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Spectroscopic characterization, theoretical treatment and antibacterial Co(II), Ni(II) and Zn(II) of phenazone derived NNO and NNN donor Schiff-bases

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ABSTRACT

A series of biologically active phenazone (4-aminoantipyrine) – derived Schiff-base ligands have been synthesized by the condensation reaction of 4-aminoantipyrine with picolinaldehyde and furan-2-carbaldehyde. Then their Cobalt (II), Nickel (II) and Zinc (II) complexes have been prepared and characterized by different analytical and spectral methods: FT-IR, electronic spectral studies, magnetic susceptibility measurements, atomic absorption, Molar conductivity measurements, molar ratio studies and melting points. The molar conductance measurements of the complexes in DMSO correspond to be electrolytic nature for all prepared complexes. On the basis of FT-IR and electronic spectral studies all complexes display an octahedral geometry around the metal center in (1:1) (L:M). A theoretical treatment of the formation of complexes in the gas phase was studied, this was done using the HYPERCHEM-6 program for the Molecular mechanics and Semi-empirical calculations. The biological evaluation of the free ligand in comparison to their complexed have been determined against bacterial strains e.g., Escherichia coli and Staphylococcus. Finally, it was found that compounds show different activity of inhibition on growth of the bacteria.

INTRODUCTION

Schiff-bases and metal complexes are important intermediates in certain biological processes[1-3]. Much work has been reported on the Schiff-bases, due to their interesting ligational as well as biological behavior[4-6]. Despite the controversy that all viruses are cancer-producing agents but, there is no longer any question that certain types of cancer are virus caused, if not all, most of the cancers have one or more viruses associated with them[5]. Science viruses contain proteins and nucleic acid units and some atoms of which are excellent coordinating agents, therefore, it attracts the attention of researches to study their interesting ligational and biological behavior. Previously we have extensively studied[7,8]. The possibility of altering the biological activity via its coordination and /or chelation to the metal atoms with the expectation that this alteration will result in the elimination or diminution of its biological activity[9,10]. In continuation to the same, we now wish to report novel biologically active Schiff-base compounds (Figure 1) chelation / coordination on their biological activity.

In view of the above in this paper we are reporting the synthesis and spectroscopic characterization of Co (II), Ni (II) and Zn (II) complexes with a novel Schiff base tridentate ligand (Figure 1).

EXPERMENTAL

Physical measurements

A Fisher-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. 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. Room temperature magnetic susceptibility measurements were carried out on a B.M 6 BRUKER type magnets, balance, Diamagnetic correction was done using pascal constants.

Materials

All the chemicals used were of Analar grade, and procured from (BDH chemicals or Sigma-Aldrich). metal salts were used as chlorides.

(A) Preparation of Schff-base ligands

The hot ethanolic solution (20 ml), of 4-amino antipyrine (0.204 g, 0.01 mole), and a hot ethanolic solution (20 ml), of picolinaldehyde (0.107 g, 0.01 mole) were mixed slowly with constant stirring. this mixture was refluxed at ~ 75°C for 2 hr. in the presence of 2-3 drops of concentrated hydrochloric acid. Cooling gave an off-white precipitate, which was filtered, washed with cold EtOH, then with ether and dried. crystallization in hot ethanol gave (L1) (yield 79%), m.p.148-150°C by using the respective reagents in the same molar ratio.

(B) Preparation of complexes of L1

The hot ethanolic solution (20 ml) of L1 (0.76 g, 0.002 mole) and hot ethanolic (20 ml) solution of corresponding metal salt (0.002 mole) were mixed together with constant stirring. the mixture was refluxed for 1 hr. at 55-80 ºC, cooling gives a colored complexes, it was filtered, washed with cold EtOH and dried under vacuum. The physical properties of prepared complexes are listed in TABLE 1. The molar ratio of the complexes was determined according to the methods[11]. All other metal complexes were prepared respectively following the same method

(C) Antibacterial studies

The synthesized complexes, in comparison to the uncomplexed Schiff-base ligands were screened for their antibacterial activity against pathogenic bacterial species, which included Escherichia coli, as gram negative (-Ve) and Staphylococcus aureus as gram positive (+Ve). the paper disc diffusion method[12] was adopted for the determination of antibacterial activity.

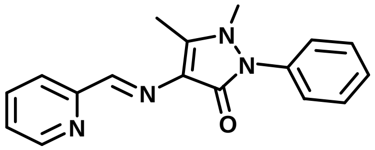
RESULT AND DISCUSION

Physical prosperities

The Schiff–bases (LI and L2) (Figure 1) were prepared by refluxing an appropriate amount of 4-aminoantipyrine and respective aldehyde in hot ethanol in 1:1 molar ratio. the structures of these Schiff-base ligands were established with the help of their IR and UV-Visible (TABLE 1). All of the metal complexes (1-6) (TABLE 2) of these Schiff-bases were an stable and prepared by the stoichiometric reaction of the respective metals as there chlorides and the respective Schiff-bases in molar ratio (M:L=1:2). The complexes are intensity coloed and amorphous solids, which decompose. They are insoluble in common organic solvents like ethanol, methanol or acetone but only soluble in DMSO and DMF. Their solubility nature and elemental analysis data suggest that they are monomers. Molar conductance values of the soluble complexes in DMSO show high value (90-110 ohm cm^2 mol^{-1}) indicating that they are all complexes electrolyteic in nature[13,14].

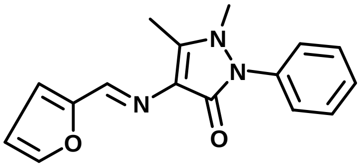
Infrared spectra

IR spectra of the Schiff-bases showed the absence of bands at 1750 and 3310 cm^{-1} due to the carbonyl



(E)-1,5-dimethyl-2-phenyl-4-(pyridin-2-ylmethyleneamino)-1H-pyrazol-3(2H)-one

L1



(E)-4-(furan-2-ylmethyleneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one

L2

Figure 1 : Structure of Schiff-base ligands.

TABLE 1 : Physical and analytical data of the metal(II) complexes

No.	Complexes/ Mol. Formula	Colour	ΔM (Ω^{-1} cm^{2}mol^{-1}) In DMSO	M.P (?C)	Yield (%)	$\mu_{eff.}$ BM	Elemental analysis % found (% Cal.) M%	Cl%
1	[Co(L1)$_2$] Cl$_2$ / $C_{34}H_{32}N_8O_2Co$ /643.60	Light brown	108	188-190	70	4.5	9.12 (9.16)	10.99 (11.03)
2	[Ni(L1)$_2$] Cl$_2$ / $C_{34}H_{32}N_8O_2Ni$ /643.36	Dark Yellow	95	200-202	65	2.98	9.07 (9.12)	10.99 (11.03)
3	[Zn(L1)] Cl$_2$ $C_{34}H_{32}N_8O_2Zn$ /650.19	Light Yellow	100	210-212	60	-	10.01 (10.06)	10.88 (10.91)
4	[Co(L2)$_2$] Cl$_2$ / $C_{32}H_{30}N_6O_4Co$ /621.55	Light brown	90	190-192	75	4.3	9.44 (9.48)	11.38 (11.42)
5	[Ni(L2)$_2$] Cl$_2$ $C_{32}H_{30}N_6O_4Ni$ /621.31	Yellow	110	215-217	70	3.0	9.41 (9.45)	11.38 (11.42)
6	[Zn(L2)] Cl$_2$ $C_{32}H_{30}N_6O_4Zn$ /628.03	Light Yellow	105	195-197	61	-	10.37 (10.42)	11.25 (11.30)

TABLE 2 : IR and electronic spectral data of the metal(II) complexes

No.	Complexes	UV/ VIS λ max (cm^{-1})	IR Spectra cm^{-1} υC=O	υC=N	υ (C-N) Py. Ring or υ(C-O) Furan Ring	υM-N	υM-O
1	[Co(L1)$_2$] Cl$_2$	8865,17410,30115	1680s	1610m	1290m	460w	530w
2	[Ni(L1)$_2$] Cl$_2$	8855,17845,30135	1670s	1605m	1295m	465w	535w
3	[Zn(L1)] Cl$_2$	28500	1665s	1600m	1285m	455w	520w
4	[Co(L2)$_2$] Cl$_2$	9865,15925,29860	1660s	1590m	1500m	460w	515w
5	[Ni(L2)$_2$] Cl$_2$	10105,16225,29815	1685s	1595m	1505m	450w	525w
6	[Zn(L2)] Cl$_2$	28450	1675s	1615m	1507m	455w	530w

υ(C=O) and υ(NH_2) stretching vibrations and instead, a strong new band appeared at ~ 1630 cm^{-1} assigned to the azomethine υ(HC=N) linkage. It is true, suggested[15] that amine and aldehyde moieties of the starting reagents no more existed and have been converted into their respective Schiff-base compounds (Figure 1). The comparison of the infrared spectra of the Schiff-bases and their metal chelates indicated that the Schiff-bases were principally coordinated to the metal atom in three ways, the representing the ligands to act as tridentate. The band appearing at 1630 and 1635 cm^{-1} due to the azomethine shifted to lower frequency by ~ 15-25 cm^{-1} indicating participation of the azomethine nitrogen in the complexation. The band at 1310 cm^{-1} assigned to the pyridine ring (C=N) nitrogen in the Schiff-base ligand (L1). The band at 1520 cm^{-1} assigned to the furan ring (C-O-C) oxygen in the Schiff-base ligand (L2).

The band appearing at 1720 cm^{-1} assigned to υ(C=O) also shifted to the lower frequency by 35-60 cm^{-1} in the spectra of its complexes indicating participation of (C=O) group in the coordination. Further conclusive evidence of the coordination of these Schiff-base compounds with the metal, was shown by the appearance of weak low frequency new bands at 515-535 cm^{-1} and 450-465 cm^{-1} (TABLE 3). These were, assigned to the metal-nitrogen υ(M-O) and metal-oxygen υ(M-N), respectively[16]. These new bands were only observable in the spectra of the metal complexes and not in the spectra of the uncomplexed Schiff-base compounds, thus, confirming participation of the groups (O or N) in the coordination.

Magnetic studies

The room temperature magnetic moment measurements of the solid cobalt (II) complexes was found at 4.3 and 4.5 B.M, indicative of three unpaired electron per Co(II) ion in an octahedral environment[14] TABLE 1..

The Ni(II) complexes showed $\mu_{eff.}$ Values 2.98 and 3.0 B.M, corresponding to two unpaired electrons per Ni(II) ion for their ideal six-coordinated configuration[17] TABLE 1. The Zn(II) complexes were all found diamagnetic.

TABLE 3 : Structural parameters, bond length (°A) and angles(°) of the [Co(L1)] Cl$_2$ complex.

Parameters		Parameters		Parameters	
Bond angles(°)		Co(45)-O(28)-C(25)	143.3443	C(3)-O(6)-Co(45)-N(37)	171.1985
N(37)-Co(45)	1.8360	Co(45)-N(15)-C(4)	69.3212	C(25)-O(28)-Co(45)-N(15)	132.5176
N(40)-Co(45)	1.8360	Co(45)-N(15)-C(16)	104.0000	C(25)-O(28)-Co(45)-N(18)	125.5426
O(6)-Co(45)	0.6000	**Bond lengths (°A)**		C(25)-O(28)-Co(45)-O(6)	175.5585
O(28)-Co(45)	0.6000	N(24)-Co(45)	3.1626	C(25)-O(28)-Co(45)-N(40)	-94.4415
N(18)-Co(45)	1.8360	C(20)-Co(45)	2.7392	C(25)-O(28)-Co(45)-N(37)	-4.4415
N(15)-Co(45)	2.6688	C(19)-Co(45)	2.9952	C(22)-N(18)-Co(45)-N(15)	147.2908
N(40)-C(39)	1.2600	C(8)-Co(45)	2.3442	C(22)-N(18)-Co(45)-O(28)	154.2657
C(44)-N(40)	1.2600	C(7)-Co(45)	2.4245	N(37)-Co(45)-N(40)	90.0000
C(43)-C(44)	1.3370	N(2)-Co(45)		N(37)-Co(45)-O(6)	180.0000
N(37)-Co(45)-N(40)	90.0000	N(37)-Co(45)	1.8360	N(37)-Co(45)-O(28)	90.0000
N(37)-Co(45)-O(6)	180.0000	N(40)-Co(45)	1.8360	N(37)-Co(45)-N(18)	90.0000
N(37)-Co(45)-O(28)	90.0000	O(6)-Co(45)	0.6000	N(37)-Co(45)-N(15)	136.9590
N(37)-Co(45)-N(18)	90.0000	O(28)-Co(45)	0.6000	N(40)-Co(45)-O(6)	90.0000
N(37)-Co(45)-N(15)	136.9590	N(18)-Co(45)	1.8360	N(40)-Co(45)-O(28)	89.7331
N(40)-Co(45)-O(6)	90.0000	N(15)-Co(45)	2.6688	N(40)-Co(45)-N(18)	90.2669
N(40)-Co(45)-O(28)	89.7331	N(40)-C(39)		N(40)-Co(45)-N(15)	133.0404
N(40)-Co(45)-N(18)	90.2669	1.2600C(4)-O(16)	1.2087	O(6)-Co(45)-O(28)	90.0000
N(40)-Co(45)-N(15)	133.0404	C(4)-C(5)	1.5232	O(6)-Co(45)-N(18)	90.0000
O(6)-Co(45)-O(28)	90.0000	N(3)-C(4)	1.3764	O(6)-Co(45)-N(15)	43.0410
O(6)-Co(45)-N(18)	90.0000	C(2)-O(15)	1.2054	O(28)-Co(45)-N(18)	180.0000
O(6)-Co(45)-N(15)	43.0410	C(2)-N(3)	1.3831	O(28)-Co(45)-N(15)	90.0000
O(28)-Co(45)-N(18)	180.0000	N(1)-C(14)	1.3912	N(18)-Co(45)-N(15)	90.0000
O(28)-Co(45)-N(15)	90.0000	N(1)-C(2)	1.3880	H(77)-C(44)-N(40)	120.0000
N(18)-Co(45)-N(15)	90.0000	N(24)-C(25)	1.2660	Co(45)-N(18)-C(17)	104.0000
H(77)-C(44)-N(40)	120.0000	N(23)-N(24)	2.8432	Co(45)-N(18)-C(22)	120.0000
H(77)-C(44)-C(43)	120.0000	N(18)-C(17)	1.2600	C(17)-N(18)-C(22)	115.0000
N(40)-C(44)-C(43)	120.0000	C(22)-N(18)	1.2600	N(18)-C(17)-C(19)	53.3897
H(76)-C(43)-C(44)	145.7395	C(21)-C(22)	1.3370	N(18)-C(17)-C(16)	130.2423
H(76)-C(43)-C(42)	145.7395	C(20)-C(21)	2.1697	C(19)-C(17)-C(16)	176.3430
C(44)-C(43)-C(42)	68.5211	C(19)-C(20)	1.3370	H(57)-C(16)-N(15)	135.4723
H(75)-C(42)-C(43)	139.3272	C(17)-C(19)	1.3370	H(57)-C(16)-C(17)	135.4723
H(75)-C(42)-C(41)	139.3272	C(4)-N(15)	1.2600	N(15)-C(16)-C(17)	89.0553
C(43)-C(42)-C(41)	81.3457	N(15)-C(16)	1.2600	Co(45)-N(15)-C(4)	69.3212
H(74)-C(41)-C(42)	120.0000	C(16)-C(17)	2.3385	Co(45)-N(15)-C(16)	104.0000
H(74)-C(41)-C(39)	120.0000	N(1)-C(14)	1.4700	C(38)-N(37)-Co(45)-N(15)	153.7041
C(42)-C(41)-C(39)	120.0000	C(5)-C(13)	1.4970	C(38)-N(37)-Co(45)-N(18)	63.7041
Co(45)-N(40)-C(39)	104.0000	N(2)-C(7)	1.2660	C(38)-N(37)-Co(45)-O(28)	-116.2959
Co(45)-N(40)-C(44)	120.0000	C(7)-C(12)	1.3370	C(38)-N(37)-Co(45)-O(6)	56.3478
C(39)-N(40)-C(44)	115.0000	C(11)-C(12)	1.3370	C(38)-N(37)-Co(45)-N(40)	-26.5628
N(40)-C(39)-C(41)	93.4500	C(10)-C(11)	1.3370	C(26)-N(37)-Co(45)-N(15)	-85.5618
N(40)-C(39)-C(38)	119.0526	C(9)-C(10)	1.3370	C(26)-N(37)-Co(45)-N(18)	-175.5618
C(41)-C(39)-C(38)	147.4939	C(8)-C(9)	1.3370	C(26)-N(37)-Co(45)-O(28)	4.4382
H(73)-C(38)-N(37)	122.7712	C(7)-C(8)	1.3370	C(26)-N(37)-Co(45)-O(6)	176.6546
H(73)-C(38)-C(39)	122.7712	C(3)-O(6)	1.2080	C(26)-N(37)-Co(45)-N(40)	94.1713
N(37)-C(38)-C(39)	114.4576	N(1)-C(5)	1.2660	C(44)-N(40)-Co(45)-N(15)	-32.1949
Co(45)-N(37)-C(26)	104.0000	C(4)-C(5)	1.3370	C(44)-N(40)-Co(45)-N(18)	58.0543
Co(45)-N(37)-C(38)	104.0000	C(3)-C(4)	1.3510	C(44)-N(40)-Co(45)-O(28)	-121.9457
C(26)-N(37)-C(38)	115.0000	N(2)-C(3)	1.2660	C(44)-N(40)-Co(45)-O(6)	-31.9457
H(72)-C(36)-H(71)	109.5200	N(1)-N(2)	1.6755	C(44)-N(40)-Co(45)-N(37)	148.0543
H(72)-C(36)-H(70)	109.4618	**Dihedral angles(°)**		C(39)-N(40)-Co(45)-N(15)	-162.5022
H(72)-C(36)-N(23)	109.4618	C(3)-O(6)-Co(45)-N(15)	73.9744	C(39)-N(40)-Co(45)-N(18)	-72.2529
H(71)-C(36)-H(70)	109.4418	C(3)-O(6)-Co(45)-N(18)	163.9744	C(39)-N(40)-Co(45)-O(28)	107.7471
H(71)-C(36)-N(23)	109.4418	C(3)-O(6)-Co(45)-O(28)	-16.0256	C(39)-N(40)-Co(45)-O(6)	-162.2529
H(70)-C(36)-N(23)	109.5000	C(3)-O(6)-Co(45)-N(40)	-105.7587	C(39)-N(40)-Co(45)-N(37)	17.7471

Electronic absorption spectroscopy

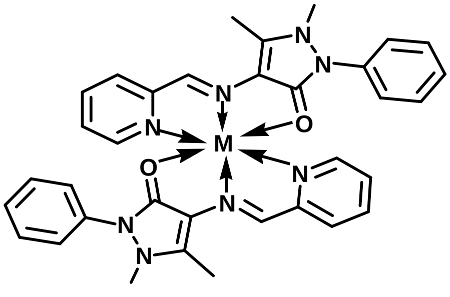
The electronic spectra of all the cobalt (II) complexes display absorption at 8765-8855, 17410-17845 and 30115-30135 cm^{-1}. these bands may be assigned to the transitions : $^4T_1g\ (F) \rightarrow {}^4T_2g\ (\upsilon_1)$, $^4T_1g \rightarrow {}^4A_2g\ (\upsilon_2)$ and $^4T_1g\ (F) \rightarrow {}^4T_2g\ (P)\ (\upsilon_3)$, respectively[18]. The position of electronic spectral bands indicates that these complexes have octahedral geometry[16,18,19] around the cobalt ions.

The electronic spectra of the Ni(II) complexes TABLE 1 exhibit three spin-allowed bands at 9865-10105, 15925-16225 and 29860-29815 cm^{-1} assignable respectively[17], to the transitions[21,23], $^3A_2g\ (F) \rightarrow {}^3T_2g\ (F)$, $^3A_2g\ (F) \rightarrow {}^3T_1g\ (F)$, $^3A_2g\ (F) \rightarrow {}^3T_1g\ (P)$ which were characteristic of their octahedral geometry[20].

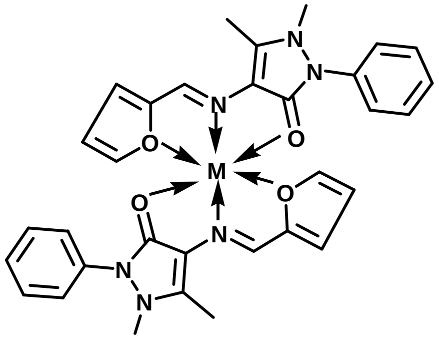
The diamagnetic Zn(II) complexes did not show any d-d bands and their spectra are dominated only by the charge transfer bands. The charge transfer band at 28450-28500 cm-1 was assigned due to transition $^2Eg \rightarrow {}^2T_2g$ possibly in an octahedral environment[21].

The proposed structure

On the basis of the above observations, it is tentatively suggested that Co(II), Ni(II) and Zn(II) complexes show an octahedral geometry (Figure 2) in which the two ligands act as tridentate and possibly accommodate themselves around the metal atom in such the way that a stable geometry of molecule is formed.



Metal complex of L1



Metal complex of L2

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

Theoretical study

The ball and cylinders and some of selected structural parameters (bond length and angles) of the optimized geometries are shown in figure 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.

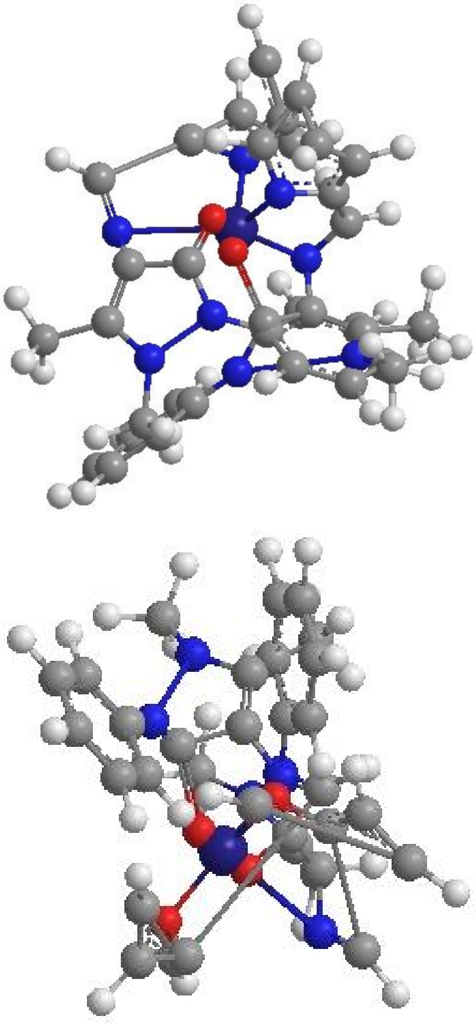


Figure 3 : The optimized structural geometry of Co(II) complex

Antibacterial properties

The Schiff-base ligands and their transition metal complexes dictates were evaluated for their antibacterial activity against bacterial species Escherichia coli and Staphylococcus aureus of bacteria[22,23]. The compounds were tested at a concentration of 10^{-3} M in DMSO solution using the paper disc diffusion method. The susceptibility zones were measured in diameter (mm) and the results are reproduced in (Figure 4). The susceptibility zones measured were the clear zones around the discs killing the bacteria.

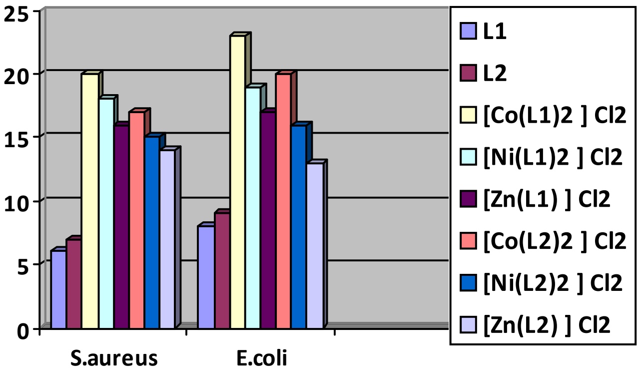


Figure 4 : The effect of ligands and their metal complexes toward bacteria

All the Schiff-bases and their complexes individually varying degrees of inhibitory effects on the growth of the tested bacterial species. The antibacterial results evidently show that the activity of the Schiff-base compounds became more pronounced when coordinated to the metal ions.

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