging) occurs at lower frequencies than $\upsilon^{(M-O)}$, $\upsilon^{(M-S)}$ (terminal) indicating these type of coordinate [24] (table 2).

Electronic Absorption Spectra: The complexes give different color from the transition metal salts and the ligands, then this was important indication to coordinate occurrence[25], therefore these colorly 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 [26,27].
The UV/visible spectra of the two prepared ligands (L1, L2) at (10^{-3}M) in ethanol were showed three absorption bands [27]. The first band (370) nm represented (n - π*) while the second band (300-310) nm represented (π - π*) and the third band (270-275) nm is called (B-band) for phenyl group [28,29].
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 [26,27].

Molar Conductance Measurements : The measurements of the molar electrical conductivity of the complexes at (25°C) in DMSO are presented in table .2. 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.

Microanalysis : The method of continuous variation mole ratio method are employed. In this work, the molar ratio of metal to ligand is 2:1 for 1-6 complexes and is 2:2 for 7-12 complexes .

The results of the physical and spectral properties of ligands are presented in Table.1. The physical properties of prepared complexes are listed in Table .2.

Table(1): The characteristic IR bands, UV-Vis. And physical properties of the Schiff base ligands

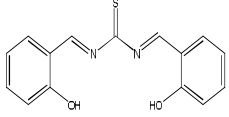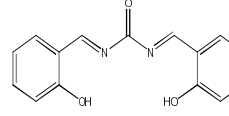| No.	Name and structure of compound	Yield %	M.P C°	Elemental analysis % found (% cal.)	colour	UV/ VIS nm	IR SPECTRA cm -1

					C	N		
L1	1,3-Bis-(2-Hydroxy-benzylidene) -thiourea	68%	153-155		63.28 (63.36)	9.68 (9.85)	Yellow	370, 310, 275	$\upsilon^{(O-H)}$3485, $\upsilon^{(C-H)}$Ar.3040, $\upsilon^{(C=N)}$1610, $\upsilon^{(C=C)}$Ar.1590, 1540, $\upsilon^{(C=S)}$1250
L2	1,3-Bis-(2-Hydroxy-benzylidene) -urea	80%	195-197		67.05 (67.16)	10.29 (10.44)	white	370, 300, 245	$\upsilon^{(O-H)}$3490, $\upsilon^{(C-H)}$Ar.3065, $\upsilon^{(C=N)}$1620, $\upsilon^{(C=C)}$Ar.1575, 1550, $\upsilon^{(C=O)}$1685

Table .2: Some physical and chemical properties of the prepared complexes

	complexes	Colour	ΔM $\Delta M/S$ cm^2 mol^{-1} In DMSO	M.P C°	UV/VIS nm	Elemental analysis (% found) % Cal		IR SPECTRA cm^{-1}							
						M%	Cl%	$\upsilon^{(O-H)}$	$\upsilon^{(C=O)}$	$\upsilon^{(C=N)}$	$\upsilon^{(C=S)}$	$\upsilon^{(C-O)}$	$\upsilon^{(M-N)}$	$\upsilon^{(M-S)}$ $\upsilon^{(M-O)}$	$\upsilon^{(M-Cl)}$
1	[Mn$_2$(L1)(Cl)$_4$(H$_2$O)$_2$]	P.B	15	183-185	285, 318, 395	18.88	25.17	3400b	-	1570	1140	1245	450	305	260
2	[Co$_2$(L1)(Cl)$_4$(H$_2$O)$_2$]	B	18	189-191	290, 315, 393	20.00	24.82	3400b	-	1560	1150	1260	470	315	270
3	[Ni$_2$(L1)(Cl)$_4$(H$_2$O)$_2$]	G	20	185-187	295, 320, 400	20.00	24.82	3400b	-	1590	1165	1250	465	320	275
4	[Mn$_2$(L2)(Cl)$_4$(H$_2$O)$_2$]	P.O	11	235-237	280, 320, 385	13.10	17.47	3400b	1615	1580	-	1255	475	380	280
5	[Co$_2$(L2)(Cl)$_4$(H$_2$O)$_2$]	R	13	225-227	285, 315, 380	20.56	25.53	3400b	1605	1575	-	1240	460	390	285
6	[Ni$_2$(L2)(Cl)$_4$(H$_2$O)$_2$]	P.G	17	217-219	290, 310, 390	20.56	25.53	3400b	1610	1565	-	1252	450	385	255
7	[Mn$_2$ (L1)2] Cl4	P.B	80	197-199	290, 320, 398	13.17	17.56	3400b	-	1585	1155	1260	455	325	-
8	[Co$_2$ (L1)2] Cl4	B	65	195-197	285, 325, 400	14.0	17.39	3400b	-	1575	1160	1255	470	335	-
9	[Ni$_2$ (L1)2] Cl4	G	70	179-181	280, 315, 395	14.0	17.39	3400b	-	1590	1170	1265	468	330	-
10	[Mn$_2$ (L2)2] Cl4	P.O	75	230-232	275, 310, 390	13.70	18.27	3400b	1620	1595	-	1248	455	370	-
11	[Co$_2$ (L2)2] Cl4	R	85	220-222	285, 318, 393	14.57	18.09	3400b	1625	1580	-	1240	475	365	-
12	[Ni$_2$ (L2)2] Cl4	P.G	90	235-237	290, 320, 385	14.57	18.09	3400b	1615	1570	-	1258	480	375	-

(P.B= pale brown, b= brown, P.O= pale orange, g=green, P.G= pale green)

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The proposed structure : According to the results obtained from (IR, UV/visible, molar ratio, molar conductivity, atomic absorption) measurements for the prepared complexes, the proposed molecular structure of the complexes has an octahedral structure as shown in Fig.2 **.**
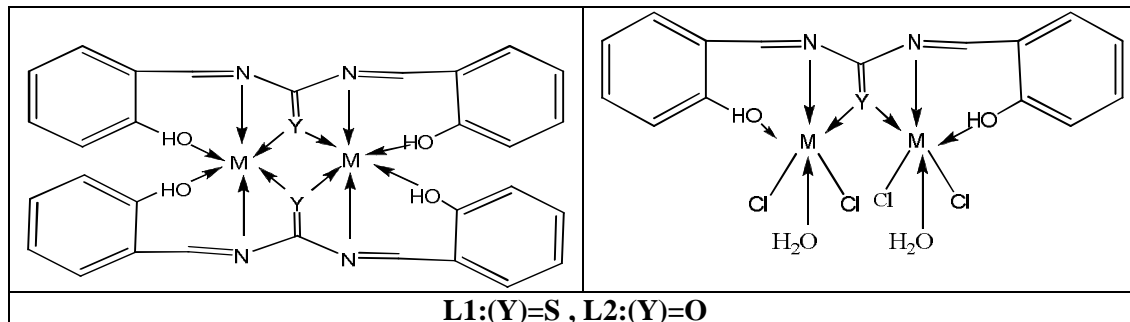

L1:(Y)=S , L2:(Y)=O

Fig.2: The proposed structure of complexes where M= Co(II), Ni(II) and Mn(II).

Theoretical Study: The ball and cylinders and some of selected structural parameters ,bond length and angles are presented in Table.3 and the optimized geometries are shown in Fig. 3. As shown in this figure, there is no obvious trend for the variation of these parameters. The values of the bond length and angles of the optimized geometries are quite similar to the experimental results of the corresponding compounds**.**
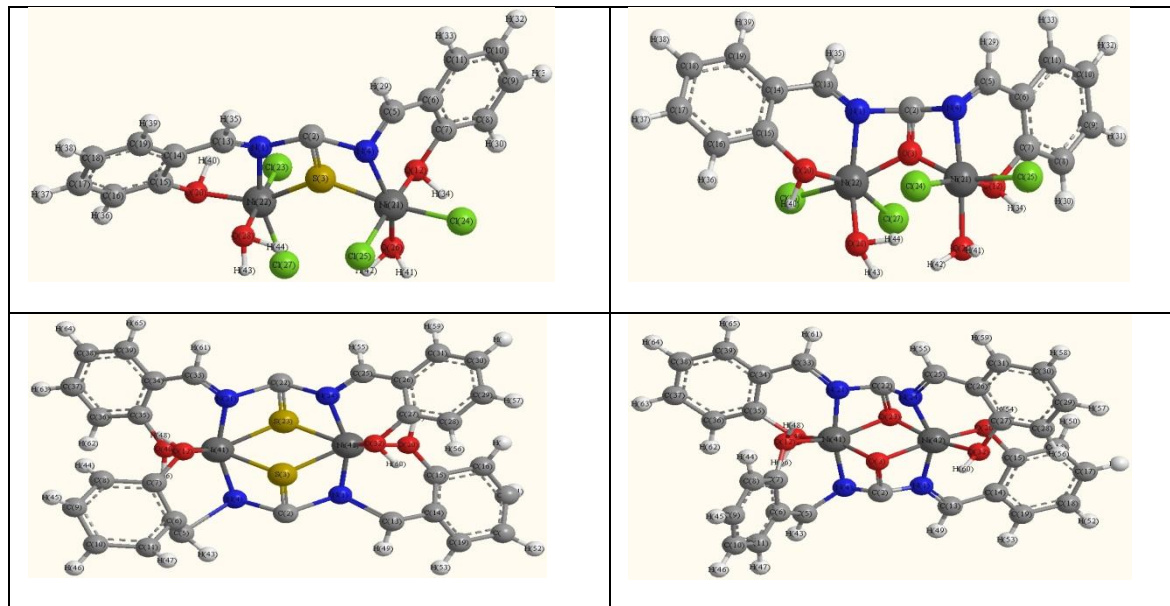

Fig.3: The optimized structural geometry of Mn (II), Co(II) and Ni(II) complexes

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Table (3) : structural parameters, bond length (ºA) and angles(º) of the studied Molecules.

Parameters	[Ni₂(L1)(Cl)₄(H₂O)₂]	[Ni₂(L2)(Cl)₄(H₂O)₂]	Parameters	[Ni₂ (L1)2] Cl4	[Ni₂ (L2)2] Cl4
Bond lengths (ºA)			Bond lengths (ºA)		
Ni(22)-O(28)	**1.8343**	**1.8299**	O(40)-Ni(41)	1.8256	1.8803
Ni(22)-Cl(27)	**2.1494**	**2.1567**	O(32)-Ni(42)	1.8353	1.8809
Ni(22)-Cl(23)	**2.1497**	**2.1533**	N(24)-Ni(42)	1.9776	1.8823
Ni(21)-O(26)	**1.8304**	**1.8307**	S(23)-Ni(42)	**2.1815**	**1.9026**
Ni(21)-Cl(25)	**2.1530**	**2.1484**	S(23)-Ni(41)	2.1782	1.9069
Ni(21)-Cl(24)	2.1469	2.1506	N(21)-Ni(41)	1.9771	1.8799
O(20)-Ni(22)	1.8383	1.8447	O(20)-Ni(42)	1.8322	1.8834
O(12)-Ni(21)	1.8390	1.8370	O(12)-Ni(41)	1.8330	1.8752
N(4)-Ni(21)	**1.9720**	1.9099	N(4)-Ni(41)	1.9544	**1.9098**
N(4)-C(5)	**1.3972**	**1.7970**	S(3)-Ni(42)	**2.1846**	1.8974
S(3)-Ni(22)	**2.1600**	1.7912	S(3)-Ni(41)	2.1863	**1.8724**
S(3)-Ni(21)	**2.1545**	**1.9122**	N(1)-Ni(42)	**1.9561**	**1.5120**
C(2)-N(4)	**1.6431**	**1.2763**	N(1)-C(13)	**2.0216**	1.2850
C(2)-S(3)	**1.5151**	1.4893	N(1)-C(2)	1.8034	
N(1)-Ni(22)	**1.9560**	**1.2763**			
N(1)-C(13)	**1.3251**	1.4893			
N(1)-C(2)	1.7026				
			Bond angles(º)		
Bond angles(º)					
H(44)-O(28)-Ni(22)	**118.6810**	**118.6810**	O(32)-Ni(42)-N(24)	**83.2091**	**163.8309**
H(43)-O(28)-Ni(22)	**90.3369**	**90.3369**	O(32)-Ni(42)-S(23)	**130.5042**	**79.4543**
H(42)-O(26)-H(41)	**69.7042**	**69.7042**	O(32)-Ni(42)-O(20)	**85.9854**	**105.6003**
H(42)-O(26)-Ni(21)	**95.3405**	**95.3405**	O(32)-Ni(42)-S(3)	**106.6801**	**84.8656**
H(41)-O(26)-Ni(21)	**114.9849**	**114.9849**	O(32)-Ni(42)-N(1)	**112.2182**	**67.1409**
O(28)-Ni(22)-Cl(27)	**98.9642**	**98.9642**	N(24)-Ni(42)-S(23)	**56.7236**	**95.1273**
O(28)-Ni(22)-Cl(23)	**83.0925**	**83.0925**	N(24)-Ni(42)-O(20)	**110.5235**	**83.4080**
O(28)-Ni(22)-O(20)	**84.2373**	**84.2373**	N(24)-Ni(42)-S(3)	**100.4707**	**107.2121**
O(28)-Ni(22)-O(3)	**104.0627**	**104.0627**	N(24)-Ni(42)-N(1)	**155.4345**	**98.1547**
O(28)-Ni(22)-N(1)	**145.3750**	**145.3750**	S(23)-Ni(42)-O(20)	**131.9970**	**165.5149**
Cl(27)-Ni(22)-Cl(23)	**84.0301**	**84.0301**	S(23)-Ni(42)-S(3)	**60.2856**	**67.0753**
Cl(27)-Ni(22)-O(20)	**161.5967**	**161.5967**	S(23)-Ni(42)-N(1)	**99.7446**	**92.5066**
Cl(27)-Ni(22)-O(3)	**118.5974**	**118.5974**	O(20)-Ni(42)-S(3)	**147.7945**	**99.5067**
Cl(27)-Ni(22)-N(1)	**84.8231**	**84.8231**	O(20)-Ni(42)-N(1)	**90.2092**	**101.9704**
Cl(23)-Ni(22)-O(20)	**80.3198**	**80.3198**	S(3)-Ni(42)-N(1)	**57.6385**	**148.3464**
Cl(23)-Ni(22)-O(3)	**150.2295**	**150.2295**	O(40)-Ni(41)-S(23)	**129.4929**	**93.6655**
Cl(23)-Ni(22)-N(1)	**109.3224**	**109.3224**	O(40)-Ni(41)-N(21)	**103.2669**	**79.6598**
O(20)-Ni(22)-O(3)	**115.8084**	**115.8084**	O(40)-Ni(41)-O(12)	**92.3550**	**155.7785**
O(20)-Ni(22)-N(1)	**78.9966**	**78.9966**	O(40)-Ni(41)-N(4)	**94.8819**	**103.9710**
O(3)-Ni(22)-N(1)	**58.4747**	**58.4747**	O(40)-Ni(41)-S(3)	**152.6107**	**71.2174**
O(26)-Ni(21)-Cl(25)	**90.0332**	**90.0332**	S(23)-Ni(41)-N(21)	**56.7769**	**149.4436**
O(26)-Ni(21)-Cl(24)	**84.5690**	**84.5690**	S(23)-Ni(41)-O(12)	**125.6774**	**94.4583**
O(26)-Ni(21)-O(12)	**85.1865**	**85.1865**	S(23)-Ni(41)-N(4)	**101.5920**	**86.9715**
O(26)-Ni(21)-N(4)	**175.4088**	**175.4088**	S(23)-Ni(41)-S(3)	**60.3083**	**105.6350**
O(26)-Ni(21)-O(3)	**114.8200**	**114.8200**	N(21)-Ni(41)-O(12)	**84.1733**	**103.7889**
Cl(25)-Ni(21)-Cl(24)	**93.6829**	**93.6829**	N(21)-Ni(41)-N(4)	**157.7395**	**66.2541**
Cl(25)-Ni(21)-O(12)	**92.7561**	**92.7561**	N(21)-Ni(41)-S(3)	**102.3574**	**100.3677**
Cl(25)-Ni(21)-N(4)	**94.4751**	**94.4751**	O(12)-Ni(41)-N(4)	**108.1177**	**99.2163**
Cl(25)-Ni(21)-O(3)	**155.1451**	**155.1451**	O(12)-Ni(41)-S(3)	**99.7158**	**84.6191**
Cl(24)-Ni(21)-O(12)	**167.8937**	**167.8937**	N(4)-Ni(41)-S(3)	58.0387	166.5818
Cl(24)-Ni(21)-N(4)	**94.2594**	**94.2594**			
Cl(24)-Ni(21)-O(3)	**88.6625**	**88.6625**			
O(12)-Ni(21)-N(4)	**95.4468**	**95.4468**			
O(12)-Ni(21)-O(3)	**89.7969**	**89.7969**			
N(4)-Ni(21)-O(3)	**60.6701**	**60.6701**			
H(40)-O(20)-Ni(22)	84.1868	84.1868			

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Biological Activity: The antibacterial activity of the Schiff bases and its complexes were tested on Gram positive bacteria, Staphylococcus aureus and Gram negative, E. coli. The antibacterial activities of the samples were evaluated by measuring the inhibition zone observed around the tested materials as shown in fig.(4).
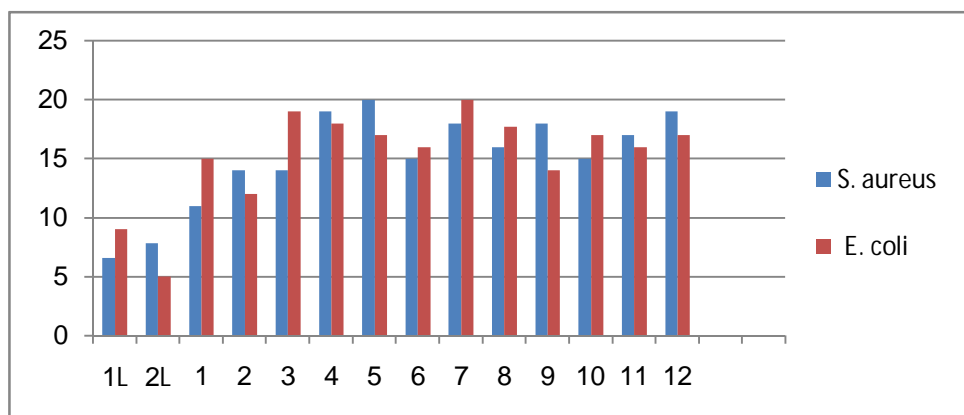
Fig(4): The effect of ligands and their metal complexes toward bacteria

APPLICATIONS

The presence of nitrogen, sulphur and oxygen atoms in the structure of an organic chelating agent has led to interesting results in the studies of coordination compounds. Prepared two types of Schiff base ligands derived from urea and thiourea and their complexes. The synthetic and structural study of above new type of octahedral complexes have bidentate ligands. The study of biological activity of the ligands and their metal complexes against two selected type of bacteria which included Escherichia coli, as gram negative (-Ve) and Staphylococcus aureus as gram positive (+Ve) to be cultivated and as control for the disc sensitivity test shows that different activity of inhibition on growth of the bacteria.

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