

SYNTHESIS, CHARACTERIZATION AND THEORETICAL TREATMENT OF SANDWICH SCHIFF BASES COMPLEXES DERIVED FROM SALICYLALDEHYDE WITH SOME TRANSITION METALS AND STUDY OF ITS BIOLOGICAL ACTIVITY

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ABSTRACT

Cobalt (II), Nickel (II) and Copper (II) complexes of Schiff Bases derived from Salicylaldehyde and 3,3'-diamino-diphenyl methane (L₁), 3,3'-diamino-diphenyl ether (L₂), 3,3'-diamino-diphenyl Sulphone (L₃), were prepared and characterized by different analytical and spectral methods: elemental analysis, IR, UV-VIS, atomic absorption, Molar conductivity measurements, molar ratio studies and melting points. The Schiff bases behave as neutral tetra dentate ligands. The chloro - complexes ligands (L₁, L₂ and L₃) with (2:2) Molar ratio showed a Sandwich structural. All complexes display an octahedral geometry around the metal center. Conductance data of the complexes suggested them to be non-electrolytes.

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 free ligand and its complexes have been tested for their antibacterial activities against Two type of human pathogenic bacteria: (*Staphylococcus aureus*), (*Escherichia coli*). The first group are Gram positive while the second group 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.

Keywords: Synthesis, Characterization, Salicylaldehyde, Complexes, Schiff Bases.

INTRODUCTION

3,3'-diamino-diphenyl-methane (DDM), known as 4,4'-methylene dianiline (MDA), is used as intermediate in the manufacture of polyurethane foams. It is preventative for iron, antioxidant for lubricating oils, rubber processing and preparation of azo-dyes^{1,2}. MDA is a hazardous substance that causes liver damage, skin and eye irritation¹⁻³. On the other hand, it was reported that some Schiff bases of aniline derivatives display anti-inflammatory and antipyretic properties. These properties increased with copper (II) complexes⁴.

Bis-(4-aminophenyl-methane) salicylaldehydeimine ligand and its metal complexes were also synthesized and characterized⁵. The complexes were found to be active against some microorganisms.

3,3'-diamino-diphenyl sulphone, a potential dyware and pharmaceutical reagent⁶⁻⁸ have been found to form octahedral and tetragonally distorted octahedral complexes with nickel (II) ion.

In the present work, metal complexes of different Schiff's bases of salicylaldehyde with 3,3'-diamino-diphenyl methane (L₁), 3,3'-diamino-diphenyl ether (L₂) or 3,3'-diamino-diphenyl Sulphone (L₃) were prepared and characterized. This is as carried out in an attempt to investigate the effect of donor atoms (N,O) on the coordination made of the ligand. The metal complexes obtained were characterized by different analytical and spectral methods.

MATERIALS AND METHODS

Instrumentation

A Fisher-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 microanalyzer 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. Room temperature magnetic susceptibility measurements were carried out on a B.M 6 BRUKER type magnets, balance, Diamagnetic correction was done using Pascal constants⁸.

Materials

All the chemicals used were reagent grade (BDH chemicals or Aldrich).

Preparation of the ligands

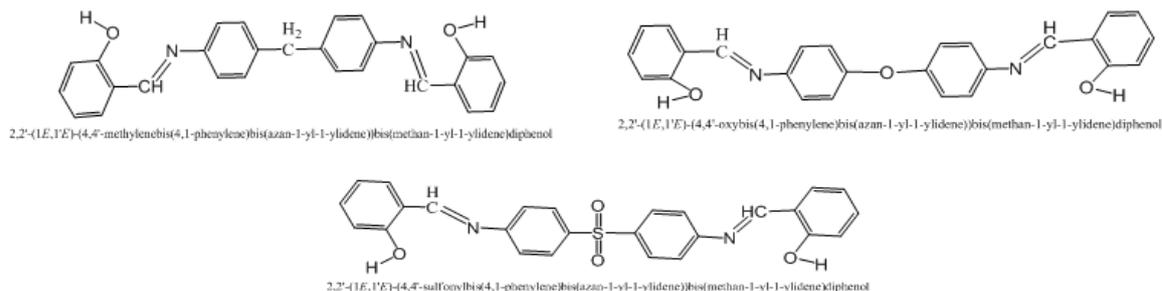
Schiff's bases were prepared according by addition of salicylaldehyde to 3,3'-diamino-diphenyl methane (L₁), 3,3'-diamino-diphenyl ether (L₂) or 3,3'-diamino-diphenyl Sulphone (L₃) in (2:1) molar ratio in ethanol. The reaction mixture was stirred in air at 50 °C for 30 min. The found precipitate was filtered off, washed with ethanol several times and dried. The general structures of ligands obtained from chemical analysis and spectral methods, are given in scheme (1). The full name of the Schiff's bases will be replaced by a number (L₁, L₂, L₃) respectively as in shown in table (1) for the rest of this paper. The physical properties of these compounds (L₁, L₂, L₃) are listed in table (1). The characters IR bands and UV/VIS spectrum in DMSO as shown in table (3).

General procedure for preparation of complexes

Co(II), Ni(II) and Cu(II) complexes of all ligands were prepared by the addition of (0.02 mole) of the metal chloride dissolved in absolute ethanol to a hot ethanol solution of (0.02 mole) of ligand. The reactants were stirred for 2h at 70 °C. The precipitates obtained were filtered off, washed with ethanol and dried in vacuum and stored in a desiccator over CaCl₂/P₄O₁₀ for two weeks to give colored complexes. The physical properties of prepared complexes are listed in table (2). The molar ratio of the complexes was determined according to the methods⁸.

Study of biological activity for ligands (L₁, L₂, L₃) and their metal complexes

The biological activity of the ligands and their metal complexes were studied against two selected types 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 test⁹, 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 37°C, the zone of inhibition of bacteria growth around the disc was observed.



Scheme 1: The general structures of ligands.

RESULT AND DISCUSSION

The structure of prepared ligands was elucidated from their spectroscopic properties and by comparing with the literature wherever possible^{10,11}. The compounds are stable with high melting point (>230 °C).

All the complexes are stable and non-hygroscopic. The metal complexes of the (L₁, L₂ and L₃) are insoluble in most organic solvents. This behavior could be attributed to the nature of the complexes⁹, the metal complexes are soluble in DMF and DMSO solvents.

Semi-empirical methods are done on hyperchem program version (6) running on a windows XP work station with a Pentium IV PC.

Geometry optimization has been carried out by using a conjugate gradient method¹².

Microanalysis

The elemental analysis data shown in table (1) for the schiff's bases found to be consistent with the expected results. The obtained data exhibited the formation of the complexes in the Molar ratio (2:2) ligand to metal (M:L) by molar-ratio method as shown in fig.(1) that is agreement with the ratio found, according to elemental analysis table(2). The stoichiometric ratio of the complexes predictable the formula of the type [M₂(L)₂Cl₄], in which M represents Co(II) ions, Ni(II) ions and Cu(II) ions complexes.

Table 1: Physical properties and IR Spectra of the ligands (L₁, L₂, L₃).

No.	Yield %	colour	M.P°C	Elemental analysis % found (% cal.)			IR Spectra cm ⁻¹
	M. Wt.	Chemical Formula		C	H	N	
L ₁	85	Pale yellow	>230	79.75 (79.80)	5.38 (5.41)	7.33 (7.38)	ν ^{C=N} 1650, ν ^{C-O} 1145, ν ^{O-H} 3400 s
	406.48	C ₂₇ H ₂₂ N ₂ O ₂					
L ₂	80	Pale yellow	>230	76.42 (76.47)	4.84 (4.90)	7.29 (7.35)	ν ^{C=N} 1640, ν ^{C-O} 1145, ν ^{O-H} 3400 s
	408.45	C ₂₆ H ₂₀ N ₂ O ₃					
L ₃	75	Pale yellow	>230	73.52 (73.58)	4.67 (4.71)	7.02 (7.07)	ν ^{C=N} 1635, ν ^{C-O} 1145, ν ^{O-H} 3400 s
	456.51	C ₂₆ H ₂₀ N ₂ O ₄ S					

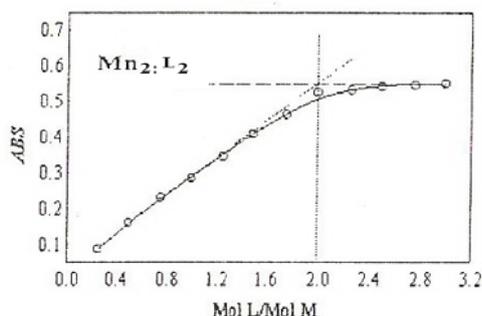


Fig. 1: Molar-ratio curve for some of prepared complexes

Molar Conductance Measurements

The molar conductance values of the complexes as shown in table (2) carried out in DMSO solvent in 10⁻³ M at 25 °C indicate that the complexes are non-electrolytic nature¹³. The values suggest that no ions present outside the coordination spheres.

IR Spectra

The spectra of the ligands show a band within the range (1635-1650) cm⁻¹ which is assigned to ν^{C=N} of azomethine group^{11,14}table (2). The observed low frequency shift of ν^{C=N} for all complexes relative to that of the corresponding free ligand is due to the participation of azomethine group in coordination. The spectra are also characterized by a new band in range (400-490) cm⁻¹ assigned to ν^{M-N}^{15,16} which indicating the involving of nitrogen atoms in coordination with metallic ion.

The infrared spectra of the complexes under investigation display a band at 950 cm⁻¹ which is due to the presence of a coordinate OH group and the band at 3400 cm⁻¹ is due to the presence of OH group in the complexes from its chemical structure. In metal complexes a new peak is found (1210-1240) cm⁻¹ for ν^{C-O} which is very characteristic and ν^{O-H} was broad at (3300) cm⁻¹¹⁷. The coordination through oxygen atom of hydroxyl group was also confirmed by the appearance of a medium new band at 500-550 cm⁻¹ which is assigned to ν^{M-O}^{15,18}.

In addition, a weak absorption band also been observed at (350-375) cm⁻¹ in all complexes which may be due to ν^{M-Cl} vibration¹⁹.

The anti symmetric and symmetric SO₂ vibrations absorb in the region (1300-1255) cm⁻¹ and (1140-1100) cm⁻¹, respectively in the free ligand^{20,21}. The unaltered position of these bands on composition suggests that sulphur is not taking part in coordination.

Table 2: Physical characterization, analytical and Molar Conductance data of the compounds

Compound	Yield %	Colour	$\Delta M/S \text{ cm}^2 \text{ mol}^{-1}$ In DMSO	M.P C°	μ_{eff} (BM)	Elemental analysis (% found) % cal	
						Cl	M
						[Co ₂ (L ₁) ₂ Cl ₄]	65
[Ni ₂ (L ₁) ₂ Cl ₄]	60	Redish.B	8	>230	3.10	(13.15) 13.20	(10.88) 10.91
[Cu ₂ (L ₁) ₂ Cl ₄]	70	Yellowish.G	6	>2390	1.75	(12.66) 12.71	(11.31) 11.36
[Co ₂ (L ₂) ₂ Cl ₄]	75	Blue	7	>230	4.90	(13.15) 13.19	(10.89) 10.94
[Ni ₂ (L ₂) ₂ Cl ₄]	66	Greensh.B	9	>230	3.28	(13.16) 13.20	(10.87) 10.91
[Cu ₂ (L ₂) ₂ Cl ₄]	80	Deep Blue	10	>230	1.02	(13.03) 13.08	(11.65) 11.70
[Co ₂ (L ₃) ₂ Cl ₄]	70	Pale Yellow	12	>230	4.85	(12.77)12.81	(10.59)10.63
[Ni ₂ (L ₃) ₂ Cl ₄]	65	Pale Yellow	11	>230	3.05	(12.78)12.82	(10.55)10.60
[Cu ₂ (L ₃) ₂ Cl ₄]	75	Deep Green	13	>230	0.99	(12.78)12.71	(11.31)11.36

Electronic Absorption Spectra and Magnetic Moment

The electronic absorption spectra of the ligands and its Ni(II) and Cu(II) complexes are recorded at room temperature using DMSO as the solvent.

The electronic absorption spectra of the schiff bases complexes as shown in table (3), from their values the following can be pointed out.

Cobalt Complexes

The spectra of cobalt (II) complexes display a strong band at (410-420) nm and another weak splitted band at (620-700) nm. these bands gather with the μ_{eff} value (4.5-4.8 B.M) indicate an octahedral geometry^{22,23}.

Nickel Complexes

The spectra of Nickel (II) complexes gave three bands in the range (330-350, 420-480 and 690-715) nm, indicating an octahedral geometry^{4,23}. The room temperature magnetic moment values in the range (3.00-3.30 B.M) table (2) These values are in tunes with an octahedral geometry^{24,25} around the Ni(II) ion in the complexes fig.(3).

Copper Complexes

The spectra of Copper (II) complexes display bands at (335-360, 420-480, 520-580 and 690-710) nm. these bands are assigned to distorted octahedral structure²⁶. The geometry obtained was also confirmed by the values of μ_{eff} .

Table 3: Infrared and UV-Visible Spectra data of the prepared compounds

Compound	UV-Visible Spectra (nm)	IR Spectra (Cm ⁻¹)					
		$\nu^{\text{C=N}}$	$\nu^{\text{C=O}}$	$\nu^{\text{O-H}}$	$\nu^{\text{M-O}}$	$\nu^{\text{M-N}}$	$\nu^{\text{M-Cl}}$
[Co ₂ (L ₁) ₂ Cl ₄]	410,620	1625	1210	3300 b	510 m	400 m	375 w
[Ni ₂ (L ₁) ₂ Cl ₄]	330,420,690	1590	1220	3300 b	550 w	450 m	350 w
[Cu ₂ (L ₁) ₂ Cl ₄]	335,425,520,690	1600	1215	3300 b	500 m	430 m	355 w
[Co ₂ (L ₂) ₂ Cl ₄]	420,650	1615	1230	3300 b	515 m	460 m	370 w
[Ni ₂ (L ₂) ₂ Cl ₄]	340,450,700	1610	1235	3300 b	520 m	490 m	365 w
[Cu ₂ (L ₂) ₂ Cl ₄]	350,450,540,700	1595	1225	3300 b	540 m	470 m	360 w
[Co ₂ (L ₃) ₂ Cl ₄]	415,700	1605	1240	3300 b	545 m	480 m	355 w
[Ni ₂ (L ₃) ₂ Cl ₄]	350,480,715	1615	1215	3300 b	530 m	425 m	370 w
[Cu ₂ (L ₃) ₂ Cl ₄]	360,460,580,710	1620	1225	3300 b	535 m	440 m	375 w

The proposed structure

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 fig. (2).

Theoretical Study

The ball and cylinders and some of selected structural parameters (bond length and angles) of the optimized geometries are shown in fig. (3), table (4).

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

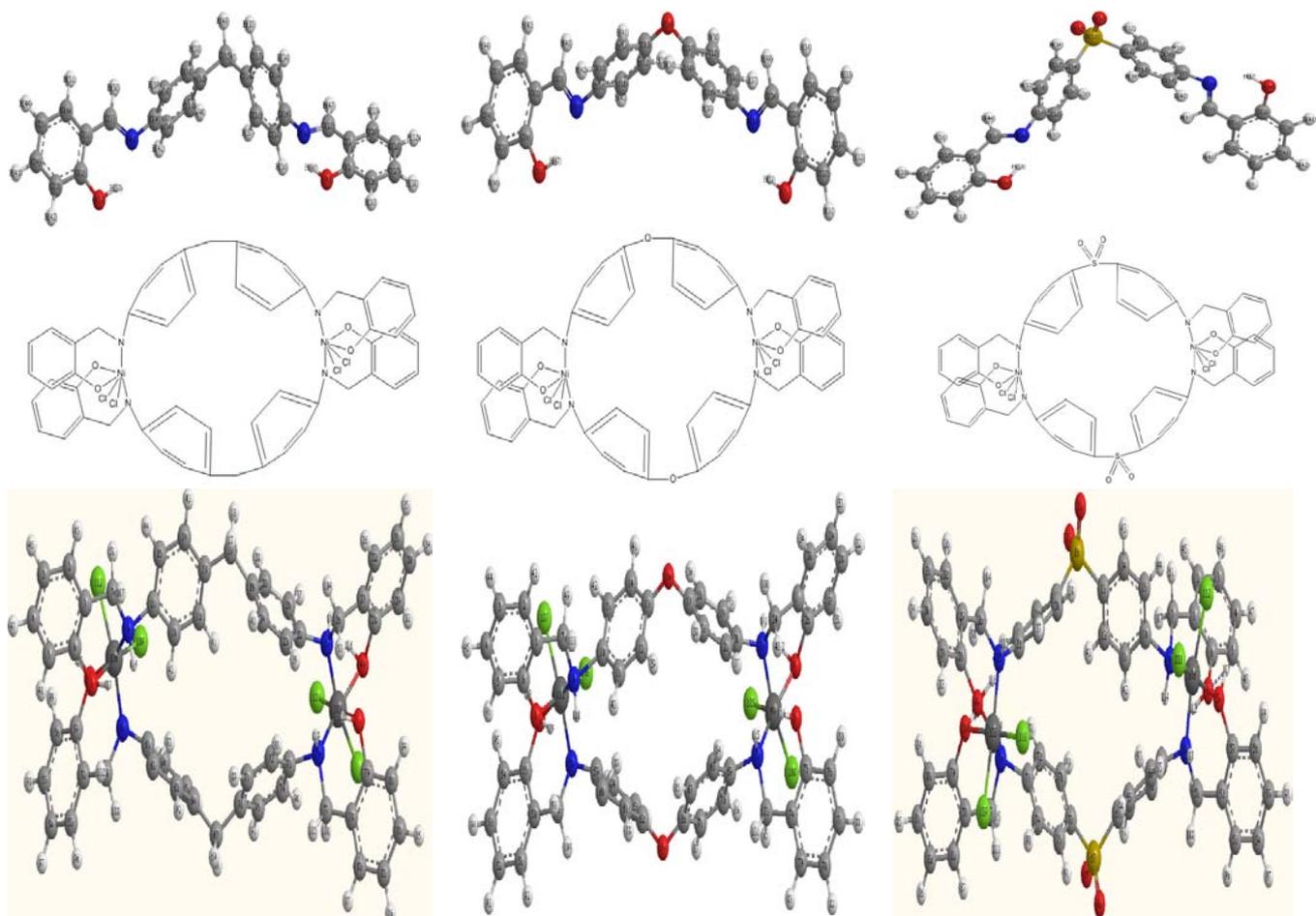


Fig. 3: The optimized structural geometry of Co(II), Ni(II) and Cu(II) complexes

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.

Table 4: structural parameters, bond length (Å) and angles(°) of the studied Molecules.

Parameter		
Bond lengths (Å)		
O(59)-Ni(106)	1.8468	
N(60)-Ni(106)	1.8478	
O(8)-Ni(106)	1.8444	
N(9)-Ni(106)	1.8446	
Cl(112)-Ni(106)	2.155	
Cl(111)-Ni(106)	2.1539	
Cl(110)-Ni(103)	2.1534	
Cl(109)-Ni(103)	2.1556	
N(76)-Ni(103)	1.845	
O(100)-Ni(103)	1.8449	
O(49)-Ni(103)	1.8491	
N(25)-Ni(103)	1.8489	
Bond angles(°)		
O(59)-Ni(106)-N(60)	79.2692	
O(59)-Ni(106)-N(9)	163.0008	
N(60)-Ni(106)-N(9)	99.2704	
Cl(109)-Ni(103)-N(25)	162.8649	
Cl(110)-Ni(103)-O(49)	88.7541	
Cl(110)-Ni(103)-N(76)	106.8336	
O(49)-Ni(103)-N(25)	78.7164	
N(76)-Ni(103)-O(100)	80.8928	
O(100)-Ni(103)-N(25)	94.0476	
H(120)-O(100)-Ni(103)	80.147	
H(120)-O(100)-C(79)	101.0006	
Ni(103)-O(100)-C(79)	127.783	
Cl(111)-Ni(106)-Cl(112)	87.2092	
Cl(111)-Ni(106)-O(8)	170.8483	
Cl(111)-Ni(106)-O(59)	88.8125	
Cl(111)-Ni(106)-N(60)	86.3145	
Cl(111)-Ni(106)-N(9)	108.0585	
Cl(112)-Ni(106)-O(8)	90.3713	
Cl(112)-Ni(106)-O(59)	85.9109	
Cl(112)-Ni(106)-N(60)	163.9308	
Cl(112)-Ni(106)-N(9)	96.7165	
O(8)-Ni(106)-O(59)	82.2091	
O(8)-Ni(106)-N(60)	93.7121	
O(8)-Ni(106)-N(9)	80.9847	
Cl(109)-Ni(103)-Cl(110)	87.0567	
Cl(109)-Ni(103)-O(49)	85.1446	
Cl(109)-Ni(103)-N(76)	97.0158	
Cl(109)-Ni(103)-O(100)	89.8015	
Cl(110)-Ni(103)-O(100)	171.9565	
Cl(110)-Ni(103)-N(25)	86.8764	
O(49)-Ni(103)-N(76)	164.3284	
O(49)-Ni(103)-O(100)	83.6004	
N(76)-Ni(103)-N(25)	100.078	
H(113)-O(8)-Ni(106)	80.4034	
C(10)-N(9)-Ni(106)	112.6949	
C(7)-N(9)-Ni(106)	121.5956	

Biological Activity

Antibacterial activity of the ligands and its complexes was tested on Gram positive bacteria, *Staphylococcus aureus* and Gram negative, *E. coli*, using nutrient agar medium by the well diffusion method²⁷. The

antibacterial activities of the samples was evaluated by measuring the inhibition zone observed around the tested materials. The values indicate that all metal complexes have higher activity than the free ligands as shown in fig.(3). Such increase activity of the metal chelates can be explained on the basis of chelation theory²⁸.

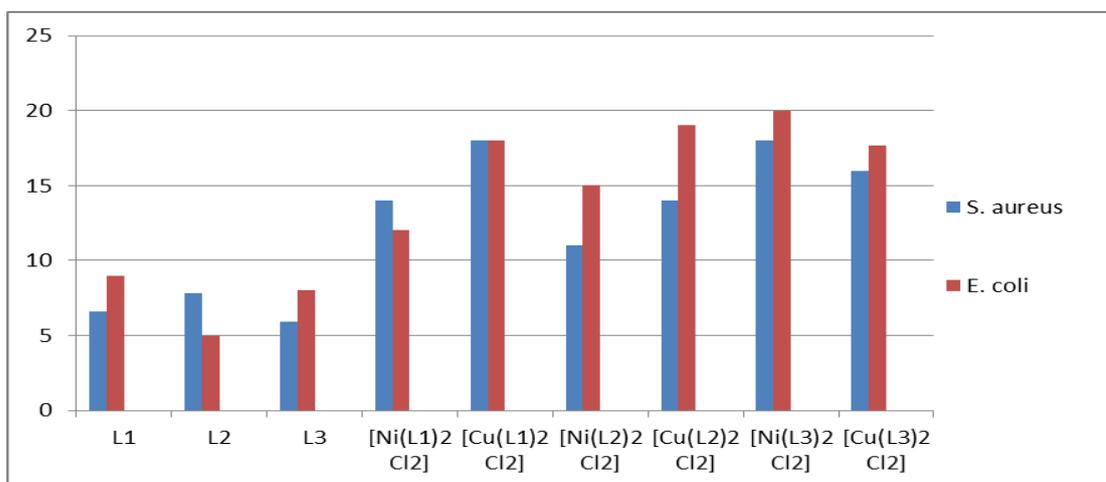


Fig. 4: The effect of ligands and their metal complexes toward bacteria

CONCLUSION

Metal complexes of Schiff's base ligands derived from Salicylaldehyde and 3,3'-diamino-diphenyl methane, 3,3'-diamino-diphenyl ether, 3,3'-diamino-diphenyl Sulphone were prepared and characterized by elemental analysis, FTIR and UV-Vis. Spectra, conductivity measurements and magnetic susceptibilities. General structures of the complexes were shown in fig.(2). The Ni(II) Cu(II) and Co(II) complexes possess show octahedral geometry around the central metal ion.

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