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Synthesis, Spectral and Biochemical Studies of New Complexes of Mixed Ligand Schiff Base and Anthranilic Acid

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ABSTRACT

In this research, new mixed ligand Schiff base complexes of Mn(II), Co(II), Ni(II), Cu(II), Cd(II), and Hg(II) are formulated from the Schiff base (L) resulting from o-phathalaldehyde (o-PA) with p-nitroaniline (p-NA) as a primary ligand and anthranilic acid as a subordinate ligand. Diagnosis of prepared ligand and its complexes is done by spectral methods as mass spectrometer; ^{1}H -NMR for ligand Schiff base FTIR, UV-Vis, molar conductance, elemental microanalyses, atomic absoption and magnetic susceptibility. The analytical studies for the all new complexes have shown octahedral geometries. The study of organicperformance of ligand Schiff base and its complexes show various activity agansit four type of bactria two gram (+) and two gram (-) .

Keyworde: ligand schiff base, microanalyses, biological activity.

INTRODUCTION

Schiff base stands for an imperative type of ligand in chemical coordinating to find comprehensive enforcement in diverse domains as biological, inorganic, analytical, and artificial chemistry branches[1,2]. Schiff bases are derived from aromatic-carbonyl compounds, and they have been more studied in linkage with metal ion[3]. Tetra dentate schiff bases (L_1-L_3), which drevied from the reaction of o-phthalaldehyde with 2-amino benzyl alcohol, 2-amino-2-methyl-1-propanol, and 2-aminobenzohydrazine, have been reacted with $[RuCl_2(DMSO)_4]$. The prepared ligand and their complexes are characterized by spctroscopic methods[4]. Macrocyclic Schiff base metal complexes, derived from o-pathalaldehyde, have recently been reported by Shaker and *et al.,* through Template method[5]. New three complexes are prepared from o-phthalaldrhde with cobalt(II), nickel(II) acetate andperchlorate salts VO(II). The complexes are diagnosed by physiochemical instrument molar conductivity, FTIR, and elemental analysis[6] . Studies towards synthesis of new coordination compounds and their catalytic activities have been continued. Ponnusamy and co-works synthesized (N_4 and

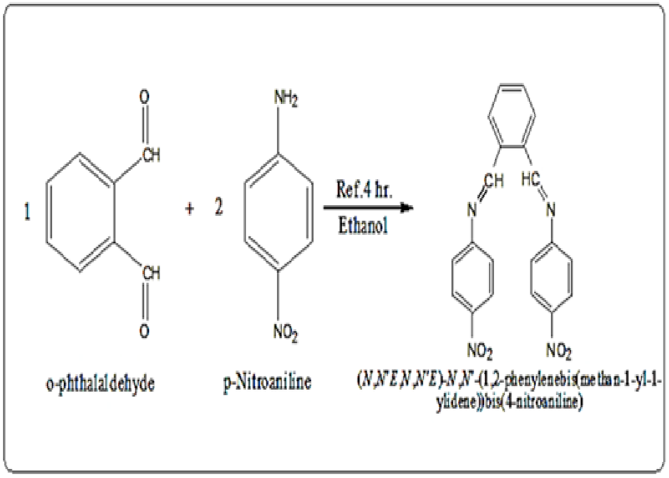
N_2O_2) tetradentate ligands of the o-pathalaldehyde (o-PA) by the non-mould method, and Co, pd and Ru complexes[7]. Schiff base ligand is derived from the concentration of o-phthalaldehyde with the glycyl glycine amino acid. The data have been described using analytical, spectral, thermal, and magnetic data. Further more, these metal complexes have also been applied as potential antibacterial agents[8]. Synthesis and catalytic applications of the Schiff base ligand with metal (II) transition are derived from o-pthalaldehyde[9]. In this work, we have prepared and characterized new complexes with mixed ligand Schiff base and anthranilicacid with some metal ions.

MATERIALS AND DEVICES

All chemicals, used in laboratory work, are of highest purity that does not need any further purity, and they have been purchased from distigushed sources. Melting points are carried out via Stuart Melting Point Kit. Elemental micro analysis of the ligand was conducted by Euro (EA 3000) instrument. ^{1}H NMR spectra are obtained using Brucker DRX system (400 MHz). UV-Vis spectra are performed on a Shimadzu UV- 160A Ultra Violet-Visible Spectrophotometer in KBr discs on (4000-400 cm^{-1} range. The IR-spectra are verified by FTIR - 8400S Spectrophotometer. Metal contents (A.A.S) of the complexes are carried out, using atomic absorption method by means of AA 620G Shimadzu spectrophotometer. The Chloride substances of compounds are specified by testing all complexes and decomposed with Nitric acid, and diluted with water. Results of the magnetic measures are found out by using Bruker BM6 instrument at room temperature and the Faraday’s method.

Synthesis of (N,N'E,N,N'E)-N,N'-(1,2-phenylenebis (methan-1-yl-1-ylidene))bis(4-nitroaniline) (L)

A solution of 4-nitroaniline (0.276g, 2 mol) in 10 ml ethanol has been inserted to a mixture solution of o-phthalaldehyde (0.134g, 1 mol) in 5 ml ethanol and three drops of glacial acetic acid, and the product combination has been refluxed for 4h[10]. The resulted brown solid is composed by filtration, recrystallisation from aceton absolute, and dried under m.p (189 °C), yield 87% Schem-1.



Scheme 1. The synthesis route of the ligand L

Synthesis of the Mixed Ligand Complexes

A solution of Schiff base ligand (0.374 g, 1 mmol) in 5 ml absolute ethanol, (anthranilic acid 0.274 g and NaOH 0.08 g) 2 mmol are added to stirred (1 mmol of metal chlorid) in 10 ml ethanol; 0.126 g Mn(II) chloride, 0.237 g Co(II) chloride.6H_2O, 0.237 g Ni(II) chloride.6H_2O, 0.17Cu(II) chloride.2H_2O, 0.201 g Cd(II) chloride.H_2O, and 0.272 g Hg(II) chloride. The product mixture is stirred for sixty minutes and, then, the result is filtered and dried through anhydrous $CaCl_2$. The physical properties of Schiff ligand and new compounds.

Biological Activity

The Schiff base and their metal compounds were investigated with four bacteria *psuedomonas* *aruginosa*, *Escharia coli*, *Staphylococcus aureus* and *Streptococcus pyogenes* by disc diffusion technique. The chemical solutions, used in the biological study, are prepared by using dimethyl sulfoxide (DMSO) as solvent, and they are provided as a single concentration of 1×10^{-3}M. The dishes were incubated at room temperature for 24 hours. The inhibition zones (IZ) in mm is formed after 24 h as a criterion for the intensity of the synthetic chemical compound effect on the outgrowth of cultivated specific bacteria strains.

RESULT AND DISCUSSION

Generally, all the complexes are soluble in DMSO and DMF but insoluble in water. The CHN analysis and the sensible features of the compounds are listed in Table-1. The complexes can be symbolized as [M (L)(Anth)$_2$] where M=metal(II) ions, (L=Schiff base ligand), and (Anth= anthranilic acid).

Table 1 : The details of Schiff base ligand and new compounds

Complexes	Code	M.wt	m.p.°C	Color	Theoretical (Calc.)				
					C	H	N	O	M
$C_{20}H_{14}N_4O$	L	347.35	187 – 189	Brown	64.17	3.77	14.97	17.10	-----
Mn (L)(Anth)$_2$ $C_{34}H_{26}MnN_6O_8$	C1	701.54	250	Pail - brown	58.21	3.74	11.98	18.24	7.83(7.03)
Co(L)(Anth)$_2$ $C_{34}H_{26}CoN_6O_8$	C2	705.54	270	Brown	57.88	3.71	11.91	18.14	8.35 (7.32)
Ni (L)(Anth)$_2$ $C_{34}H_{26}NiN_6O_8$	C3	705.30	250	Pail-brown	57.90	3.72	11.92	18.15	8.32(7.03)
Cu(L)(Anth)$_2$ $C_{34}H_{26}CuN_6O_8$	C4	710.15	230	Orange	57.50	3.69	11.83	18.12	8.95(7.96)
Cd(L)(Anth)$_2$ $C_{34}H_{26}CdN_6O_8$	C5	759.02	250	Pail-brown	53.80	3.45	11.07	16.86	14.81(13.57)
Hg(L)(Anth)$_2$ $C_{34}H_{26}HgN_6O_8$	C6	847.20	170 - 172	Dark brown	48.20	3.09	9.92	15.11	23.68(22.23)

Mass Spectrum

Mass Spectrum of Schiff base ligand is carried out to determine its molecular weight and fragmentation pattern as explained in Fig. 2 and Table 2.[11,12]

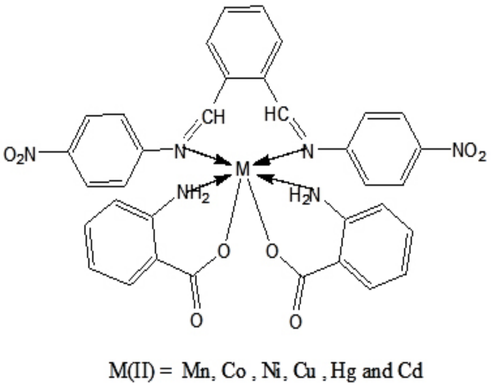


Fig.1. The synthesis route of [L1(M)(Anth)$_2$] complexes

Table 2: The fragmentation data for the (L)

Ligand	Assignments	Peak m/z
L	M= ($C_{20}H_{14}N_4O_2$)	373
	M- N_2O_4 = M_1	281
	M_1 – C_6H_4 = M_2	206
	M_2 – N=CH = M_3	179
	M_3 – C_7H_5N = M_4	76

^{1}H-NMR Spectral Data of Ligand

The ^{1}H-NMR spectrums of the synthesized Schiff base ligand (L) in DMSO-d6 are shown in Fig. 3 and Table 3. The singlet signal appeared at (δ= 2.45 ppm) can be assigned to the solvent DMSO. The multiple signals, ranged between (δ= 6.55-8.36), are assigned to the aromatic protons of the phenyl, and the doublet signal at (δ= 8.44) is attributed to the azomethine proton (HC=N)[13, 14].

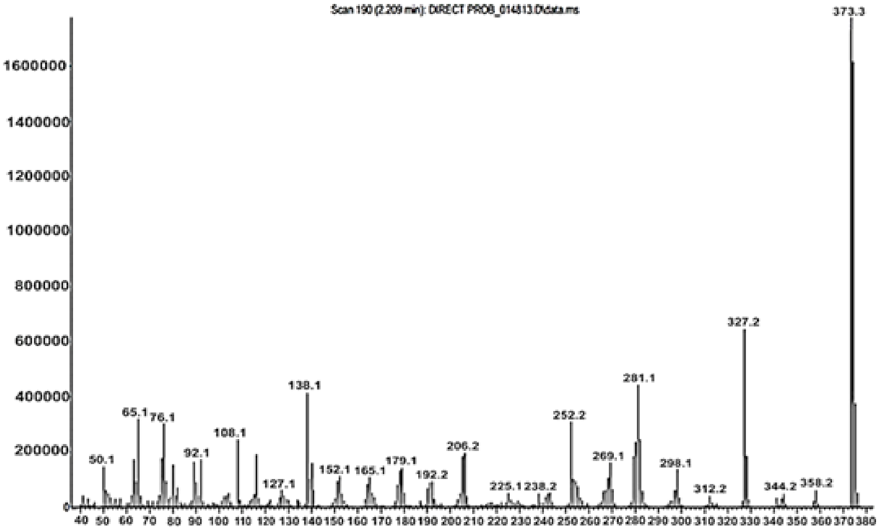


Fig. 2. Mass spectrum of ligand

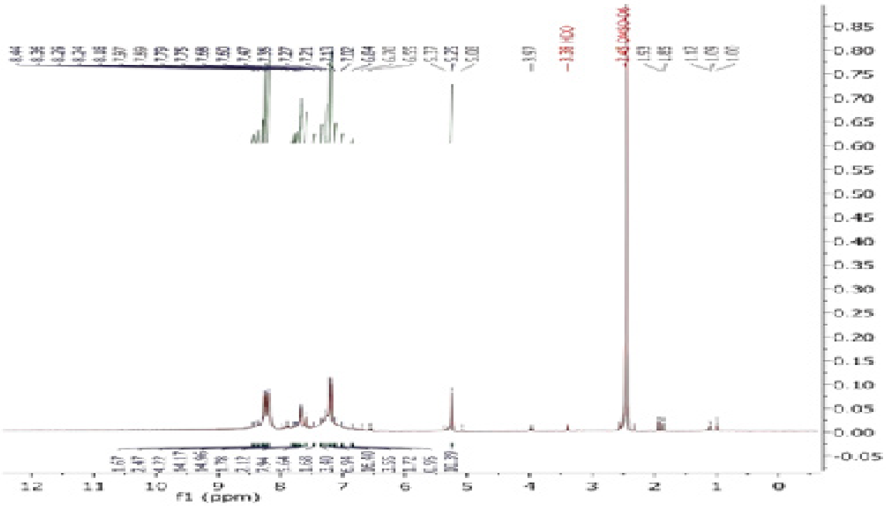


Fig. 3. ^{1}H-NMR spctrum of ligand (L)

Table 3: 1H-NMR Spectral data for measured L and chemical shift in ppm

Ligand	Functional group	δ(ppm)
	DMSO-d6	2.45
L	Ar-H	6.55 – 8.36 (12H, m)
	N=C-H	8.44(2H, s)

FTIR Spectra

The FTIR spectrum of (L) is in KBr disc in range of (4000-400) cm^{-1}. Fig. 4 shows the weak absorption band at 3111 cm^{-1} which has been consigned for the (C-H) aromatic stretching vibration. The medium band at 1622 cm^{-1} is assigned to the (HC=N) stretching vibration, and the band at 1577 cm^{-1} is allocated for the (C=C) stretching vibration[15]. The FTIR spectrum of Anthranilic acid shows bands of υ(O-H), υ(NH_2), υas (COO), and υs (COO) at (3390) and (3324, 3240), 1679, and 1486 cm^{-1} respectively[16]. In complexes, υ(O-H) is disappeared, and υ(NH_2) is shifted to higher frequencies for all complexes without C1 and C2, making NH_2 in an active location of coordinate . The bands of υas and υs(COO) in all these complexes shifted to higher frequencies for υasy(COO), and lower frequencies for υsym(COO). Therefore, the difference between Δas-s is equal to (235-247) cm^{-1} that indicates the carboxlate ion coordination with the metal ions, and it is considered as mono dentate donor[17,18]. New spectra have been appeared in the bands of all compounds in the regions (559-570) cm^{-1} which refer to υ(M-O) mode[19]. The bands at (486-489) cm^{-1} refer to υ(M-N) mode[20, 21].

Table 4: FTIR details of cm-1 free ligands and its compounds

Comp.	υ(O-H)	υ(N-H)	υ(C-H) arom.	υ(COO) as & s	Δ as-s	υ(C=N)	υ(M-N)	υ(M-O)
L1	----	----	3111	----	----	1622	----	----
Anth	3390	3321	2586	1679	-----	------	----	----
		3210		1486				
C1	---	3305	3143	1693	239	1654	559	489
		3232	3082	1454			536	
C2	----	3303	3136	1693	235	1654	563	489
		3224	3086	1458				
C3	----	3363	3120	1693	239	1654	567	489
		3302	3082	1454				
C4	----	3402	3120	1693	235	1600	574	489
		3275	2924	1458				
C5	----	3360	3136	1693	243	1654	574	489
		3290	3086	1450				
C6	----	3329	3113	1693	247	1654	563	489
		3263	3078	1446				

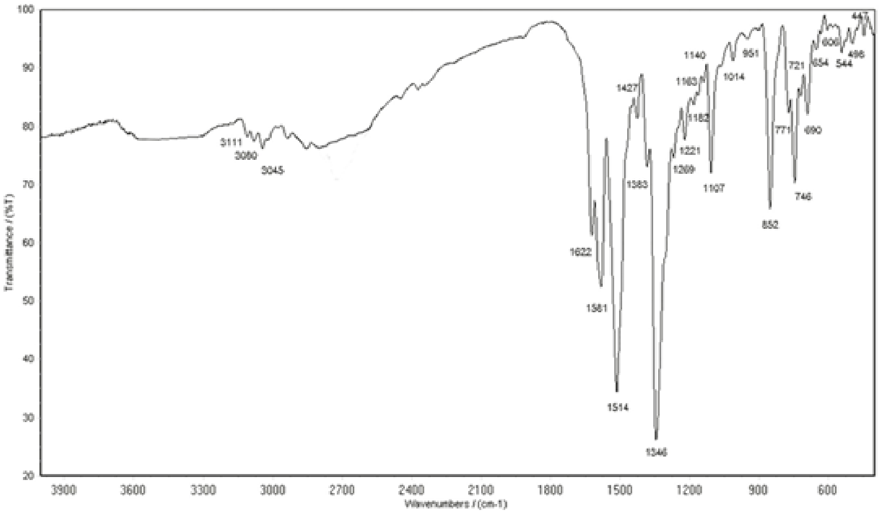


Fig. 4. FTIR spectrum of ligand L

Electrnic Spectra, Molar Conductivity, and Magnetic Moments

The UV-Vis. band of ligand (L) is shown in Fig. 5. The spectrum exhibits three peaks; one of them is in (286 nm) due to ($\pi \rightarrow \pi^*$) electronic shift while the others are in (345, and 358 nm) due to ($n \rightarrow \pi^*$) electronic shift[22,23]. The UV-Vis. spectrum of C1 complex shows five absorption peaks. The three absorption peaks at (264, 329 and 345) nm are due to intra ligand comparably with the spectrum of (L1). The fourth absorption peak is at (380 nm) assigned for charge transfer (C. T), and the last one has a weak intense peak at (448 nm), which indicates that there is a (d-d) electronic transition type $^6A1g \rightarrow {}^4T_2g(G)$, and this proves an octahedral structure around Mn(II) complex[24]. The UV-Vis band of C2 compound has five absorption peaks; three absorption peaks are at (279, 327 and 347) nm assigned for intra ligand, and two new absorption peaks, with weak intensity, are at (739 and 790 nm) due to (d-d) type $^4T_1g(F) \rightarrow {}^4A_2g(F)$ transition; this indicates that there is an octahedral structure around Co(II) complex[25,26]. The UV-Vis. band of C3 compound shows five absorption peaks, the low absorption peaks are at (267 and 345) nm assigned for intra ligand. The absorption peak at (357 nm) is attributed to charge transfer (C.T). C3 has weak intensity (777 and 826) nm due to types $^3A_2g(F) \rightarrow {}^3T_1g(F)$ and $^3A_2g(F) \rightarrow {}^3T_2g(F)$ transitions, which support the existence of an octahedral structure around Ni(II) complex[27]. The UV-Vis. spectrum of C4 complex displays three absorption peaks; the highest absorption peaks at (345 nm) is assigned to charge transfer (C.T), and the peak at (270 nm) is due to intra ligand. The third absorption peak with weak intensity at (800 nm) is attributed to $^2Eg \rightarrow {}^2T_2g$. These peaks are congruence in location with the researches of octahedral Cu(II)[28]. The UV-Vis. spectra of C5 and C6 complexes, show absorption peaks at (264 and 266) nm, respectively, and are assigned to intra ligand. The peaks at (342 and 345) nm are due to charge transfer (C.T) that shows diamagnetic as perspective from their electronic arranging. They support that there is an octahedral structure around Cd(II) and Hg(II) complexes[29]. The molar conductivities indicate that all complexes are non-electrolytes. Magnetic moment values show that there is an octahedral arrangement around the metal (II) ions[18] as revealed in Table 5.

Boiological Activity

The Schiff base ligand [L] and the corresponding metal compounds under study are tested against four antimicrobial activities; *psuedomonas aruginosa* and *Escharia coli* (*gram-*), *Staphylococcus aureus* and *Streptococcus pyogenes* (*gram+*) by plate well into agar nutrient method. Antimicrobial activity is expressed in millimeters by measuring the diameters of the inhibitory region and contrasting with the DMSO control; the values are explained in Table 6, Fig. 5 and chart-[30,31].

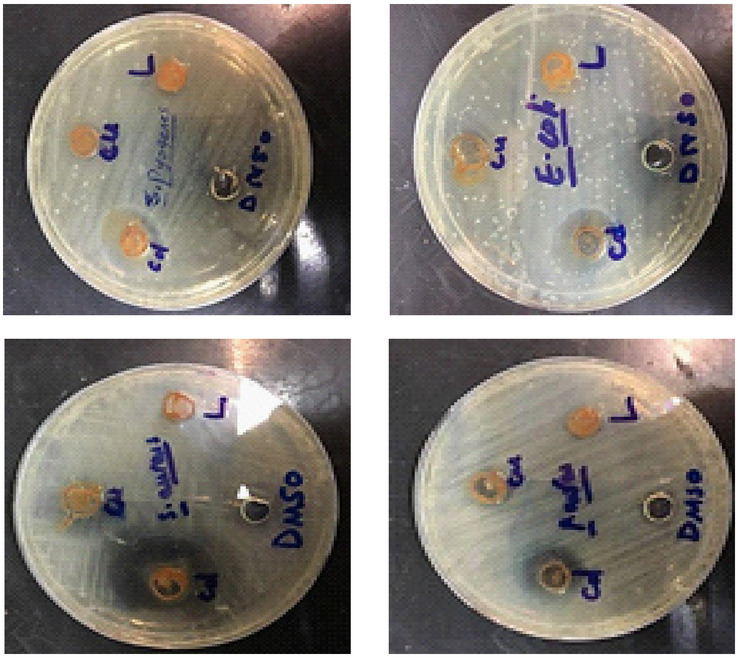


Fig. 5. The zone of inhibition for all compounds

Table 5: Spectral and magnetic moments (nm) of the complexes

Compounds	λmax.	υcm^{-1}	λmax. $mol^{-1}. L.cm^{-1}$	Assignments	Molar Conductivity	μeff (BM)
L	286	34965	893	$\pi \rightarrow \pi^*$	---	---
	345	28986	2019	$n \rightarrow \pi^*$		
	358	27933	1134	$n \rightarrow \pi^*$		
C1	264	37879	1006	Intra-ligand		5.72
	329	30395	1783	Intra-ligand		
	345	28986	1973	Intra-ligand	0.95	
	380	26316	75	C.T		
	448	22321	22	$^6A_1g \rightarrow {}^4T_2g(G)$		
C2	279	35842	1051	Intra-ligand	1.09	4.72
	327	30581	1228	Intra-ligand		
	347	28818	1454	C.T.		
	739	13532	38	$^4T_1g(F) \rightarrow {}^4A_2g(f)$		
	790	12658	35	$^4T_1g(F) \rightarrow {}^4T_2g(f)$		
C3	267	37435	1000	Intra-ligand	1.83	4.61
	345	28986	1635	Intra-ligand		
	357	28011	1011	C.T.		
	777	12870	15	$^3A_2g(F) \rightarrow {}^3T_1g(F)$		
	826	12107	13	$^3A_2g(F) \rightarrow {}^3T_2g(F)$		
C4	270	37037	1182	Intra-ligand	0.89	1.83
	345	28986	2023	C.T.		
	800	12500	49	$^2Eg \rightarrow {}^2T_2g$		
C5	264	37879	1010	Intra ligand	0.87	Dia.
	342	29239	2312	C.T.		
C6	266	37594	1143	Intra ligand	1.57	Dia
	345	28986	2063	C.T.		

Table 6: Antibacterial performance of the ligand and their metal compounds

Comp.	*Staphylococcus aureus*	*Streptococcus pyogenes*	*Psuedomonas aruginosa*	*Escharia coli*
DMSO	zero	zero	zero	Zero
L	zero	zero	zero	Zero
C1	zero	zero	zero	Zero
C2	16	14	20	17
C3	zero	zero	zero	Zero
C4	25	zero	zero	Zero
C5	30	21	17	20
C6	30	25	18	17

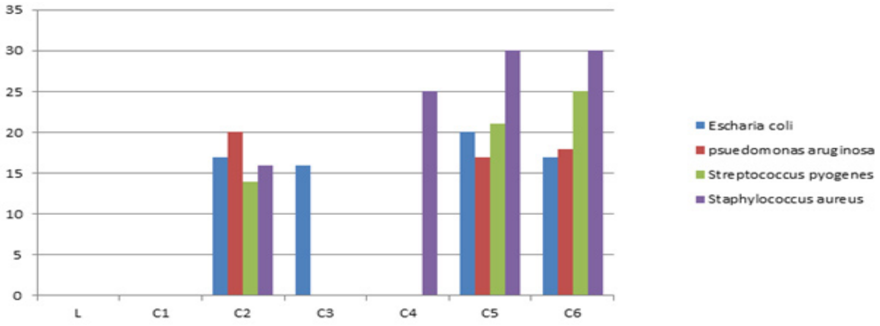


Chart 1 : The inhibition zones of the compounds

CONCLUSION

The new Schiff base derived from o-phathalaldehyde with p-nitroaniline is synthesized and characterized. The results show the coordination of L format with metal ions through the N as a donor atom. The results of the electron spectra and the magnetic susceptibility of all complexes show that these complexes are of octagonal geometry. The composite compounds are studied as antimicrobial, and the results reveal that C2,C5 and C6 complexes have various activities against bacteria, while L, C1 and C2 are inactive against two types of bactria.

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