Synthesis, characterization and biological evaluation of mixed ligand metal complexes derived from 4,6-diacetylresorcinol

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ABSTRACT

In the present study two new series of Copper(II), Nickel(II) and Cobalt(II) complexes with synthesized Schiff base ligands 4,6-bis(1-(4-chlorophenylimino) ethyl) benzene-1,3-diol (H_2L^1), 4,6-bis(1-(4-fluorophenylimino) ethyl) benzene-1,3-diol (H_2L^2), 4,6-bis(1-(4-methylphenylimino) ethyl) benzene-1,3-diol (H_2L^3) and organic ligands 8-hydroxy quinoline, 1,10-phenanthroline have been prepared. The Schiff bases H_2L^1, H_2L^2 and H_2L^3 ligands were synthesized by the condensation of 4,6-diacetyl resorcinol with 4-chloroaniline, 4-fluoroaniline and 4-methylaniline. The metal complexes were synthesized by the reaction of Schiff base ligands and organic ligands with metal salts. The metal complexes have been characterized by FT-IR, UV-Vis., elemental analysis, ESR and Thermal gravimetric analysis. The mixed ligand metal complexes were tested for antimicrobial activity against gram positive bacteria *Staphylococcus aureus, Streptococcus Pyogenes* and gram negative bacteria *Escherichia coli, Pseudomonas aeruginosa* and fungus *Candida albicans, Aspergillus Niger* and *Aspergillus clavatus* using broth dilution method.   © 2010 Trade Science Inc. - INDIA

INTRODUCTION

Metal chelation is involved in many important biological processes where the coordination can occur between a variety of the metal ions and a wide range of ligands[1,2]. Generally, the chelating ligand is a polyfunctional molecule which can encase the metal in an organic sphere. Many types of the Schiff base ligands are known and the properties of their derived metal chelates have been investigated[3]. Acyclic ligands having nitrogen, oxygen and sulphur donor atoms in their structures can act as good chelating agents for transition and non-transition metal ions[4-6]. Alkyl resorcinol and aromatic resorcinol are reported to possess valuable therapeutic and antiseptic properties. In particular, 4-alkyl resorcinol is reported to have skin beautifying effect, low toxicity and irritation when applied on to human skin[7,8]. 8-Hydroxyquinoline and 1,10-Phenanthroline have been extensively used as a ligand in both analytical and preparative coordination chemistry. As an important building block, both the ligands units play an important role in the development of the

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supramolecular chemistry[9-11]. The metal chelating properties of 1,10-phenanthroline have been widely utilized in all aspects of coordination chemistry as well as in its recent applications to develop biomimetic models of metalloenzymes and to prepare supramolecules, self-assembling systems or metal complexes with interesting anticancer properties[12,13]. The present work, is extension to our work[14] where the ligands were synthesized by the condensation of 4,6-diacetylresorcinol with 4-chloroaniline, 4-fluoroaniline 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. Reaction of the Schiff base, H_2L^1, H_2L^2 and H_2L^3, ligands with copper(II), nickel(II) and cobalt(II) ions and further react with another organic ligands in molar 1:2:2 ratio afforded the corresponding transition metal complexes.

EXPERIMENTAL

Materials

4,6-diacetyl resorcinol and Schiff base ligands were synthesized according to the method reported in literature[14]. Copper(II), Nickel(II) and Cobalt (II) were used as nitrate salts and were obtained from Rankem. All amines and organic ligands were Merck; organic solvents EtOH, MeOH, DMF and DMSO were reagent grade.

Physical measurements

IR spectra (4000-400 cm^{-1}) of the metal chelates were obtained using KBr discs, on 8400 FTIR SHIMADZU Spectrometer. Mass spectra were recorded on QP 2010 SHIMADZU GCMS spectrometer. Electronic spectra of the metal complexes in DMF were recorded on a Perkin Elmer Lambda 19 spectrophotometer, and ESR was recorded on E-112 ESR spectrometer, at X-band microwave frequency (9.5 GHz) with sensitivity of 5×10^{10} ΔH spins. Thermal Gravimetric Analyses (TGA) was carried out by using Perkin Elmer (Pyris 1 TGA) from 50°C to 800°C under heating rate of 10°C/min. Elemental analysis (C, H and N) were carried out on Elemental Analyzer PERKIN ELMER 2400, and analysis of metal was carried out by EDTA titration method, in which the metal complex first evaporate in conc. Nitric acid and pre-pare a stock solution. This solution with ammonia then titrates against EDTA by using appropriate indicator. Magnetic moment of the compound was measured by GOUY balance using Hg[Co(CNS)] as standard.
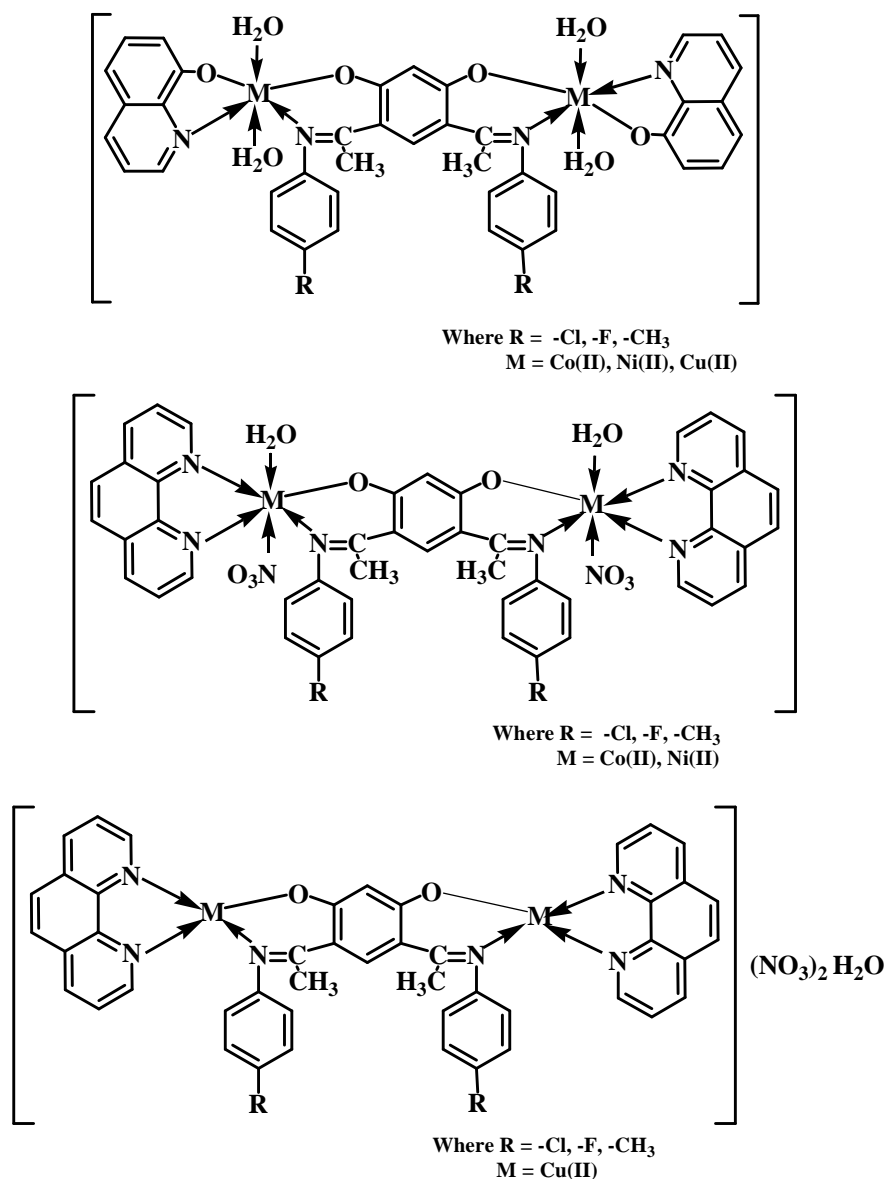
Synthesis of metal complexes

An ethanolic solution of the metal (II) nitrate (hexahydrate) (20 ml) was gradually added to an ethanolic (30 ml) solution of the Schiff base ligand in 2:1 molar ratio and the solution was stirred for 1 h. An ethanolic solution of the other ligands L' (L' = 8-HQ, 1,10-Phen) was then added to the previous solution in the molar ratio 2:1. The solution was continuously stirred for 4h, during which the metal complex precipitated. The resulting precipitates were filtered off, washed with ethanol then diethyl ether and finally air-dried. The complex is air stable in the solid state and soluble in DMF and/or DMSO. The progress of reaction was monitored by TLC. M.P. of these complexes are >300°C. (Scheme 1).

Antimicrobial screening

All newly synthesized compounds were tested for their antibacterial activities against gram positive bacteria *Staphylococcus aureus, Streptococcus Pyogenes* and gram negative bacteria *Escherichia coli, Pseudomonas aeruginosa* and antifungal activity against *Candida albicans, Aspergillus Niger* and *Aspergillus clavatus*. The method used to evaluate the antimicrobial activity was 'Broth Dilution Method'. It is one of the non-automated *in vitro* susceptibility tests. Serial dilutions were prepared in primary and secondary screening[25,26]. The MIC of the control organism is read to check the accuracy of the drug concentrations. The lowest concentration inhibiting growth of the organism is recorded as the MIC. The MIC values of the newly synthesized compounds have been comapered with the standard drugs Ampicillin, Chloramphenicol, Nystatin and Greseofulvin.

RESULTS AND DISCUSSION

The metal complexes were confirmed by various analytical techniques such as IR, ESR, UV-Vis. Spectroscopy and TG analysis. (TABLE 1) lists the physical and analytical data of metal complexes. The antimicro-

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Where R = -Cl, -F, -CH$_3$
M = Co(II), Ni(II), Cu(II)

Where R = -Cl, -F, -CH$_3$
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Where R = -Cl, -F, -CH$_3$
M = Cu(II)

Scheme 1 : Structure of metal complexes

bial activities of metal complexes are depicted in (TABLE 2).

Characterization of metal complexes

IR spectra

IR spectra of the complexes were recorded to confirm their structures. The assignments were aided by comparison with the vibrational frequencies of the free ligand and their related compounds. There are three conceptual features in the infrared spectra of the complexes. The former one is the shift of the stretching frequencies of the azomethine (–C=N–) group of the transition metal complexes to lower frequencies and lie in the range of 1610-1630 cm^{-1}, compared with the free ligand bands at 1642 and 1631 cm^{-1}, which may be due to the coordination of the two azomethine groups to metal ions. This lowering shift is not significant in most cases as expected and it is believed that, this is due to the interference with the deformation of the water molecules associated with the complexes. The second feature is the bands in the range of 3352–3572 cm^{-1} which can be assigned to the stretching frequencies of the ν(OH) of water molecules associated to the complexes which are also confirmed by the TG analysis. The third feature is the weak to medium bands in the two ranges 440–560 and 576–610 cm^{-1}, which could be assigned

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

No.	Complex	Formula	M.W.	Color	Yield (%)	Elemental analysis, % Found/(Calcd)			
						C	H	N	M
1	$[Co_2(L^1)(8\text{-}HQ)_2 (H_2O)_4]$	$C_{40}H_{36}Cl_2Co_2N_4O_8$	889.51	Reddish brown	85%	54.01 (53.94)	4.08 (3.00)	6.30 (6.37)	13.25 (13.28)
2	$[Ni_2(L^1)(8\text{-}HQ)_2 (H_2O)_4]$	$C_{40}H_{36}Cl_2N_4Ni_2O_8$	889.03	Green	81%	54.04 (53.98)	4.08 (4.17)	6.30 (6.23)	13.20 (13.13)
3	$[Cu_2(L^1)(8\text{-}HQ)_2 (H_2O)_4]$	$C_{40}H_{36}Cl_2Cu_2N_4O_8$	898.73	Deep blue	86%	53.46 (53.52)	4.04 (4.11)	6.23 (6.19)	14.14 (14.09)
4	$[Co_2(L^2)(8\text{-}HQ)_2 (H_2O)_4]$	$C_{40}H_{36}Co_2F_2N_4O_8$	856.6	Reddish brown	79%	56.09 (56.17)	4.24 (4.15)	6.54 (6.47)	13.76 (13.83)
5	$[Ni_2(L^2)(8\text{-}HQ)_2 (H_2O)_4]$	$C_{40}H_{36}F_2N_4Ni_2O_8$	856.12	Green	84%	56.12 (56.03)	4.24 (4.31)	6.54 (6.61)	13.71 (13.63)
6	$[Cu_2(L^2)(8\text{-}HQ)_2 (H_2O)_4]$	$C_{40}H_{36}Cu_2F_2N_4O_8$	865.82	Deep blue	80%	55.49 (55.57)	4.19 (4.08)	6.47 (6.39)	14.68 (14.74)
7	$[Co_2(L^3)(8\text{-}HQ)_2 (H_2O)_4]$	$C_{42}H_{42}Co_2N_4O_8$	848.67	Reddish brown	81%	59.44 (59.37)	4.99 (5.07)	6.60 (6.71)	13.89 (14.00)
8	$[Ni_2(L^3)(8\text{-}HQ)_2 (H_2O)_4]$	$C_{42}H_{42}N_4Ni_2O_8$	848.19	Green	79%	59.47 (59.56)	4.99 (5.10)	6.61 (6.54)	13.84 (13.91)
9	$[Cu_2(L^3)(8\text{-}HQ)_2 (H_2O)_4]$	$C_{42}H_{42}Cu_2N_4O_8$	857.9	Deep blue	83%	58.80 (58.71)	4.93 (5.03)	6.53 (6.61)	14.81 (14.92)
10	$[Co_2(L^1)(1,10\text{-}Phen)_2 (NO_3)_2(H_2O)_2]$	$C_{46}H_{36}Cl_2Co_2N_8O_{10}$	1049.6	Reddish brown	78%	52.64 (52.73)	3.46 (3.41)	10.68 (10.59)	11.23 (11.31)
11	$[Ni_2(L^1)(1,10\text{-}Phen)_2 (NO_3)_2(H_2O)_2]$	$C_{46}H_{36}Cl_2N_8Ni_2O_{10}$	1049.12	Green	76%	52.66 (52.59)	3.46 (3.52)	10.68 (10.73)	11.19 (11.30)
12	$[Cu_2(L^1)(1,10\text{-}Phen)_2] (NO_3)_2(H_2O)$	$C_{46}H_{32}Cl_2Cu_2N_6O_2$	898.78	Deep blue	84%	61.47 (61.44)	3.59 (3.50)	9.35 (9.28)	14.14 (14.23)
13	$[Co_2(L^2)(1,10\text{-}Phen)_2 (NO_3)_2(H_2O)_2]$	$C_{46}H_{36}Co_2F_2N_8O_{10}$	1016.69	Reddish brown	91%	54.34 (54.41)	3.57 (3.61)	11.02 (11.11)	11.59 (11.66)
14	$[Ni_2(L^2)(1,10\text{-}Phen)_2 (NO_3)_2(H_2O)_2]$	$C_{46}H_{36}F_2N_8Ni_2O_{10}$	1016.21	Green	86%	54.37 (54.44)	3.57 (3.51)	11.03 (10.92)	11.55 (11.63)
15	$[Cu_2(L^2)(1,10\text{-}Phen)_2] (NO_3)_2(H_2O)$	$C_{46}H_{32}Cu_2F_2N_6O_2$	865.87	Deep blue	83%	63.81 (63.92)	3.73 (3.68)	9.71 (9.62)	14.68 (14.74)
16	$[Co_2(L^3)(1,10\text{-}Phen)_2 (NO_3)_2(H_2O)_2]$	$C_{48}H_{42}Co_2N_8O_{10}$	1008.76	Reddish brown	79%	57.15 (57.09)	4.20 (4.16)	11.11 (11.19)	11.68 (11.61)
17	$[Ni_2(L^3)(1,10\text{-}Phen)_2 (NO_3)_2(H_2O)_2]$	$C_{48}H_{42}N_8Ni_2O_{10}$	1008.28	Green	78%	57.18 (57.25)	4.20 (4.13)	11.11 (11.22)	11.64 (11.57)
18	$[Cu_2(L^3)(1,10\text{-}Phen)_2] (NO_3)_2(H_2O)$	$C_{48}H_{38}Cu_2N_6O_2$	857.95	Deep blue	79%	67.20 (67.13)	4.46 (4.52)	9.80 (9.71)	14.81 (14.90)

to the stretching frequencies of the ν(M–O) and (M–N) bands, respectively, supporting that the bonding of the ligands to the metal ions is achieved by the phenolic oxygen, and azomethine nitrogen atoms of the ligands[15,16]. In case of organic ligand 1,10-phenanthroline, the NO_3^- ion is attached to coordination sphere as anion. The complexes contain 1,10-phenanthroline, IR frequency of NO_3^- ion in complexes show three weak bands at 1340, 1050 and 990 cm^{-1}. The IR frequency of NO_3^- in copper complexes show band at 1400 cm^{-1}. (Figure 1).

Electronic spectra and magnetic moments

The electronic spectra of the complexes showed several absorption bands, including absorption bands of the ligands and d-d transitions of the metal ions.

The electronic spectrum of Co (II) complex has multiple bands observed at 428nm, 390-410nm and 480-500nm. These bands are ascribed to $^4T_{1g}(F){\rightarrow}^4T_{2g}$; $^4T_{1g}(F){\rightarrow}^4A_{2g}$ and $^4T_{1g}(F){\rightarrow}^4T_{1g}(P)$ transitions respectively, which is consistent with the octahedral geometry. The Ni(II) complex has three spin allowed transitions at 250nm, 462nm, 520-581nm and 735nm. These bands are correlated to $^3A_{2g}{\rightarrow}^3T_{2g}$; $^3A_{2g}{\rightarrow}^3T_{1g}(F)$ and $^3A_{2g}{\rightarrow}^3T_{1g}(P)$ transitions respectively in an octahedral stereochemistry. The electronic spectrum of Cu(II) complex shows a multiple structured broad band in the range 331-435nm 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 for complexes **(3)**, **(6)** and **(9)**, and $^2B_{1g} \rightarrow {}^2A_{1g}$ in a square planar geometry for com-

TABLE 2 : Antimicrobial activity of metal complexes

		Minimal inhibition concentration (MIC) (μg/ml)						
		Antibacterial activity				Antifungal activity		
Sr. No	Complex	E. Coli	P. Aeruginosa	S. Aureus	S. Pyogenus	C. Albicans	A. Niger	A. Clavatus
		MTCC-443	MTCC-441	MTCC-96	MTCC-442	MTCC-227	MTCC-282	MTCC-1323
1	$[Co_2(L^1)(8\text{-}HQ)_2 (H_2O)_4]$	250	250	500	500	500	400	1000
2	$[Ni_2(L^1)(8\text{-}HQ)_2 (H_2O)_4]$	500	500	1000	1000	500	500	250
3	$[Cu_2(L^1)(8\text{-}HQ)_2 (H_2O)_4]$	125	250	250	500	500	250	500
4	$[Co_2(L^2)(8\text{-}HQ)_2 (H_2O)_4]$	250	100	250	500	1000	1000	500
5	$[Ni_2(L^2)(8\text{-}HQ)_2 (H_2O)_4]$	100	500	500	100	500	500	250
6	$[Cu_2(L^2)(8\text{-}HQ)_2 (H_2O)_4]$	500	250	500	250	500	100	500
7	$[Co_2(L^3)(8\text{-}HQ)_2 (H_2O)_4]$	62.5	125	200	250	250	250	100
8	$[Ni_2(L^3)(8\text{-}HQ)_2 (H_2O)_4]$	100	125	500	500	250	250	500
9	$[Cu_2(L^3)(8\text{-}HQ)_2 (H_2O)_4]$	500	500	250	250	500	500	100
10	$[Co_2(L^1)(1,10\text{-}Phen)_2 (NO_3)_2(H_2O)_2]$	250	250	100	500	250	250	500
11	$[Ni_2(L^1)(1,10\text{-}Phen)_2 (NO_3)_2(H_2O)_2]$	250	500	500	500	100	500	500
12	$[Cu_2(L^1)(1,10\text{-}Phen)_2] (NO_3)_2(H_2O)$	500	250	100	250	500	100	250
13	$[Co_2(L^2)(1,10\text{-}Phen)_2 (NO_3)_2(H_2O)_2]$	100	125	500	500	250	250	500
14	$[Ni_2(L^2)(1,10\text{-}Phen)_2 (NO_3)_2(H_2O)_2]$	500	500	250	250	500	500	100
15	$[Cu_2(L^2)(1,10\text{-}Phen)_2] (NO_3)_2(H_2O)$	250	250	100	500	250	250	500
16	$[Co_2(L^3)(1,10\text{-}Phen)_2 (NO_3)_2(H_2O)_2]$	500	500	1000	1000	500	500	250
17	$[Ni_2(L^3)(1,10\text{-}Phen)_2(NO_3)_2(H_2O)_2]$	125	250	250	500	500	250	500
18	$[Cu_2(L^3)(1,10\text{-}Phen)_2] (NO_3)_2(H_2O)$	100	500	500	100	500	500	250
	Standard Drugs							
1	Ampicillin	100	100	250	100	-	-	-
2	Chloramphenicol	50	50	50	50	-	-	-
3	Nystatin	-	-	-	-	100	100	100
4	Greseofulvin	-	-	-	-	500	100	100

plexes **(12)**, **(15)** and **(18)**[17-19].

The magnetic moment value of the Cu(II) complexes 3, 6 & 9 (1.70 B.M.) is very close to the spin value (1.73 B.M.) expected for one unpaired electron which offers the possibility of an octahedral geometry. The magnetic moment of Cu(II) complexes **(12)**, **(15)** & **(18)** show less value (1.64 B.M.). The larger variation in the magnetic moment values (2.9-3.4 B.M.) for a high-spin Ni(II) complex (2.83 B.M.) depends on the magnitude of the orbital contribution. The magnetic moment value (2.88 B.M.) in the present work is within the range expected for similar octahedral Ni(II) ions. The magnetic moment values for the Co(II) complexes have been used as criterion to determine the type of coordination around the metal ion. Due to the intrinsic orbital angular momentum in the ground state, there is consistently a considerable orbital contribution and the effective magnetic moment lies between 4.7 and 5.2 B.M. at room temperature. In the present complexes the magnetic moment value (4.74 B.M.) suggest an octahedral geometry for the Co(II) complex in the high-spin state[20,21].

Thermal analysis

Thermal methods of analysis open a new possibility for the investigation of metal complexes. The thermal behavior of all the metal complexes was studied by using thermo gravimetric techniques at a 50-800°C temperature range. The data from the thermo gravimetric analyses indicated that the decomposition of the complexes **(1)** to **(9)** proceeds in three steps. The complexes lost water molecules between 50-120°C, the decomposition of complex between 120-500°C and formed metal oxides above 500°C for the Cu(II), Ni(II)
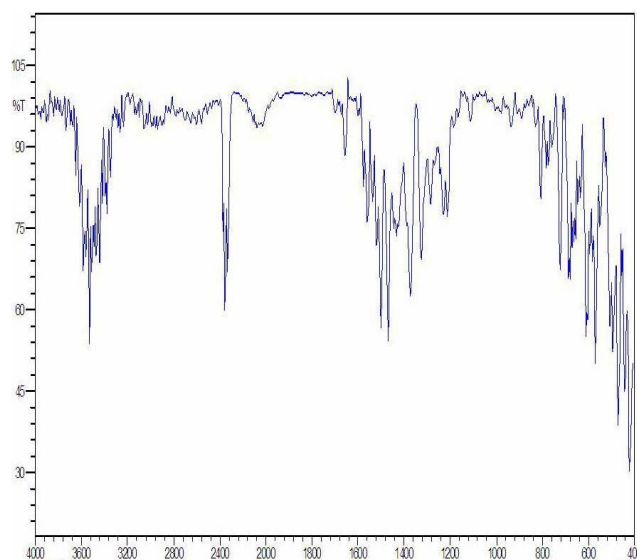
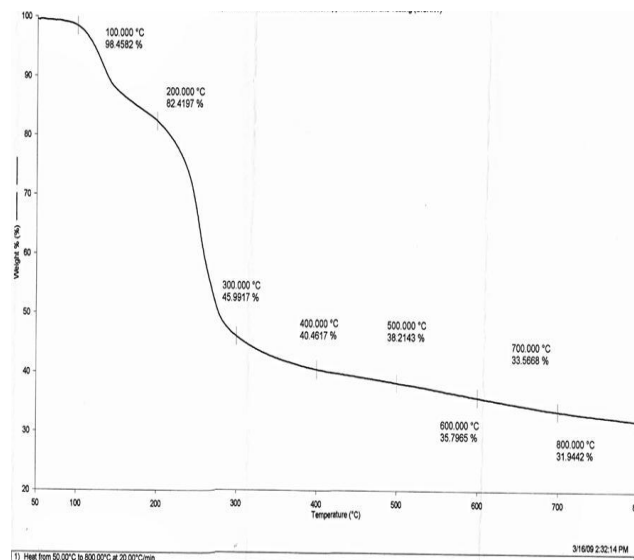Figure 1 : IR spectra of metal complex

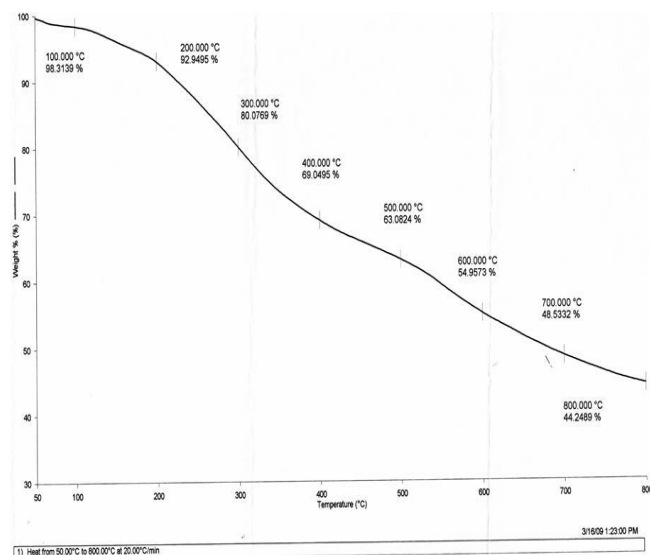

Figure 2 : TG analysis of metal complex 9
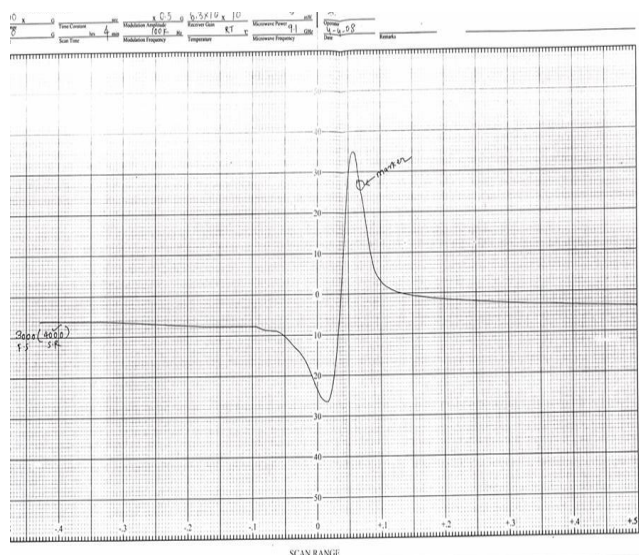

Figure 3 : TG analysis of complex 10

Figure 4 : ESR spectra of metal complex 6

and Co(II) complexes. Water of hydration is associated with complex formation and is found outside the coordination sphere formed around the central metal ion[22]. The thermal gravimetric analysis of metal complexes **(10)** to **(18)** proceed in four stages. The TGA curve of the complexes show loss of lattice/coordinate water molecule between 50-200°C followed by removal of NO_3^- ion between 200-300°C in the second stage. The third stage corresponds to the decomposition of complexes between 300-500°C. the curve at 500°C and above can be assign to the formation of metal oxide of Cu(II), Ni(II), Co(II) in the forth stage. (Figure 2 & 3).

ESR spectra

The ESR spectra of all copper complex show intense broad bands with g = 2.00255-2.00277, the value of g and the shape of the ESR signals suggest octahedral in complexes **(3)**, **(6)** & **(9)** and show bands with g = 2.00223 for complexes **(12)**, **(15)** & **(18)** suggest square planar in coordination around the Cu(II) ions[24] (Figure 4).

Antimicrobial activities

Anti bacterial and antifungal activities of the metal complexes were carried out against the bacteria *Staphylococcus aureus, Streptococcus Pyogenes*, *Es-*

cherichia coli and Pseudomonas aeruginosa and the fungus *Candida albicans, Aspergillus Niger* and *Aspergillus clavatus* by the 'Broth Dilution Method' using Ampicillin, Chloramphenicol, Nystatin and Greseofulvin as standards[27]. The Minimal Inhibitory Concentration (MIC) against bacteria and fungi of metal complexes were compared with the MIC values of standard drugs.

The MIC values of metal complexes **(3)**, **(17)** (125μg/ml) and **(5)**, **(8)**, **(13)**, **(18)** (100μg/ml) (100μg/ml) are equivalent to the MIC value of ampicillin against *E. Coli*, while the MIC value of complex **(7)** (62.5μg/ml) is slightly more than the standard drug Chloramphenicol against *E. Coli*. The MIC values of the metal complexes **(4)** (100μg/ml) and **(7)**, **(8)**, **(13)** (125μg/ml) are nearly equivalent to the MIC value of ampicillin against *P. Aeruginosa*. The MIC values of the complexes **(3)**, **(4)**, **(7)**, **(9)**, **(14)**, **(17)** (250μg/ml) against *S. Aureus* are similar to that of standard drug ampicillin, while the complexes 10, 12, 15 (100μg/ml) show relatively low MIC value. The MIC value of complex **(5)** and **(18)** (100μg/ml) reveals identical MIC value against *S. Pyogenus* with reference to ampicillin. The MIC values of metal complexes **(1)**, **(2)**, **(3)**, **(5)**, **(6)**, **(9)**, **(12)**, **(14)**, **(16)**, **(17)**, **(18)** (500μg/ml) against *C. Albicans* are similar to that of standard drug Greseofulvin while the complexes **(7)**, **(8)**, **(10)**, **(13)**, **(15)** (250μg/ml) show relatively half MIC values. The metal complex **(11)** (100μg/ml) reveals identical MIC value against *C. Albicans* with reference to Nystatin. The MIC values of complexes **(6)** and **(12)** (100μg/ml) against *A. Niger* are comparable to the standard drugs Nystatin and Greseofulvin. The MIC values of the complexes **(7)**, **(9)** and **(14)** (100μg/ml) against *A. Clavatus* are comparable to standard drugs Nystatin and Greseofulvin.

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 ligand: metal: ligand ratio of 1:2:2. Coordinated water molecule is found in all the divalent complexes. On the basis of ana-

lytical, magnetic and electronic spectral data polymeric octahedral/distorted octahedral geometries have been proposed for all the complexes. The results of the biological screening of metal complexes reveal that the antimicrobial activities of the chelated ligands are enhanced as compared to the free ligands.

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