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Studies on biologically active transition metal complexes of N, N'-bis[1,3-benzodioxol-5-ylmethylene]butane-1,4-diamine

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ABSTRACT

The Co(II), Ni(II) and Cu(II) complexes of the bidentate chelating Schiff base ligand, N,N'-bis-1,3-benzodioxol-5-ylmethylene]butane-1,4-diamine were synthesised using acetates, chlorides, bromides, nitrates and perchlorates of the metals. They were characterised by elemental analysis, conductance and magnetic susceptibility measurements UV-Vis and IR spectra, and thermogravimetric analysis. The thermograms of three complexes were analysed and the kinetic parameters for the different stages of decompositions were determined. The *in vitro* antibacterial activity against gram-positive *Bacillus subtilis* and gram-negative *Escherichia coli* and *in vitro* antifungal activity against *Aspergillus ficuum and Candida albicans* of three complexes and the lignad were investigated.

KEYWORDS

Schiff base;
Diamine;
Piperonal;
Transition metal complexes;
Thermal decomposition;
Antimicrobial activity.

INTRODUCTION

The chelating Schiff base ligands derived from diamines and various carbonyl compounds, encompass a highly remarkable class of compounds having a wide range of applications in catalytic[1], synthetic[2], analytical[3,4], clinical[5] and biochemical[6] areas and they possess considerable physiological activities[7,8]. Schiff base derivatives of 1,4-butanediamine and their metal complexes, also find a number of catalytic[9] and biological[10] applications. A perusal of earlier work revealed that the coordinating possibility of 1,4-butanediamine is enhanced by condensing with a variety of carbonyl compounds[11-13]. A search through literature revealed that no work had been done on Schiff bases derived from diamines and piperonaldehyde. Therefore, a new Schiff base ligand derived from piperonal and 1,4-butanediamine and its Cr(III), Mn(II) and Fe(III) complexes were synthesised and characterised by the same authors in an earlier work[14]. The use of piperonal as the carbonyl compound in these studies owed to the fact that several compounds containing the 3,4-methylenedioxy group possessed various biological activities[15,16]. As a continuation of this study, Co(II), Ni(II) and Cu(II) complexes of this ligand were synthesised using acetates, chlorides, bromides, nitrates and perchlorates of the metals. Investigations on ther-

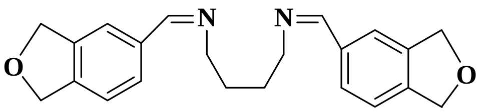

Figure 1: N,N'-bis-1,3-benzodioxol-5-ylmethylene]butane-1,4-diamine(L)

mal decomposition behaviour and antimicrobiall activities of some of these complexes were also done. The ligand named as N,N'-bis-1,3-benzodioxol-5-ylmethylene]butane-1,4-diamine (L), (Figure 1) has two donor sites, two nitrogen atoms as azomethine groups.

EXPERIMENTALS

Materials and measurements

All chemicals used in the present work *viz*, piperonaldehyde, butane-1,4-diamine, metal salts, solvents etc., were of A R grade (E.Merck or B D H).

Carbon, hydrogen and nitrogen analyses were carried out by using Hitachi CHN-O rapid analyzer at CDRI, Lucknow. The anions present in complexes were estimated by standard methods[17]. ^{1}H- NMR spectra of the ligand was recorded on a Varien-300 nuclear magnetic

resonance instrument using DMSO-d_6 as solvent. Infrared spectra were measured in the range 4000-400 cm^{-1} on a Schimadzu FTIR-8101 spectrophotometer with KBr pellets. The solid-state electronic spectra of complexes were recorded using a Schimadzu UV-1601 spectrophotometer. The magnetic measurements were made at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as calibrant. The thermal decomposition behaviours of complexes were monitored using a Perkin Elmer TGA-7 Analyser.

Synthesis of the compounds

The ligand was synthesized in the earlier work[14] and the method is given here for information. 1,4-butanediamine (20 mmol, 176 mg) solution in ethanol (50 mL) was mixed with a solution of piperonaldehyde (40 mmol, 604 mg) in ethanol (50 mL) in 1:2 molar ratio and was refluxed for about 1h and then cooled. The white precipitate formed was filtered off, washed with water and a few ml of alcohol and then purified by recrystallising from ethanol (yield = 678 mg, 87 %).

Complexes of Co(II), Ni(II) and Cu(II) with this ligand were synthesised using acetate, chloride, bromide, nitrate and perchlorate salts of these metals. Solutions of the ligand and Ni(II) and Cu(II) salts in methanol (10 mmol in 50 ml) (1:1 molar ratio) were refluxed for 2 to 3 h. Acetates of these metals were dissolved in methanol-water mixture and added to refluxing solutions of the ligand in methanol. In the case of Co(II), solutions of the salts and ligand in acetone were used. Acetate of Co(II) was dissolved in acetone-water mixture and added to refluxing solutions of the ligand in acetone. The complexes, synthesised using metal chlorides, precipitated during refluxing and were filtered off. In other cases, the reaction mixtures were concentrated and the pasty mass obtained in each case was repeatedly washed with diethyl ether and/or petroleum ether and/or acetone to get the solid complexes separated. The complexes were filtered, washed with suitable solvents and then dried over anhydrous $CaCl_2$.

RESULTS AND DISCUSSION

Characterisation of ligand

The characterization of the ligand was done in the earlier work[14] and is described here for information. The ^{1}H- NMR spectrum of the ligand was recorded in DMSO-d_6 and it showed a number of characteristic signals of the compound[18]. The peak observed at a δ value of 8.01 ppm was assigned to the azomethine protons in the molecule. The signals due to the aromatic protons were observed in the range 7.30-6.83 ppm. The singlet peak at 5.96 ppm was assigned to the methylinic protons of the dioxymethylene groups of the piperonal moieties present in the ligand. The inductive effect of the two oxygen atoms deshielded the methylenic protons and this resulted in the higher δ value for these protons. The peaks in the ranges of 3.71-3.65and 1.95-1.91 ppm were assigned to the methylinic protons of the butanediamine moiety of the ligand. The IR spectrum of the ligand showed bands at 3050 and 2983 cm^{-1} assigned to the C-H stretching of aromatic and methylene groups, respectively. The bands present at 1640 and 1255 cm^{-1} were assigned to the C=N and C-N stretchings, respectively[19]. Bands at 1191 and 1099 cm^{-1} were assigned to the in plane bending of the aromatic C-H and those at 872 and 816 cm^{-1} to the out of plane bending vibration of the aromatic C-H. The characteristic absorption frequency of the dioxymethylene group of piperonal moiety[20] was present at 926 cm^{-1}. The absence of the characteristic stretching frequency of C=O of the aromatic aldehyde group[19], indicated that the condensation was complete.

TABLE 1 : Formulae, general properties and micro analytical data of ligand and complexes

No.	Compound	Colour	Yield %	M.P ^oC	μ_{eff} B.M.	Λ_m ohm^{-1} cm^2mol^{-1}	Microanalytical data found(calculated) %				
							Metal	C	H	N	Anion
1	$C_{20}H_{20}O_4N_2$(L)	Pale yellow	87	172				68.3(68.2)	5.62(5.68)	7.89(7.95)	
2	$[CoL(AcO)_2(H_2O)_2]$	Pink	78	268	4.78	3.82	10.7(10.4)	50.2(51.0)	5.12(5.31)	4.68(4.96)	
3	$[CoLCl_2(H_2O)_2]$	Pink	64	274	4.72	15.2	11.9(11.4)	45.1(46.3)	4.42(4.63)	5.19(5.41)	13.9(13.7)
4	$[CoLBr_2(H_2O)_2]$	Pink	71	291	5.08	22.3	9.52(9.72)	40.2(39.5)	3.99(3.95)	4.72(4.61)	25.8(26.4)
5	$[CoL(NO_3)_2\ (H_2O)_2]$	Pink	68	285	4.92	48.6	9.96(10.3)	42.9(42.0)	4.31(4.20)	9.98(9.81)	
6	$[CoL(ClO_4)_2(H_2O)_2]$	Pink	64	>300	4.82	38.4	9.37(9.13)	36.1(37.2)	3.64(3.72)	4.26(4.33)	31.9(30.8)
7	$[NiL(AcO)_2(H_2O)_2]$	Yellowish green	78	254	3.23	10.2	10.8(10.4)	49.9(51.0)	5.12(5.31)	4.74(4.96)	
8	$[NiLCl_2(H_2O)_2]$	Yellowish green	69	265	3.29	7.42	11.1(11.3)	47.1(46.4)	4.69(4.64)	5.46(5.41)	13.4(13.7)
9	$[NiLBr_2(H_2O)_2]$	Green	73	276	3.11	12.4	9.83(9.68)	38.8(39.6)	3.87(3.96)	4.58(4.62)	27.2 (26.4)
10	$[NiL(H_2O)_4](NO_3)_2$	Green	71	>300	3.19	152.4	9.91(9.68)	38.7(39.6)	4.55(4.62)	9.14(9.23)	
11	$[NiL(ClO_4)_2(H_2O)_2]$	Yellowish green	68	>300	3.15	38.9	9.15(9.09)	36.1(37.2)	3.59(3.72)	4.22(4.34)	31.7(30.8)
12	$[CuL(AcO)_2(H_2O)_2]$	Greenish blue	74	269	1.98	8.56	11.9(11.2)	49.4(50.6)	5.12(5.27)	4.69(4.92)	
13	$[CuLCl_2(H_2O)_2]$	Blue	69	273	1.96	6.32	12.9(12.2)	44.7(45.9)	4.42(4.59)	5.18(5.36)	14.1(13.6)
14	$[CuLBr_2(H_2O)_2]$	Greenish blue	71	285	2.08	18.4	9.84(10.4)	40.2(39.2)	3.99(3.92)	4.62(4.58)	35.8(26.2)
15	$[CuL(H_2O)_4](NO_3)_2$	Blue	74	>300	2.05	149.8	10.9(10.4)	38.3(39.2)	4.43(4.58)	8.96(9.16)	
16	$[CuL(ClO_4)_2(H_2O)_2]$	Blue	71	>300	1.99	24.6	10.1(9.76)	35.6(36.9)	3.47(3.69)	4.12(4.30)	31.9(30.6)

*AcO^- = CH_3COO^-

The elemental analysis and spectral data for L are consistent with the formula $C_{20}H_{20}O_4N_2$ and the structure given in figure 1.

Formulae and general properties of complexes

The reaction of the ligand (L) with different salts of Co(II), Ni(II) and Cu(II), ions in 1:1 molar ratios gave metal complexes of the given formulae, as evidenced by the micro-analytical and spectral data.

1. $[MLA_2(H_2O)_2]$, where M = Co(II) and A^- = CH_3COO^-, Cl^-, Br^-, NO_3^- or ClO_4^- or Ni(II) or Cu(II) and A^- = CH_3COO^-, Cl^-, Br^- or ClO_4^-
2. $[ML(H_2O)_4]\ (NO_3^-)_2$, where M = Ni(II) or Cu(II)

The colours, magnetic susceptibilities and molar conductivities and melting points and the micro-analytical data of the complexes are listed in TABLE 1. These air stable metal complexes were non-hygroscopic, partially soluble in most organic solvents, but freely soluble in DMF and DMSO. The molar conductivities in DMF (10^{-3} M) solution showed that all the complexes except two behaved as nonelectrolytes, indicating the coordinated nature of the anions, while the nitrato complexes of Ni(II) and Cu(II) behaved as a 1:2 electrolyte[21].

IR spectra of complexes

TABLE 2 lists the most important IR spectral bands of the ligand and metal complexes. In the spectra of all the complexes the ν(C=N) was shifted to lower frequency, due to its involvement in coordination. Instead of the band at 1640 cm^{-1} present in the spectrum of the free ligand, new bands appeared in the ranges of 1624-1599, 1614-1593 and 1606-1589 cm^{-1} in the Co(II), Ni(II) and Cu(II) complexes, respectively, and were assigned to the coordinated azomethine groups[22-24].

The characteristic absorption frequency of the dioxymethylyne group was found to be present in the spectra of all the complexes at the same frequency as it was observed in the ligand spectrum. This indicated the non-involvement of dioxymethylene groups in coordination in these complexes[20]. The IR spectra of all the complexes revealed new bands at 612-511 and 508-439 cm^{-1}, assigned to ν(M-N) and ν(M-O), respectively[22,25,26]. The M-O band may be either due to coordinated nitrate- or perchlorate- ions or water molecules. The inclusion of water molecules in the coordination sphere of all the complexes was supported by

TABLE 2 : Significant IR spectral bands of ligand and Co(II), Ni(II) and Cu(II) complexes

No.	Compound	Assignments and band frequencies* (cm^{-1})										
		(coordinated water)			ν C=N	ν CO (coordinated AcO^-)	νNO_3^-		νClO_4^- (coordinated)	δ O-CH_2-O	νM-N	νM-O
		ν O-H	ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			νNO(asy) (free NO_3^-)	νNO_3^- (coordinated)				
1	$C_{20}H_{20}O_4N_2$(L)				1640s					927m		
2	[CoL(AcO)$_2$ (H_2O)$_2$]	3428b	965m	640w	1611m	1588m 1432w				928m	511w	439m
3	[CoLCl$_2$(H_2O)$_2$]	3413b	962	637	1624m					928m	519m	452w
4	[CoLBr$_2$(H_2O)$_2$]	3401b	957m	636w	1614s					927w	573w	446w
5	[CoL(NO_3)$_2$ (H_2O)$_2$]	3402b	956m	639w	1599m			1421m 1354w 1032sh		927m	564w	462m
6	[CoL(ClO_4)$_2$ (H_2O)$_2$]	3414b	963m	635w	1604m				1124m 1063w 946w	927w	542w	463m
7	[NiL(AcO)$_2$ (H_2O)$_2$]	3393b	961m	633w	1593m					928m	592w	491m
8	[NiLCl$_2$(H_2O)$_2$]	3417b	964m	639w	1614m	1597w 1441m				927m	606m	483w
9	[NiLBr$_2$(H_2O)$_2$]	3403b	959m	639w	1608s					928m	558w	472w
10	[NiL (H_2O)$_4$](NO_3)$_2$	3392b	961m	638w	1599m		1385s			927w	571w	459m
11	[NiL(ClO_4)$_2$ (H_2O)$_2$]	3408b	959m	636w	1611m				1116m 1087w 941w	927w	612w	483m
12	[CuL(AcO)$_2$ (H_2O)$_2$]	3398b	961m	634w	1602m	1592m 1438w				928m	543w	498m
13	[CuLCl$_2$(H_2O)$_2$]	3396b	959m	637w	1589m					927w	581m	501w
14	[CuLBr$_2$(H_2O)$_2$]	3417b	963m	635w	1606m					928m	559w	479w
15	[CuL(H_2O)$_4$] (NO_3)$_2$	3402b	964m	639w	1596m		1385s			927m	582w	508m
16	[CuL(ClO_4)$_2$ (H_2O)$_2$]	3421b	959m	636w	1601s				1119m 1039w 937w	928w	578w	463m

the appearance of broad bands in the range 3428-3392 and medium or weak bands at 965-956 and 640-633 cm^{-1}, owing to ν(OH), $\rho K_{rock}(H_2O)$ and ρ_{wagg} (H_2O), respectively of coordinated water molecules[24, 26].

Coordination of anions

The spectra of the acetato complexes of Co(II) and Ni(II) showed bands in the ranges of 1597-1588 and 1441-1432 cm^{-1}. The separation between these two bands was much larger than the separation for the bands due to asymmetric and symmetric stretchings of free acetate ion. Therefore, the bands were assigned to the C-O stretching vibrations of the unidentately coordinated acetate ions present in them[25,27-29]. Microanalytical data and the non-conducting nature of these complexes further supported this.

The IR spectra of nitrato complexes of Ni(II) and Cu(II) showed sharp bands at 1385 cm^{-1}, which corresponded to the $\nu NO_{(asy)}$ of free nitrate ion[25,30,31]. The conductance value of the complex confirmed the presence free nitrate ions. But in the IR spectra of nitrato complex of Co(II) such bands were absent and new bands appeared at 1421, 1354, 1032 cm^{-1} and were assigned to νNO_3^- of unidentate nitrate ions[25,31]. The non-conducting nature of the complex also indicated coordinated nature of nitrate ions in it.

The spectra of all the perchlorato complexes, investigated here, showed bands corresponding to unidentate perchlorate ions. These bands were found to be present in the ranges 1124-1116, 1087-1039 and 946-937 cm^{-1} and were assigned to the Cl-O stretchings of the monodentate perchlorate ion of C_{3v} symme-

TABLE 3: Electronic spectral bands of complexes and their assignments

No.	Compound	Bands (nm)	Assignment	Geometry
2	$[CoL(AcO)_2(H_2O)_2]$	1102 668 464	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
3	$[CoLCl_2(H_2O)_2]$	1093 676 461	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P$	Octahedral
4	$[CoLBr_2(H_2O)_2]$	1089 631 476	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
5	$[CoL(H_2O)_4](NO_3)_2$	1037 582 448	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P$	Octahedral
6	$[CoL(ClO_4)_2(H_2O)_2]$	1068 597 454	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
7	$[NiL(AcO)_2(H_2O)_2]$	1151 722 412	$^3A_2g(F) \rightarrow {}^3T_{2g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
8	$[NiLCl_2(H_2O)_2]$	1146 708 414	$^3A_2g(F) \rightarrow {}^3T_{2g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
9	$[NiLBr_2(H_2O)_2]$	1138 724 394	$^3A_2g(F) \rightarrow {}^3T_{2g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
10	$[NiL(H_2O)_4](NO_3)_2$	1153 713 408	$^3A_2g(F) \rightarrow {}^3T_{2g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
11	$[NiL(ClO_4)_2(H_2O)_2]$	1142 718 399	$^3A_2g(F) \rightarrow {}^3T_{2g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
12	$[CuL(AcO)_2(H_2O)_2]]$	762b	$^2E_g \rightarrow {}^2T2_g$	Distorted octahedral
13	$[CuLCl_2(H_2O)_2]$	741b	$^2E_g \rightarrow {}^2T2_g$	Distorted octahedral
14	$[CuLBr_2(H_2O)_2]$	743b	$^2E_g \rightarrow {}^2T2_g$	Distorted octahedral
15	$[CuL(H_2O)_2](NO_3)_2$	723b	$^2E_g \rightarrow {}^2T2_g$	Distorted octahedral
16	$[CuL(ClO_4)_2(H_2O)_2]$	738b	$^2E_g \rightarrow {}^2T2_g$	Distorted octahedral

try[25,32]. The non-conducting nature and the microanalytical data of these complexes also indicated coordinated nature of perchlorate ions.

$AcO^- = CH_3COO^-$

Magnetic- and electronic spectral studies

The solid-state electronic spectra of the complexes were recorded by the procedure recommended by Venenzi[33]. TABLE 3 lists the important electronic spectral bands of the complexes and their assignments

Co(II) complexes

The spectra of all the Co(II) complexes which were investigated here, showed bands in the ranges 1102-1037, 676-582, 476-448 nm. These bands were assigned to the $^4T_1g(F) \rightarrow {}^4T_2g(F)$, $^4T_1g(F) \rightarrow {}^4A2g(F)$ and $^4T_1g(F) \rightarrow {}^4T_1g(P)$ transitions, respectively, in an octahedral geometry[23,24]. The magnetic moment values in the range 4.72-5.08 B.M. also indicated high-spin octahedral geometries[23,34]. In the high-spin octahedral complexes of Co(II), the ground term $^4T_{1g}$ results in considerable orbital contribution.

Ni(II) complexes

The spectra of the Ni(II) complexes showed bands in the ranges 1153-1138, 724-708 and 414-394 nm. which were assigned respectively to the $^3A_2g(F) \rightarrow {}^3T_2g(F)$, $^3A_2g(F) \rightarrow {}^3T_1g(F)$ and $^3A_2g(F) \rightarrow {}^3T_1g(P)$ transitions in an octahedral geometry. The ratio of wave numbers of the first two transitions was found to be in the range 1.6-1.8, which further supported octahedral geometries for these complexes[24,35]. With the ground term ^3A_2g for octahedral complexes, no orbital contribution is expected but a slightly higher value than the spin-only moment is observed for them because of the spin-orbit coupling or by the mixing of higher states with ground state. All the Ni(II) complexes investigated here showed magnetic moments in the range 3.29 to 3.11 B.M as expected for octahedral geometries[23,36].

Cu(II) complexes

The spectra of all the Cu(II) complexes showed broad bands in the range 762 to 723nm, and were assigned to the $^2E \rightarrow {}^2T_2$ transitions in a distorted-octahedral geometry[35,37]. The greenish blue colour of the complexes also was indicative of octahedral geometries[38]. No orbital contribution is expected for regular octahedral Cu(II) complexes with the ground term but due to the spin-orbit coupling values slightly higher than spin-only value are usually observed[34]. All the Cu(II) complexes investigated here showed magnetic moments in the range 1.96 to 2.09 B.M.

Thermogravimetric analysis

Thermograms of three complexes, viz, $[CoLCl_2$

TABLE 4 : Thermal decomposition data of Co(II), Ni(II) and Cu(II) complexes

Complex	Stage	Temp. range in TG	Peak temp.	Loss of mass %			Assignments
				From TG	Theoretical	From pyrolysis	
$[CoLCl_2(H_20)_2]$	I	100-180	150	6.8	6.9		Loss of 2 H_2O
	II	200-400	300	22.9	22.1		Loss of 1 piperonal moiety
	III	400-580	520	54.1	55.5		Loss of rest of the ligand and 2 Cl^- ions and formation of 1/3 Co_3O_4
	Total			83.8	84.5	83.1	
$[NiLCl_2(H_2O)_2]$	I	100-180	150	7.2	7.0		Loss of 2 H_2O
	II	220-400	320	22.2	23.0		Loss of 1 piperonal moiety
	III	420-600	540	55.6	55.6		Loss of rest of the ligand and 2 Cl^- ions & formation of NiO
	Total			85.0	85.6		
$[CuLCl_2(H_20)_2]$	I	110-220	160	7.1	6.9		Loss of 2 H_2O
	II	260-480	370	44.9	455		Loss of 2 piperonal moieties
	III	480-620	560	32.2	32.4		Loss of rest of the ligand and 2 Cl^- ions and formation of CuO
	Total			84.2	84.8	83.9	

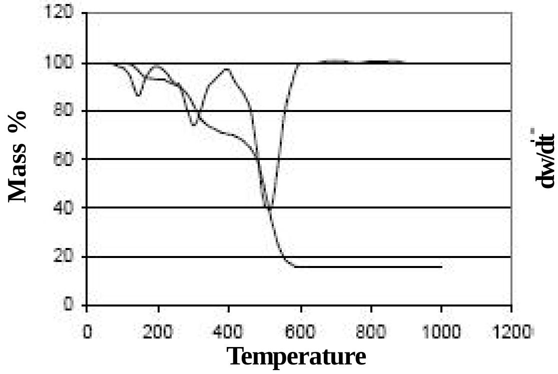

Figure 2 : TG-dTG traces of $[CoLCl_2(H_2O)_2]$

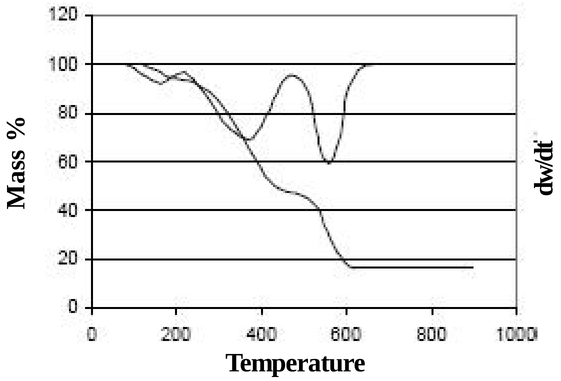

Figure 4 : TG-dTG traces of $[CuLCl_2(H_2O)_2]$

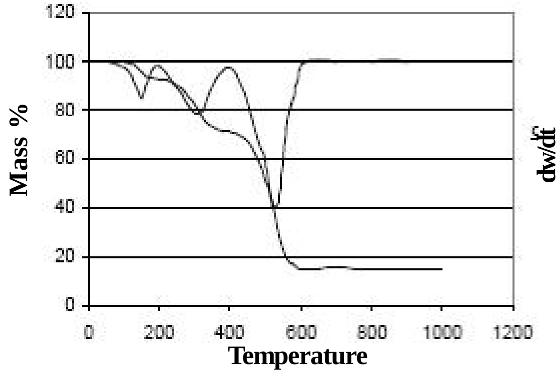

Figure 3 : TG-dTG traces of $[NiLCl_2(H_2O)_2]$

$(H_20)_2]$, $[NiLCl_2(H_2O)_2]$and $[CuLCl_2(H_20)_2]$ were analysed. All the complexes exhibited 3-stage decomposition patterns. They underwent dehydration reactions around 150^0C, losing two molecules of water each, thus confirming the presence of coordinated water molecules in them. The second stage in the case of Co(II) and Ni(II) complexes matched to the loss of one piperonal moiety and that in the case of Cu(II) complex indicated the lose of two piperonal moieties. They gave Co_3O_4, NiO and CuO, respectively, as the end products at temperatures around 600^0C. The decomposition patterns were in good agreement with the suggested formulae. By the analysis of the non-isothermal TG, using the integral method of Coats-Redfern, kinetic parameters, viz, order of reaction(n), activation energy(E_a), frequency factor(A) and entropy of activation(ΔS^*) were calculated. The enthalpies and free energies of activation for various decomposition stages have also been calculated using the relations, $\Delta H^* - E_a - RT_s$ and $\Delta G^* - \Delta H^* - T_s\Delta S^*$ where T_s is the peak temperature of the decomposition stage investigated[39]. Figures 3-5 give the TG-DTG traces of the complexes, the TABLE 5 gives the different stages of decomposition and the TABLE 6 gives the kinetic parameters. Based on inception temperature and free energy of activation, stabilities of the complexes were found to be in the order,

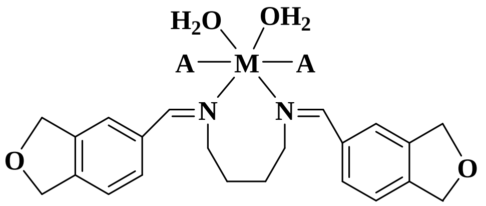

Figure 5: Structure suggested for $MLA_3(H_2O)]$, where M = Co(II) or Ni(II) and $A^- = CH_3COO^-$, Cl^-, Br^- or ClO_4^- and M = Cu(II) and $A^- = CH_3COO^-$, Cl^-, Br^-, NO_3^- or ClO_4^-

TABLE 6 : *In vitro* antimicrobial activity of ligand and complexes(MIC in μg/ml)

Compound	Antibacterial activity*		Antifungal activity*	
	B.subtilis	*E.coli*	*A.ficuum*	*C.albicans*
Ligand	>50	25	12.5	12.5
$[CoLCl_2(H_2O)_2]$	50	25	25	12.5
$[NiLCl_2(H_2O)_2]$	25	12.5	12.5	6.25
$[CuLCl_2(H_2O)_2]$	12.5	6.25	6.25	<3.12

***The MIC of standard drugs for antibacterial activity (Tetracycline and Choramphenicol) and antifungal activity (Cyclohexamide and Flucanazole) were found to be < 3.12 μg/ml**

TABLE 5 : Kinetic parameters for the decomposition of Co(II), Ni(II) and Cu(II) Complexes

Complex	Stage	Ea kJ/mol	A s^{-1}	ΔS* J/K/mol	ΔH* kJ/K/mol	ΔG* kJ/K/mol	γ	n
$[CoLCl_2(H_20)_2]$	I	78.1	4.2×10^7	-101.9	74.6	117.7	-0.99973	1
	II	70.1	5.7×10^3	-178.4	65.3	167.5	-0.99276	1
	III	192.1	8.5×10^{-3}	-292.7	12.6	244.7	-0.99262	1
$[NiLCl_2(H_2O)_2]$	I	69.6	2.6×10^6	-125.2	66.1	119.0	-0.99357	1
	II	68.8	4.6×10^3	-180.4	63.8	170.8	-0.99695	1
	III	191.5	6.9×10^{-3}	-294.6	12.4	251.9	-.99182	1
$[CuLCl_2(H_20)_2]$	I	52.0	6.2×10^3	-174.4	48.8	116.5	-0.99637	1
	II	61.2	2.5×10^2	-205.2	55.8	187.8	-0.99776	1
	II	195.4	7.0×10^9	-64.9	188.5	242.6	-0.99506	1

Cu > Ni > Co.

Antimicrobial activity

The biological activity of the ligand and three of its complexes was explored with the evaluation of their antimicrobial activity. The new ligand (1) and its chloro complexes of Co(II), Ni(II) and Cu(II) complexes (3, 8 and 13) were evaluated for *in vitro* antibacterial activity against Gram-positive *Bacillus subtilis* [MTCC 2063], and Gram-negative *Escherichia coli* [MTCC 1652] and *in vitro* antifungal activity against *Aspergillus ficuum* [MTCC 8184], *Candida albicans* [MTCC 183]. Double strength nutrient broth-I.P. and Sabouraud dextrose broth-I.P[40] were employed for bacterial and fungal growth, respectively. Minimum Inhibitory Concentrations (MIC) were determined by means of standard serial dilution method[41] and are presented in Table. All compounds exhibited moderate to appreciable *in vitro* activity against the tested strains.

The tested compounds showed mild to moderate antibacterial activity against *Bacillus subtilis* and *Escherichia coli.* The complexes were generally more effective. The copper complex displayed considerable antibacterial activity against *Escherichia coli.* All the tested compounds showed moderate to good antifungal avtivity against *Aspergillus ficuum* and *Candida albicans*. Interestingly the copper complex was found to exhibit significant antifungal activity against *Candida albicans*. It was also noticed that all the compounds, ligands and metal complexes were more active as antifungal than as antibacterial.

CONCLUSION

A total of 15 complexes of N,N'-bis-1,3-benzodioxol-5-ylmethylene]butane-1,4-diamine were synthesised, characterised and screened for their antibacterial activity against *B.subtilis* (gram positive) and *E. coli* (gram negative) bacteria and antifungal activity against *A.ficuum and C.albicans*. The minimal inhibitory concentrations (MIC) of all the compounds were determined by serial dilution method. Compounds were found to have moderate to significant antimicrobial activity.

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