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Synthesis, characterization and biological evaluation of *bis*-bidentate Schiff base metal complexes

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ABSTRACT

A novel series of 4,6-bis(1-(4-substitutedphenylimino)ethyl)benzene-1,3-diols *bis*-bident Schiff base transition metal complexes, H_2L^1 , H_2L^2 and H_2L^3 were synthesized. The Schiff base H_2L^1 , H_2L^2 and H_2L^3 , ligands were synthesized by the condensation of 4,6-diacetylresorcinol with 4-chloroaniline, 4-flouroaniline and 4-methylaniline respectively. The ligands behave as dibasic bis-bidentates yielding polymeric complexes. The ligands and their metal complexes have been characterized by 1H NMR, IR, mass, ESR and elemental analysis. The bonding sites are the azomethine and phenolic oxygen atoms. The metal complexes exhibit different geometrical arrangements such as square planar, tetrahedral, octahedral and distorted octahedral arrangement. The Schiff base and its new complexes were tested for antibacterial activity against gram positive bacteria; *Staphylococcus aureus* and gram negative bacteria; *Escherichia coli* including the resistance bacteria *Pseudomonas aeruginosa*.

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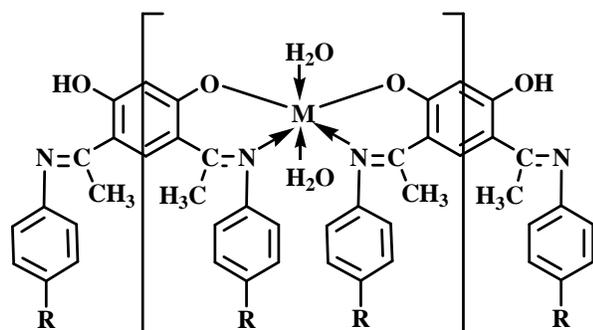
KEYWORDS

Bis-schiff-base complexes;
Diacetyl resorcinol;
Anti-bacterial activity.

INTRODUCTION

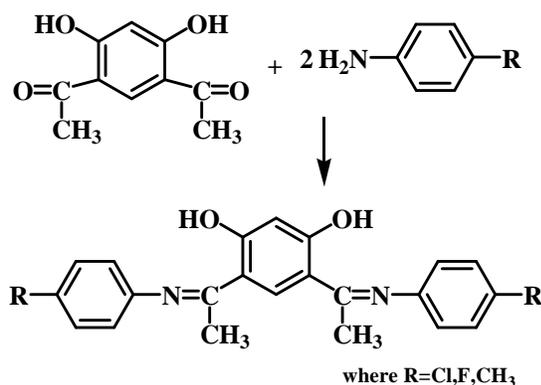
The interest of the coordination complexes of Schiff bases stems from their versatile catalytic reactions for organic synthesis^[1-4] and its use in degradation of organic substances^[5] and in radiopharmaceuticals^[6] and their ability to reversibly bind oxygen^[7] and photochromic properties^[8], and the complexing ability towards transition metals. Due to such a wide range of applications, new three series of binuclear complexes of copper(II), nickel(II), and cobalt(II) ions with three Schiff base, H_2L^1 , H_2L^2 and H_2L^3 ligands are of particular interest. The purpose is to alter the metal ion coordination environment, which is primarily responsible for the properties exhibited by the complex.

Due to such a wide range of applications^[9,10], new three series of binuclear complexes of 4,6-bis(1-(4-substitutedphenylimino)ethyl)benzene-1,3-diols have been prepared by the condensation of 4,6-diacetylresorcinol with 4-chloroaniline, 4-flouroaniline and 4-methylaniline, to afford the corresponding Schiff base ligands, which serves as tetradentate Schiff base ligands, abbreviated as H_2L^1 , H_2L^2 and H_2L^3 , respectively. The ligands are either di- or tetra-basic with two symmetrical sets of either OON or NNO tridentate chelating sites. Reaction of the Schiff base, H_2L^1 , H_2L^2 and H_2L^3 , ligands with copper(II), nickel(II), cobalt(II), in molar 2:1 ratio afforded the corresponding transition metal complexes (SCHEME 1). The structures of the ligands and the newly prepared complexes were iden-



Where R= Cl, F, CH₃ and M= Cu(II), Co(II) and Ni(II)

SCHEME 1: Structure of metal complex



where R=Cl,F,CH₃

SCHEME 2: General reaction for Schiff base ligands

tified by elemental analyses, infrared, electronic, mass, ¹H-N.M.R. and ESR spectra as well as thermal gravimetric analysis (TGA). The bonding sites are the azomethine and phenolic and alcoholic oxygen atoms, the metal complexes exhibit different geometrical arrangements such as tetrahedral, octahedral and distorted octahedral arrangement. The biological evaluation of the ligands and metal complexes against some pathogenic bacteria are also reported^[23].

EXPERIMENTAL

Materials

4,6-Diacetylresorcinol was synthesized according to the literature method^[11,12]. Copper(II), nickel(II) and cobalt(II) were used as nitrate salts and were Merck or BDH. Organic solvents EtOH, absolute EtOH, MeOH, acetone, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were reagent grade and were used without further purification.

Synthesis of the Schiff base ligand

The Schiff base, H₂L¹, H₂L² and H₂L³, Ligands were synthesized by adding 4,6-diacetylresorcinol (4.85g, 25.0mmol) dissolved in hot absolute EtOH (20cm³) to 4-chloroaniline (6.37g, 50.0mmol), 4-fluoroaniline (5.55g, 50.0 mmol) and 4-methylaniline (5.35g, 50.0mmol) respectively, in absolute EtOH (20cm³). The reaction mixtures were heated to reflux for 3h. The products obtained were filtered off and washed several times with a few amount of EtOH then ether and air dried. The products were kept in a desiccator until used. Recrystallization was carried out in EtOH. The yields were 8.4 g (75%), for H₂L¹ and 7.8g (75%) for H₂L² and H₂L³. m.p. of these three ligands are >170°C. A general chemical reaction for ligand is formulated as in (SCHEME 2).

Synthesis of metal complexes

The metal chelates were prepared by refluxing the respective metal(II) nitrate(hexahydrate) (1mmol) in 20 ml of methanol with the ligand, H₂L (2 mmol) in 20ml of methanol on a water bath for about 4hrs. The pH of the solution was adjusted to 7 by drop wise addition of 10% methanol ammonia solution. The metal chelates got separated after cooling the solution overnight. The metal chelates thus separated were washed with methanol followed by pet ether (60-80°) and dried in vacuum. The yield is 72-79%. The complexes (SCHEME 1) are insoluble in water and alcohol but soluble in DMSO^[13].

Bacterial culture

The strains of bacteria used were *Escherichia coli*, *B.Spinzini*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus*. All strains were used standard. The identity of all the strains was confirmed^[24]. A bacterial pension was prepared and added to the sterilized medium before solidification. The media with bacteria was poured into sterilized Petri dishes under aseptic condition. Different weights of Schiff base, Co(II), Cu(II), Ni(II) Schiff bases complexes; (1mg, 5mg and 10mg) were placed on the surface of the culture and incubated at 37°C for 24 h. After incubation the inhibition (mm) and the average of inhibition zones recorded.

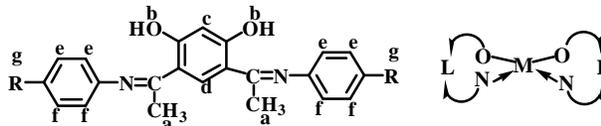
RESULTS AND DISCUSSION

UV-vis spectra of the metal complexes in DMF

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TABLE 1: The analytical and physical data of the ligand and metal complexes

Ligand or complex	Formula	M.W.	Color	Yield (%)	m.p. (°C)	Elemental analysis, % found/(Calc'd)				
						C	H	N	M	
1	H ₂ L ¹	C ₂₂ H ₁₈ Cl ₂ N ₂ O ₂	413.3	Reddish brown	75%	170	63.90 (63.93)	4.37 (4.39)	6.75 (6.78)	-
2	H ₂ L ²	C ₂₂ H ₁₈ F ₂ N ₂ O ₂	380.39	Reddish brown	75%	210	69.44 (69.46)	4.73 (4.77)	7.34 (7.36)	-
3	H ₂ L ³	C ₂₄ H ₂₄ N ₂ O ₂	372.46	Reddish brown	75%	190	77.36 (77.39)	6.47 (6.49)	7.49 (7.52)	-
4	[NiL ¹ (H ₂ O)] _n	C ₄₄ H ₃₄ Cl ₄ N ₄ NiO ₄	883.27	Green	78%	>300	59.78 (59.83)	3.85 (3.88)	6.33 (6.34)	6.61 (6.65)
5	[NiL ² (H ₂ O)] _n	C ₄₄ H ₃₄ F ₄ N ₄ NiO ₄	817.45	Green	76%	>300	64.61 (64.65)	4.17 (4.19)	6.83 (6.85)	7.13 (7.18)
6	[NiL ³ (H ₂ O)] _n	C ₄₈ H ₄₆ N ₄ NiO ₄	801.6	Green	75%	>300	71.90 (71.92)	5.75 (5.78)	6.96 (6.99)	7.28 (7.32)
7	[CuL ¹ (H ₂ O)] _n	C ₄₄ H ₃₄ Cl ₄ CuN ₄ O ₄	888.12	Deep brown	79%	>300	59.47 (59.50)	3.82 (3.86)	6.28 (6.31)	7.12 (7.16)
8	[CuL ² (H ₂ O)] _n	C ₄₄ H ₃₄ CuF ₄ N ₄ O ₄	822.3	Deep brown	78%	>300	64.24 (64.27)	4.16 (4.17)	6.79 (6.81)	7.67 (7.73)
9	[CuL ³ (H ₂ O)] _n	C ₄₈ H ₄₆ CuN ₄ O ₄	806.45	Deep brown	79%	>300	71.48 (71.49)	5.74 (5.75)	6.93 (6.95)	7.83 (7.88)
10	[CoL ¹ (H ₂ O)] _n	C ₄₄ H ₃₄ Cl ₄ CoN ₄ O ₄	883.51	Reddish brown	72%	>300	59.76 (59.81)	3.84 (3.88)	6.33 (6.34)	6.60 (6.67)
11	[CoL ² (H ₂ O)] _n	C ₄₄ H ₃₄ CoF ₄ N ₄ O ₄	817.69	Reddish brown	72%	>300	64.60 (64.63)	4.17 (4.19)	6.81 (6.85)	7.17 (7.21)
12	[CoL ³ (H ₂ O)] _n	C ₄₈ H ₄₆ CoN ₄ O ₄	801.84	Reddish brown	69%	>300	71.89 (71.90)	5.75 (5.78)	6.97 (6.99)	7.28 (7.35)

TABLE 2: ¹HNMR spectral data of ligand and metal complexes


Assignment	H ₂ L ¹	H ₂ L ²	H ₂ L ³	Complexes
H ^a	2.1(6H)	2.1(6H)	2.1(6H)	2.1(6H)
H ^b	12.92(1H)	12.92(1H)	12.92(1H)	-
H ^c	6.36(1H)	6.36(1H)	6.36(1H)	6.36(1H)
H ^d	7.64(1H)	7.64(1H)	7.64(1H)	7.64(1H)
H ^e	6.61(2H)	6.61(2H)	6.61(2H)	6.61(2H)
H ^f	7.0(2H)	7.0(2H)	7.0(2H)	7.0(2H)
H ^g	-	-	2.35(6H)	2.35(6H) (H ₂ L ³ complex)

were recorded on a Jasco 550 Spectrophotometer. IR spectra of the ligands and their metal complexes, as KBr discs, were recorded on an 8400 FTIR Simadzu Spectrometer. ¹HNMR spectra of the ligand and its complexes, in DMSO-d₆, were recorded on a Bruker Avance II 400 Spectrometer at room temperature using TMS as internal standard. Mass spectra were recorded at QP 2010 Shimadzu GCMS Spectrometer. and ESR was recorded on E-112 ESR Spectrometer, at X-band microwave frequency (9.5 GHz) with sensitivity of 5 × 10¹⁰ ΔH spins. TG and DT analyses^[14] were

recorded on NETZSCH TGA-DTA/DSC instrument.

The reactions of the Schiff-base, H₂L, with different metal ions produce a new series of binuclear metal complexes, M^{1/2}, Ni(II), Cu(II), and Co(II). The analytical and physical data of the Ligand and Metal complexes are listed in (TABLE 1).

Characterization of the ligands and metal complexes

Mass spectroscopy was performed on the H₂L ligand to determine its molecular weight and fragmentation pattern. The molecular ion peak was observed at m/e 412, m/e 380, m/e 372, confirming its formula weight (FW) 413, 380, 372 for H₂L¹, H₂L² and H₂L³ respectively. Which are same as the calculated m⁺ values. The general schematic fragmentation of the ligand is depicted in (SCHEME 3).

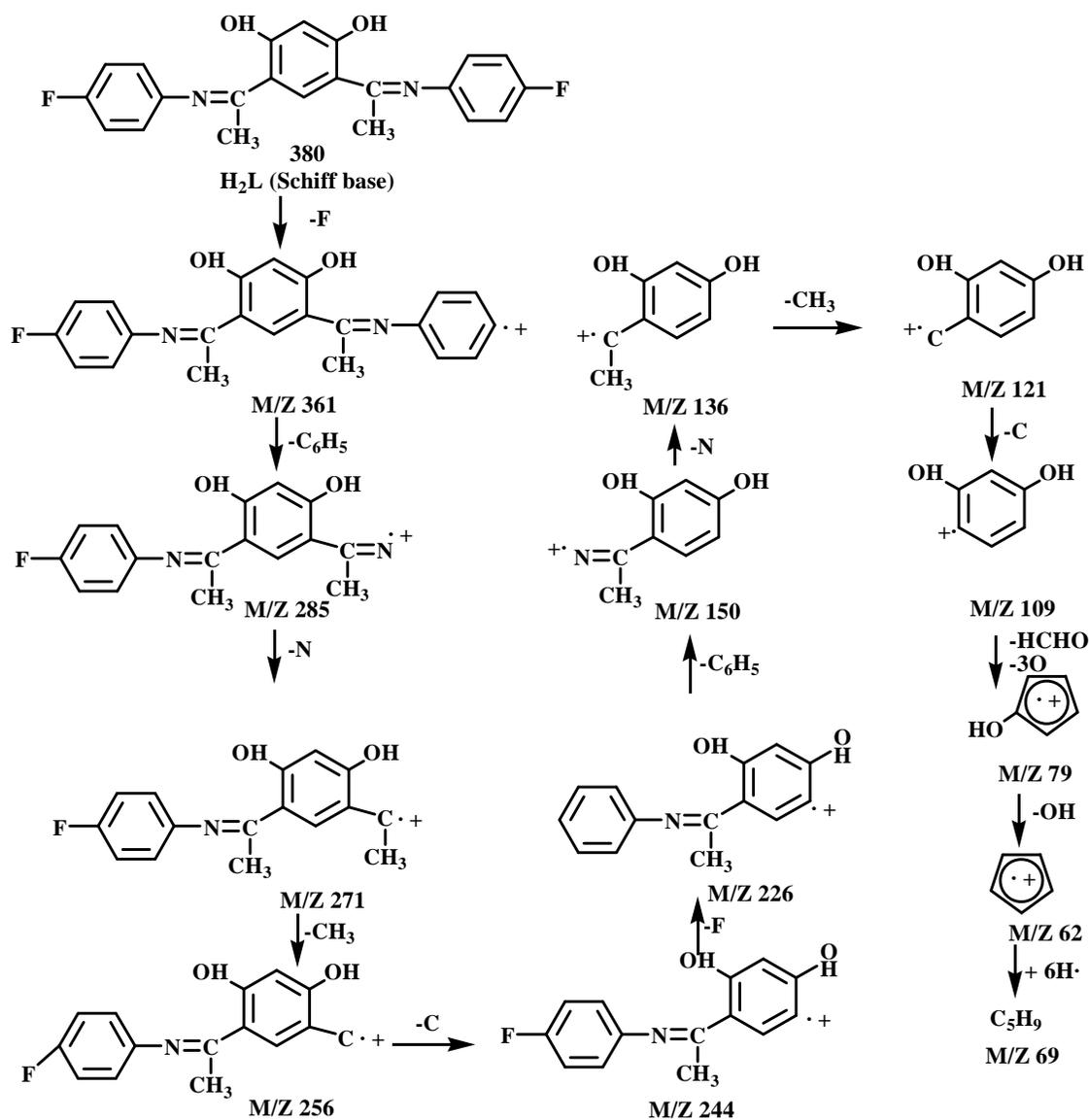
The ¹H NMR spectrum of H₂L and complexes in DMSO-d₆ (TABLE 2) showed signals at δ (ppm) 2.1 (3H, CH₃^a), 12.92 (1H, OH-phenolic^b), 6.36 (1H, Ar-H^c), 7.64 (1H, Ar-H^d), 6.61 (2H, Ar-H^e), 7.0(2H, Ar-H^f), and 2.35 (3H, CH₃^g). It is observed that the signal due to the proton (12.92, phenolic-OH^b) completely disappeared on adding D₂O, while the other signals still

exist at their expected positions. The integral ratio of the protons is in agreement with the expected structure of the ligand and metal complex^[15].

The IR spectrum of the ligand shows a broad band at 3430 cm^{-1} due to the stretching vibrations of phenolic hydroxyl groups. The broadness is due to intermolecular hydrogen bonding between the phenolic groups and the azomethine groups. The band at 1246 cm^{-1} is ascribed to the $\nu(\text{C}-\text{O})$ stretching vibrations, where the strong band observed at 1610 cm^{-1} is assigned to the stretching vibrations of the azomethine group. The band for p-substitution at 686 & 770^[16].

The characteristic bands of the infrared spectra the

metal complexes are listed in (TABLE 3). The IR spectra of complexes (4–12) exhibit a broad band around 3200–3463 cm^{-1} assigned to $\nu(\text{OH})$ of water molecules associated with the complex, which are also confirmed by elemental and thermal analyses. The IR spectra of the complexes show a shift of the $\nu(\text{C}=\text{N})$ band towards lower wavenumbers of 1635–1665 cm^{-1} compared with the free ligand band at 1680 cm^{-1} . This shift indicates coordination of the two azomethine groups to the metal ions. Coordination through the phenolic oxygen after deprotonation is revealed by the appearance of a band due to $\nu(\text{C}-\text{O})$ at much lower frequencies (1205–1225 cm^{-1}) in all the complexes compared to



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that of H_2L (1236 cm^{-1}), suggesting that the hydroxyl groups of the Schiff-base coordinate^[17] with the metal ions.

Thermo gravimetric analysis shows that the weight loss is observed in all the divalent complexes^[18]. The weight loss is found to be two mole of coordinated water per mole of the complex. Differential thermal analysis shows that one endothermic peak is observed in each complex. This indicates that the weight loss occurs in a single step. The loss of coordinated water occurs at 130°C for Cu(II) , 140°C for Ni(II) , 150°C for Co(II) , complexes respectively.

The electronic spectrum of the ligand H_2L (10^{-3}M in DMF), shows mainly three bands at 210, 242 and 370nm due to (${}^1L_a \rightarrow {}^1A_1$) and (${}^1L_b \rightarrow {}^1A_1$) transitions of

the phenyl ring and $\pi-\pi^*$ transition within the C=N group. In addition, a broad band at 410nm is due to the $n-\pi^*$ transition which is overlapping with the intermolecular CT from the phenyl ring to the azomethine group.

The electronic spectrum of Co(II) complex has multiple bands observed at $20000-19230$, $16393-5625$ and 7143 cm^{-1} . These bands are ascribed to ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{v}1)$; ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{v}2)$ and ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})(\text{v}3)$ transitions respectively. The $\text{v}2/\text{v}1$ ratio is in the range. $2.95-2.187$, which is consistent with the octahedral geometry^[19]. The Ni(II) complex has three spin allowed transitions at 10000 , 18518 , $20833-23256$ and 29412 cm^{-1} . These bands are correlated to ${}^3A_{2g} \rightarrow {}^3T_{2g}$; ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$ transitions respectively in an octahedral stereochemistry^[20]. The electronic spectrum of Cu(II) complex shows a multiple structured broad band in the range $13250-17390\text{ cm}^{-1}$ which may be assigned as a combination of three transitions ${}^2B_{1g} \rightarrow {}^2A_{2g}$; ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ in a distorted octahedral geometry^[21]. Based on the magnetic data and electronic spectral data octahedral geometries have been proposed for all the complexes.

ESR spectrum of Cu(II) complex was recorded at room temperature using DPPH as the standard. The spectrum consists of a single intense signal. The g value has been found to be 2.0027 , which is greater than the free electron value^[22]. This indicates that the unpaired electron is largely localized on the metal ion.

Antibacterial activity

TABLE 4 exhibits the zone of bacterial growth inhibition of the Schiff base which synthesized from

TABLE 3: The characterization bands of the infrared spectrum of H_2L , and their metal complexes

Ligand or complex	-OH (Phenolic or crystalline)	$\nu(\text{C=N})$ $\nu(\text{M-O})$ $\nu(\text{M-N})$			
1 H_2L^1	3430br	1680s	-	-	
2 H_2L^2	3409br	1680s	-	-	
3 H_2L^3	3356br	1680s	-	-	
4 $[\text{NiL}^1(\text{H}_2\text{O})]_n$	3240br	1654s	558m	390w	
5 $[\text{NiL}^2(\text{H}_2\text{O})]_n$	3370br	1660s	467m	372w	
6 $[\text{NiL}^3(\text{H}_2\text{O})]_n$	3380br	1640s	495m	-	
7 $[\text{CuL}^1(\text{H}_2\text{O})]_n$	3463br	1635s	467m	365w	
8 $[\text{CuL}^2(\text{H}_2\text{O})]_n$	3430br	1653s	455m	370w	
9 $[\text{CuL}^3(\text{H}_2\text{O})]_n$	3433br	1645s	465m	372w	
10 $[\text{CoL}^1(\text{H}_2\text{O})]_n$	3200br	1645s	504m	346w	
11 $[\text{CoL}^2(\text{H}_2\text{O})]_n$	3233m	1652s	416m	-	
12 $[\text{CoL}^3(\text{H}_2\text{O})]_n$	3238br	1655s	480m	370w	

S=Strong, w=weak, m=medium and br=broad.

TABLE 4: Antibacterial activities of ligand and metal complexes

Compound/Organism	<i>E-Coli</i>	<i>E-aeroges</i>	<i>B.spinzinii</i>	<i>Pseudomonas aeruginosa</i> <i>Staphylococcus aureus</i>		
				Zone of inhibition in mm		
1 H_2L^1	5	-	6	-	-	7
2 H_2L^2	-	-	5	-	-	6
3 H_2L^3	-	-	8	5	-	7
4 $[\text{NiL}^1(\text{H}_2\text{O})]_n$	5	-	6	-	-	5
5 $[\text{NiL}^2(\text{H}_2\text{O})]_n$	5	-	5	-	-	4
6 $[\text{NiL}^3(\text{H}_2\text{O})]_n$	6	-	7	3	-	6
7 $[\text{CuL}^1(\text{H}_2\text{O})]_n$	9	8	8	7	-	7
8 $[\text{CuL}^2(\text{H}_2\text{O})]_n$	6	5	5	-	-	5
9 $[\text{CuL}^3(\text{H}_2\text{O})]_n$	8	5	9	7	-	9
10 $[\text{CoL}^1(\text{H}_2\text{O})]_n$	7	5	8	5	-	8
11 $[\text{CoL}^2(\text{H}_2\text{O})]_n$	4	4	7	4	-	7
12 $[\text{CoL}^3(\text{H}_2\text{O})]_n$	9	6	8	5	-	9

E.Coli = *Escherichia coli*

Diacetyl resorcinol and its complexes of Co(II), Cu(II) and Ni(II) against the tested bacteria. The Schiff base (H_2L) and metal complexes displays effect against all bacteria tested. The test results presented in TABLE 4 show that moderate effect against both gram positive and gram negative bacteria in comparison with standard drugs ampicillin, amoxicillin, and sefalexin in this study. The study indicates that the Cu(II), Co(II) solid complex has antibacterial activity against all bacteria used^[23,24].

CONCLUSION

The ligand H_2L behaves as a dibasic tetradentate ligand with O:N:N:O donor sequence coordinating through the nitrogen of the azomethine free and both oxygen of phenol groups. All the complexes have a polymeric octahedral geometry with a metal to ligand ratio of 1:2 Coordinated water molecule is found in all the divalent complexes. On the basis of analytical, magnetic and electronic spectral data polymeric octahedral geometries have been proposed for all the complexes (SCHEME 1). The complex screen for antibacterial activity and result show moderate in comparison with standard drugs.

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