



Synthesis, characterisation, thermal decomposition and antifungal studies of Co(II), Ni(II) and Cu(II) complexes of N,N'-bis[1,3-benzodioxol-5-ylmethylene]propane-1,3-diamine

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ABSTRACT

Co(II), Ni(II) and Cu(II) Complexes of a bidentate chelating / bridging Schiff base ligand, namely N,N'-bis[1,3-benzodioxol-5-ylmethylene]propane-1,3-diamine were synthesised using acetates, chlorides, bromides, nitrates and perchlorates of the metals. The complexes were characterised by elemental analysis, UV-Vis and IR spectra, conductance and magnetic susceptibility measurements and thermogravimetric analysis. The ligand showed bridging nature in some of its complexes, as evidenced by magnetic- and microanalytical data. The thermograms of three complexes were analysed and the kinetic parameters for the different stages of decompositions were determined. The antifungal activities of the ligand and three complexes against *Phytophthora capsici* were tested in carrot agar medium.

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KEYWORDS

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

INTRODUCTION

1,3-propanediamine, its Schiff base derivatives and their metal complexes, find a variety of synthetic^[1-3], catalytic^[4], analytical^[5-7] and biological^[8-10] applications and have been studied extensively. A perusal of earlier works revealed that the coordinating possibility of 1,3-propanediamine is enhanced by condensing with a variety of carbonyl compounds^[11-15]. Literature survey also showed that piperonal and other compounds containing the 3,4-methylenedioxy groups possessed various biological activities^[16-18], but no work had been done on the transition metal complexes of the Schiff base derived from 1,3-propanediamine and piperonaldehyde. Therefore, the Schiff base ligand, derived from piperonal and propane-1,3-diamine named as N,N'-bis[1,3-

benzodioxol-5-ylmethylene]propane-1,3-diamine (L) and its Cr(III), Mn(II) and Fe(III) complexes were synthesized and characterized in an earlier work by the same authors.^[19] The ligand (**Figure 1**) has 4 potential donor sites, two nitrogen atoms as azomethine groups and two oxygen atoms as two dioxymethylene groups. Schiff base complexes of Co(II), Ni(II) and Cu(II) are well known and a good number of them show significant biological^[20,21] and catalytic activities^[22,23]. Hence as a continuation of the earlier study^[19] complexes Co(II), Ni(II) and Cu(II) with the above ligand were synthesised using acetates, chlorides, bromides, nitrates and perchlorates of these metals. Investigations on thermal decomposition behaviour and antifungal activities of some of these complexes were also done.

EXPERIMENTAL

Materials and measurements

All chemicals used in the present work viz, piperonaldehyde, propane-1,3-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^[24]. Infrared spectra were measured in the range 4000-400cm⁻¹ on a Shimadzu FTIR-8101 spectrophotometer with KBr pellets. The solid-state electronic spectra of complexes were recorded using a Shimadzu 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 complexes

The synthesis of ligand was carried out in the previous work^[19], by mixing propane-1,3-diamine (20 mmol, 148 mg) solution in ethanol (50 mL) with a solution of piperonaldehyde (40 mmol, 604 mg) in ethanol (50 mL) in 1:2 molar ratio and was refluxing for about 1h. The reaction mixture was then cooled and the white precipitate formed, was filtered off, washed with water and a few ml of alcohol and then purified by recrystallising from ethanol (yield = 684 mg, 91 %).

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 metal salts in methanol (10 mmol in 50 ml) (1:1 molar ratio) were refluxed for 2 to 3 h. Metal acetates were dissolved in methanol-water mixture and added to refluxing solutions of the ligand in methanol. 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 CaCl₂.

Biological assay

The antifungal activities of the ligand, its Co(II),

Ni(II) and Cu(II) complexes on the four stages of growth of *Phytophthora capsici*, the pathogen which causes foot-rot or quick-wilt disease in black pepper, viz, mycelial growth, sporangial production, zoospore release and zoospore germination were investigated by incorporating the test solutions in DMSO-water (1:40) mixtures to carrot-agar media. DMSO of corresponding concentration was used as control.

RESULTS AND DISCUSSION

Characterisation of ligand

The ligand was characterised by elemental analysis, ¹H NMR and IR spectral studies in the earlier work^[19] and is reported here for information. The ¹H-NMR spectrum of the ligand, was recorded in DMSO-d₆ and it showed a number of characteristic signals of the compound^[25]. The peak observed at a δ value of 8.04 ppm was assigned to the azomethine protons in the molecule. The signals due to the aromatic protons were observed in the range 7.33-6.84 ppm. The singlet peak at 5.96 ppm was assigned to the methylenic 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 3.72-3.66 and 1.96-1.92 ppm were assigned to the methylenic protons of the propylenediamine moiety of the ligand. The IR spectrum of the ligand showed bands at 3050 and 2981cm⁻¹ assigned to the C-H stretching of aromatic and methylene groups, respectively. The bands present at 1641 and 1256 cm⁻¹ were assigned to the C=N and C-N stretchings, respectively^[26]. Bands at 1191 and 1099 cm⁻¹ were assigned to the in plane bending of the aromatic C-H and those at 871 and 813cm⁻¹ to the out of plane bending vibration of the aromatic C-H. The characteristic absorption frequency of the dioxymethylene group of piperonal moiety^[27] was present at 927cm⁻¹. The absence of the characteristic stretching frequency of C=O of the aromatic aldehyde group^[26], indicated that the condensation was complete. The elemental analysis and spectral data for L are consistent with the formula C₁₉H₁₈O₄N₂ 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 appropriate molar

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ratios gave different types of metal complexes of the given formulae, as evidenced by the micro-analytical and spectral data. The reaction of chlorides of Co(II), Ni(II) and Cu(II) with the ligand in 2:1 molar ratios produced bimetallic complexes as evidenced by micro analytical data and effective magnetic moment per metal atom. When copper acetate was used for the synthesis hydroxo complex was obtained instead of the acetato complex. All other metal acetates gave the acetato complexes. The hydroxo complex of Cu(II) also showed

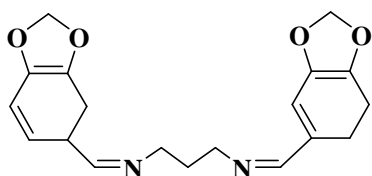


Figure 1: N,N'-bis[1,3-benzodioxol-5-ylmethylene]propane-1,3-diamine (L)

bimetallic nature.

1. $[MLA_2(H_2O)_2]$, where M = Mn(II) or Co(II) and A = CH_3COO^- , Br^- or ClO_4^- or M = Ni(II) and A = Br^- or NO_3^- or M = Cu(II) and A = Br^-
2. $[ML(H_2O)_4]A_2$, where M = Co(II) and A = NO_3^-
3. $[M_2LA_4]$, where M = Co(II) and A = Cl^- or M = Cu(II) and A = OH^-
4. $[M_2LA_4(H_2O)_2]$, where M = Ni(II) or Cu(II) and A = Cl^-
5. $[MLA_2]$, where M = Ni(II) and A = AcO^- or ClO_4^- or M = Cu(II) and A = ClO_4^-
6. $[ML(H_2O)_2]A_2$, where M = Cu(II) and A = NO_3^-

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 of them behaved as nonelectrolytes, indicating the

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

No.	Compound	Colour	Yield %	M.P °C	μ_{eff} B.M.	Δ_m ohm ⁻¹ cm ² mol ⁻¹	Microanalytical data found(calculated) %				
							Metal	C	H	N	Anion
1	$C_{19}H_{18}O_4N_2(L)$	Pale yellow	91	140			68.46 (68.01)	5.42 (5.33)	7.83 (7.94)		
2	$[CoL(AcO)_2(H_2O)_2]^*$	Pink	73	279	4.69	15.62	11.14 (10.71)	48.97 (50.09)	4.89 (5.08)	4.91 (5.08)	
3	$[Co_2LCl_4]$	Bright green	71	288	3.60	5.43	20.46 (19.73)	37.62 (38.13)	2.96 (3.01)	4.49 (4.68)	24.61 (23.74)
4	$[CoLBr_2(H_2O)_2]$	Pink	76	235	5.02	47.25	10.73 (9.95)	37.54 (38.45)	3.51 (3.71)	4.58 (4.72)	27.81 (26.98)
5	$[CoL(H_2O)_4](NO_3)_2$	Pink	72	>300	4.86	139.23	10.42 (9.95)	37.56 (38.45)	4.19 (4.38)	9.28 (9.44)	
6	$[CoL(ClO_4)_2(H_2O)_2]$	Pink	69	>300	4.74	56.84	10.16 (9.34)	35.32 (36.08)	3.37 (3.48)	4.19 (4.43)	32.72 (31.49)
7	$[NiL(AcO)_2]^*$	Brown	74	216	D**	24.61	12.02 (11.40)	52.58 (53.62)	4.47 (4.66)	5.23 (5.44)	
8	$[Ni_2LCl_4(H_2O)_2]$	Yellowish green	68	232	2.61	4.42	19.42 (18.53)	37.10 (36.00)	3.32 (3.47)	4.31 (4.42)	23.12 (22.42)
9	$[NiLBr_2(H_2O)_2]$	Green	75	>300	3.26	48.62	10.22 (9.90)	37.81 (38.47)	3.54 (3.71)	4.61 (4.72)	28.01 (27.00)
10	$[NiL(NO_3)_2(H_2O)_2]$	Green	78	>300	3.14	51.81	11.03 (10.54)	40.12 (40.96)	3.74 (3.95)	9.61 (10.06)	
11	$[NiL(ClO_4)_2]$	Brown	71	>300	D**	19.85	9.67 (9.85)	37.42 (38.27)	2.89 (3.02)	4.57 (4.70)	34.12 (33.41)
12	$[Cu_2L(OH)_4]$	Brown	74	>300	1.43	12.98	24.1 (23.83)	41.8 (42.78)	3.94 (4.13)	5.12 (5.25)	
13	$[Cu_2LCl_4(H_2O)_2]$	Blue	68	>300	1.54	2.78	20.5 (19.75)	34.73 (35.46)	3.34 (3.42)	4.23 (4.35)	23.0 (22.08)
14	$[CuLBr_2(H_2O)_2]$	Green	78	>300	2.02	38.32	11.3 (10.61)	37.2 (38.10)	3.52 (3.84)	4.53 (4.68)	28.1 (26.73)
15	$[CuL(H_2O)_2](NO_3)_2$	Violet	74	>300	1.98	146.24	11.7 (11.31)	39.8 (40.61)	3.79 (3.92)	9.72 (9.97)	
16	$[CuL(ClO_4)_2]$	Brown	69	>300	2.11	38.68	11.3 (10.57)	36.8 (37.97)	2.87 (3.00)	4.43 (4.66)	34.2 (33.14)

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

No.	Compound	Assignments and band frequencies* (cm ⁻¹)												
		vO-H (coord- inated H ₂ O)	(coordinated water) ρK _{rock} (H ₂ O) ρ _{wagg} (H ₂ O)		v C=N	v CO (coord- inated AcO ⁻)	vNO ₃ ⁻ (free NO ₃ ⁻)	vNO ₃ ⁻ (coord- inated)	vClO ₄ ⁻ (coord- inated)	δ O-CH ₂ -O	v M-N	v M-O		
1	C ₁₉ H ₁₈ O ₄ N ₂ (L)				1641s							927m		
2	[CoL(AcO) ₂ (H ₂ O) ₂]	3408b	959m	634w	1598m	1586w						927m	464w	417m
3	[Co ₂ LCl ₄]	-	-	-	1629m							927m	469m	-
4	[CoLBr ₂ (H ₂ O) ₂]	3410b	956m	637w	1598s							929w	558w	436w
5	[CoL(H ₂ O) ₄](NO ₃) ₂	3396b	961m	632w	1596m		1384s					928w	546w	447m
6	[CoL(ClO ₄) ₂ (H ₂ O) ₂]	3428b	963m	635w	1597m				1118m			929w	510w	440m
7	[NiL(AcO) ₂]	-	-	-	1591m	1587m						928m	564w	487m
8	[Ni ₂ LCl ₄ (H ₂ O) ₂]	3412b	964m	639w	1599m	1430w							619m	462w
9	[NiLBr ₂ (H ₂ O) ₂]	3424b	958m	641w	1596s							929w	527w	453w
10	[NiL(NO ₃) ₂ (H ₂ O) ₂]	3429b	961m	634w	1592m				1423w			929w	542w	431m
									1354w					
									1026w					
11	[NiL(ClO ₄) ₂]	-	-	-	1599m				1120m			928m	622w	456m
									1048w					
									932w					
12	[Cu ₂ L(OH) ₄]	3439s	-	-	1598m							928m	524w	482m
13	[Cu ₂ LCl ₄ (H ₂ O) ₂]	3412b	958m	639w	1570m							-	557m	498w
14	[CuLBr ₂ (H ₂ O) ₂]	3422b	959m	640w	1594m							927w	532w	467w
15	[CuL(H ₂ O) ₂](NO ₃) ₂	3386b	962m	637w	1587m		1384s					928w	557w	505m
16	[CuL(ClO ₄) ₂]	-	-	-	1593s				1142m			927w	549w	463m
									1114w					
									931w					

coordinated nature of the anions, but the nitrate complexes of Co(II) and Cu(II) behaved as a 1:2 electrolytes^[28].

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 1641 cm⁻¹ present in the spectrum of the free ligand, new bands appeared in the ranges of 1629-1596, 1599-1591 and 1598-1570 cm⁻¹ in the Co(II), Ni(II) and Cu(II) complexes, respectively, and were assigned to the coordinated azomethine groups^[29-31].

The characteristic absorption frequency of the dioxymethylene group was found to be present in the spectra of majority of 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^[27]. But the chloro complexes of Ni(II) and Cu(II) showed significant shift

or absence of this band. Hence, it was concluded that one of the oxygen atoms of the dioxymethylene group of the ligand was coordinated in these complexes^[27].

The IR spectra of all the complexes showed two new bands in the range 622-464 and 505-417 cm⁻¹, assigned to ν(M-N) and ν(M-O), respectively^[29,32,33]. The M-O band may be either due to coordinated nitrate-, perchlorate- or hydroxyl anion or water molecule or oxygen atom of dioxymethylene group. But the spectrum of chloro complex of Co(II), didn't show a band that can be assigned to ν(M-O). The inclusion of water molecules in the coordination sphere of the acetato, bromo, nitrate and perchlorato complexes of Co(II), the chloro, bromo and nitrate complexes of Ni(II) and Cu(II), was supported by the appearance of broad bands in the range 3439-3386 and medium or weak bands at 964-956 and 641-632 cm⁻¹, owing to ν(OH), ρK_{rock}(H₂O) and ρ_{wagg}(H₂O), respectively of coordinated water molecules^[31,33]. In the chloro complex of Co(II), ν(M-O) band could not be identified, indicating the absence of Co-O bond.

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TABLE 3: Electronic spectral bands of Co(III), Ni(II) and Cu(II) complexes and their assignments

No.	Compound	Bands (nm)	Assignment	Geometry
2	[CoL(AcO) ₂ (H ₂ O) ₂]	1080	⁴ T _{1g} (F) → ⁴ T _{2g} (F)	Octahedral
		687	⁴ T _{1g} (F) → ⁴ A _{2g} (F)	
		484	⁴ T _{1g} (F) → ⁴ T _{1g} (P)	
3	[Co ₂ LCl ₄]	1612	⁴ A ₂ (F) → ⁴ T ₂ (F)	Tetrahedral
		665	⁴ A ₂ (F) → ⁴ T ₁ (F)	
		510	⁴ A ₂ (F) → ⁴ T ₁ (P)	
4	[CoLBr ₂ (H ₂ O) ₂]	1105	⁴ T _{1g} (F) → ⁴ T _{2g} (F)	Octahedral
		623	⁴ T _{1g} (F) → ⁴ A _{2g} (F)	
		453	⁴ T _{1g} (F) → ⁴ T _{1g} (P)	
5	[CoL(H ₂ O) ₄](NO ₃) ₂	1028	⁴ T _{1g} (F) → ⁴ T _{2g} (F)	Octahedral
		587	⁴ T _{1g} (F) → ⁴ A _{2g} (F)	
		434	⁴ T _{1g} (F) → ⁴ T _{1g} (P)	
6	[CoL(ClO ₄) ₂ (H ₂ O) ₂]	1073	⁴ T _{1g} (F) → ⁴ T _{2g} (F)	Octahedral
		558	⁴ T _{1g} (F) → ⁴ A _{2g} (F)	
		443	⁴ T _{1g} (F) → ⁴ T _{1g} (P)	
7	[NiL(AcO) ₂]	539	¹ A _{1g} → ¹ B _{1g}	Square-planar
		1140	³ A _{2g} (F) → ³ T _{2g} (F)	
8	[Ni ₂ LCl ₄ (H ₂ O) ₂]	700	³ A _{2g} (F) → ³ T _{1g} (F)	Octahedral
		412	³ A _{2g} (F) → ³ T _{1g} (P)	
		1132	³ A _{2g} (F) → ³ T _{2g} (F)	
9	[NiLBr ₂ (H ₂ O) ₂]	710	³ A _{2g} (F) → ³ T _{1g} (F)	Octahedral
		389	³ A _{2g} (F) → ³ T _{1g} (P)	
		1154	³ A _{2g} (F) → ³ T _{2g} (F)	
10	[NiL(NO ₃) ₂ (H ₂ O) ₂]	721	³ A _{2g} (F) → ³ T _{1g} (F)	Octahedral
		392	³ A _{2g} (F) → ³ T _{1g} (P)	
		534	¹ A _{1g} → ¹ B _{1g}	
11	[NiL(ClO ₄) ₂]	534	¹ A _{1g} → ¹ B _{1g}	Square-planar
12	[Cu ₂ L(OH) ₄]	542	² B _{1g} → ² A _{1g}	Square-planar
13	[Cu ₂ LCl ₄ (H ₂ O)]	714b	² E _g → ² T _{2g}	Distorted octahedral
			² E _g → ² T _{2g}	Distorted octahedral
14	[CuLBr ₂ (H ₂ O) ₂]	743b	² E _g → ² T _{2g}	Distorted octahedral
15	[CuL(H ₂ O) ₂](NO ₃) ₂	572	² B _{1g} → ² A _{1g}	Square-planar
16	[CuL(ClO ₄) ₂]	536	² B _{1g} → ² A _{1g}	Square-planar

Coordination of anions

The spectra of the acetato complexes of Co(II) and Ni(II) showed bands in the ranges of 1587-1586 and 1443-1430 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^[34-36]. Microanalytical data and the non-conducting nature of these complexes further supported this. The strong band present at 3439 cm⁻¹ in the case of the hydroxo complex of Cu(II) was assigned to the O-H stretching frequency of the coordinated hydroxo group^[31,36]. The complex was synthesised using copper acetate, but in its spectrum, the characteristic bands of either free or coordinated acetate ion could not be identified^[31,37]. Element-

tal analysis data also indicated the presence of hydroxyl ions in the complex and corresponded to the formula proposed for it.

The IR spectra of nitrate complexes of Co(II) and Cu(II) showed sharp bands at 1385 cm⁻¹, which corresponded to the νNO_(asy) of free nitrate ion^[37-38]. The conductance value of the complex confirmed the presence free nitrate ions. But in the IR spectra of nitrate complex of Ni(II) such bands were absent and new bands appeared at 1423, 1354, 1026 cm⁻¹ and were assigned to νNO₃⁻ of unidentate nitrate ions^[32,38]. The non-conducting nature of these complexes also indicated coordinated nature of nitrate ions in them.

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 1142-1118, 1114-1036 and 941-931 cm⁻¹ and were assigned to the Cl-O stretchings of the monodentate perchlorate ion of C_{3v} symmetry^[32,39]. The non-conducting nature and the microanalytical data of these complexes also indicated coordinated nature of perchlorate ions.

Magnetic- and electronic spectral studies

The solid-state electronic spectra of the complexes were recorded by the procedure recommended by Venenzi^[40]. TABLE 3 lists the important electronic spectral bands of the complexes and their assignments.

Co(II) complexes

Among the Co(II) complexes which were investigated here, the spectra of the acetato, bromo, nitrate and perchlorato complexes showed bands in the ranges 1105-1028, 687-558, 484-434 nm. These bands were assigned to the ⁴T_{1g}(F) → ⁴T_{2g}(F), ⁴T_{1g}(F) → ⁴A_{2g}(F) and ⁴T_{1g}(F) → ⁴T_{1g}(P) transitions, respectively, in an octahedral geometry^[30,31]. The magnetic moment values in the range 4.69-5.02 B.M. also indicated high-spin octahedral geometries^[30,31]. The chloro complex of Co(II) was bright-green in colour and its electronic spectrum showed intense bands at 1612, 665 and 510 nm assigned, respectively, to the ⁴A₂(F) → ⁴T₂(F), ⁴A₂(F) → ⁴T₁(F) and ⁴A₂(F) → ⁴T₁(P) transitions, characteristic of tetrahedral geometry^[41,42]. But the chloro complex of Co(II) showed a magnetic moment of 3.60 B.M. only, which was slightly lower than the value expected for tetrahedral complex. The slightly lower value could be due to bridging nature of the ligands, resulting in

bimetallic character and anti-ferromagnetic coupling [42-44].

Ni(II) complexes

In the present investigation, the spectra of acetato and perchlorato complexes of Ni(II) showed bands at 539 and 534 nm, respectively, assigned to the $^1A_{1g} \rightarrow ^1B_{1g}$ transitions in a square-planar geometry^[33,45]. The diamagnetic nature of the complexes also supported this geometry^[33,45]. The spectra of the chloro, bromo and nitrate complexes of Ni(II) showed transitions in the ranges 1132-1154, 700-721 and 412-389 nm. These were assigned 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^[31,46]. The chloro complex showed a magnetic moment of 2.61 B.M., lower than that expected for an octahedral complex. The lower value could be, probably due to the bimetallic nature and the subsequent anti-ferromagnetic coupling in them^[47,48]. The bromato and nitrate complexes showed magnetic moments of 3.26 and 3.14 B.M., respectively, in the range expected for octahedral geometries^[30,49].

Cu(II) complexes

In the electronic spectra of hydroxo, nitrate and perchlorato complexes broad bands appeared at 542, 572 and 536 nm respectively, which were assigned to the $^2B_{1g} \rightarrow ^2A_{1g}$ transitions in a square-planar geometry^[31,33,46]. The spectra of chloro and bromo complexes of Cu(II) showed bands at 714 and 743 nm, respectively, and these were assigned to the $^2E \rightarrow ^2T_2$ transition in a distorted-octahedral geometry^[46,50]. The hydroxo and chloro complexes of Cu(II) showed magnetic moments of 1.43 and 1.54 B.M., respectively. The lower values indicated some sort of molecular association that could be achieved through either a direct copper-copper interaction and/or magnetic exchange interaction through bridging ligands^[31,47]. The bromato, nitrate and perchlorato complexes showed magnetic moments in the range 1.98 to 2.11 B.M. indicating sufficient magnetic dilution in these complexes^[31,47].

Thermogravimetric analysis

Thermograms of three complexes, viz, $[Co_2LCl_4]$, $[Ni_2LCl_4(H_2O)_2]$ and $[Cu_2LCl_4(H_2O)_2]$ were analysed. The total mass-losses in each case indicated the forma-

tion Co_3O_4 , NiO and CuO, respectively around 600°C., which were confirmed by chemical analysis. The Ni(II) and Cu(II) complexes exhibited 3-stage decomposition patterns. Around 150°C they underwent dehydration reactions, losing two molecules of water each, thus confirming the presence of coordinated water molecules in them. The second stage in the case of the Ni(II) complex matched to the loss of one piperonal moiety and that in the case of Cu(II) complex indicated the loss of two piperonal moieties. In both cases, the rest of the ligand and four chloride ions were removed, with the simultaneous formation of metal oxides in the third stage. No mass-loss was detected for the Co(II) complex up to a temperature of 200°C indicating the absence of water molecules in it. It decomposed in two stages, which were similar to the second and third stages of decomposition of the Ni(II) complex. The decomposition patterns were in good agreement with the suggested formulae and the total mass-loss in independent pyrolytic studies also agreed with the thermograms. 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

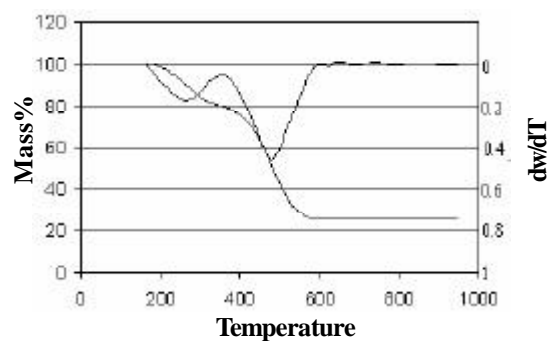


Figure 2 : TG-dTG traces of $[Co_2LCl_4]$

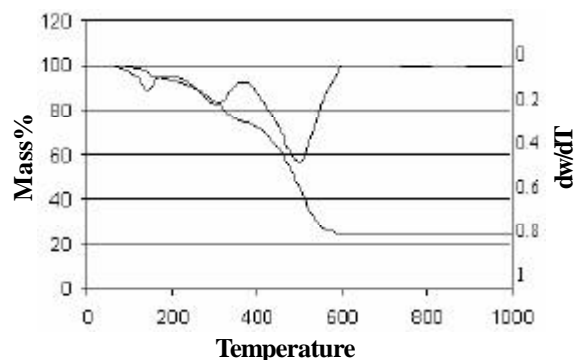


Figure 3: TG-dTG traces of $[Ni_2LCl_4(H_2O)_2]$

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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^[51]. Figures 2-4 give the TG-DTG traces of the complexes, the TABLE 4 gives the different stages of decomposition and the TABLE 5 gives the kinetic parameters. Based on inception temperature and activation energy, for the first stage of decomposition excluding the dehydration stage, stabilities of the complexes were found to be in the order, Cu > Ni > Co.

The structures suggested for different complexes are given in figures 5-10.

Anti fungal studies

Black pepper or *Piper nigrum L*, a perennial climber, belonging to the family, *Piperacia* is one of the main exports earning spice crops of Kerala state in India. Several diseases caused by fungi, bacteria, virus and mycoplasma, affect black pepper. Among them, foot-rot caused by *Phytophthora capsici*, is highly prevalent in almost all the pepper growing areas and is reported to inflict considerable damage to the plants. Crop lose due to foot-rot in Kerala is estimated to be about 10 % of the total production and in India it ranges from 20 to 30 percentage^[52-54]. The ligand and the Co(II) and Ni(II) acetato complexes and the Cu(II) hydroxo complex were screened for antifungal activities against *Phytophthora capsici* and were found to be active on different stages of growth of the microorganism. In all

the four stages, the metal complexes were generally found to show more antifungal activity than the free ligand. The complex of Cu(II) was found to be the more effective in inhibiting the growth of *Phytophthora capsici*, compared to those of the other metal ions in all

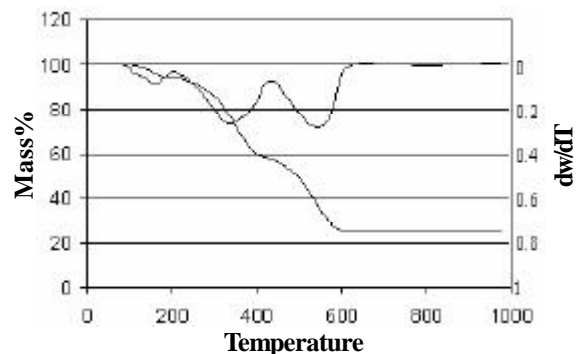
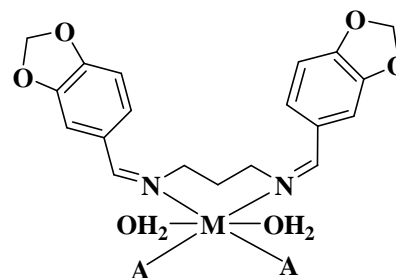


Figure 4: TG-dTG traces of $[\text{Cu}_2\text{LCl}_4(\text{H}_2\text{O})_2]$



Where M = Co(II) and A = CH_3COO^- , Br⁻ or ClO_4^- or M = Ni(II) and A = Br⁻ or NO_3^- or M = Cu(II) and A = Br⁻

Figure 5: Structure suggested for $[\text{CoL}(\text{OOC}-\text{CH}_3)_2(\text{H}_2\text{O})_2]$, $[\text{CoLBr}_2(\text{H}_2\text{O})_2]$, $[\text{CoL}(\text{ClO}_4)_2(\text{H}_2\text{O})_2]$, $[\text{NiLBr}_2(\text{H}_2\text{O})_2]$, $[\text{NiL}(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ and $[\text{CuLBr}_2(\text{H}_2\text{O})_2]$

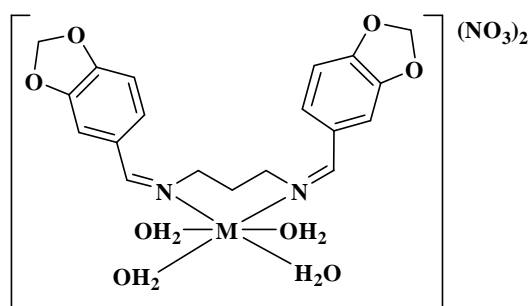
TABLE 4: Thermal decomposition data of Co(II), Ni(II) and Cu(II) complexes

Complex	Stage	Temp. range in TG	Peak temp.	Loss of mass			Assignments
				From TG	Theoretical	From Pyrolysis	
$[\text{Co}_2\text{LCl}_4]$	I	200-340	310	20.9	20.2		Loss of 1 piperonal moiety
	II	340-560	490	53.2	53.0		Loss of rest of the ligand, 4Cl^- ions and subsequent formation of metal oxide
	Total			74.1	73.2	73.5	$\text{Co}_2\text{LCl}_4 \rightarrow ? \text{Co}_3\text{O}_4$
$[\text{Ni}_2\text{LCl}_4(\text{H}_2\text{O})_2]$	I	100-180	150	5.9	5.7		Loss of $2\text{H}_2\text{O}$
	II	180-380 (220-380)*	320	20.6	19.1		Loss of 1 piperonal moiety
	III	380-590	500	50.0	51.6		Loss of remaining ligand, 4Cl^- ions and formation of metal oxide
Total				75.5	76.4	74.8	$\text{Ni}_2\text{LCl}_4 \cdot 2\text{H}_2\text{O} \rightarrow 2 \text{NiO}$
$[\text{Cu}_2\text{LCl}_4(\text{H}_2\text{O})_2]$	I	110-200	115	5.8	5.6		Loss of $2\text{H}_2\text{O}$
	II	220-440	330	37.9	37.6		Loss of 2 piperonal moiety
	III	440-600	550	31.1	32.1		Loss of remaining ligand, 4Cl^- and formation MO
Total				74.8	75.3	74.2	$[\text{Cu}_2\text{LCl}_4(\text{H}_2\text{O})_2] \rightarrow 2 \text{CuO}$

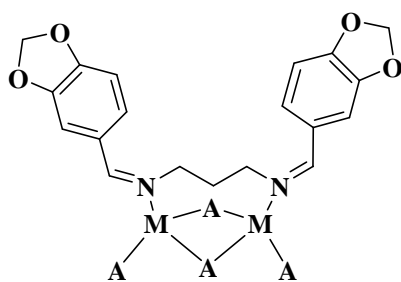
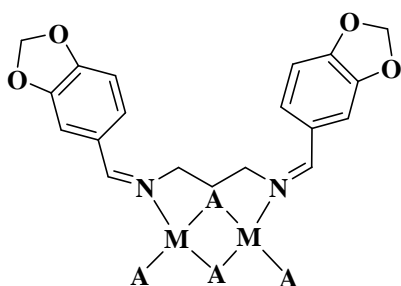
*Temperature range of significant mass-loss in the stage

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

Complex	Stage	E _a kJ/mol	As ⁻¹	ΔS* J/K/mol	ΔH* kJ/mol	ΔG*kJ/mol	γ	n
[Co ₂ LCl ₄]	I	55.11	4.93 × 10 ²	-198.93	50.26	166.23	-0.9939207	1
	II	113.12	1.73 × 10 ⁵	-152.46	106.78	223.11	-0.9931158	1
	I	72.36	7.72 × 10 ⁶	-115.97	68.84	117.90	-0.9980618	1
[Ni ₂ LCl ₄ (H ₂ O) ₂]	II	56.73	3.71 × 10 ²	-201.42	51.80	171.25	-0.9997985	1
	III	111.39	1.06 × 10 ⁵	-156.82	104.80	229.16	-0.9967919	1
	I	66.80	7.06 × 10 ⁵	-135.14	63.57	116.01	-0.9957561	1
[Cu ₂ LCl ₄ (H ₂ O) ₂]	II	59.61	2.65 × 10 ²	-204.38	54.60	177.84	-0.9990715	1
	III	145.59	8.83 × 10 ⁶	-120.38	138.75	237.82	-0.9970325	1



where M = Co(II)

Figure 6 : Structure suggested for [CoL(H₂O)₄](NO₃)₂M = Co(II) and A = Cl⁻Figure 7 : Structure suggested for [Co₂LCl₄]Where M = Cu(II) and A = OH⁻Figure 8 : Structure suggested for [Cu₂L(OH)₄]

the four stages of investigation. The Ni(II) and Co(II) complexes followed it. The acetates of Co(II), Ni(II) and Cu(II), were also reported to be antifungal in nature, capable of inhibiting the mycelial growth of *Phytophthora capsici*, but the activities were generally far lower than those of the complexes^[55]. Among the four stages, the inhibition was more pronounced in

TABLE 6: The inhibitory effects of the ligand and its metal complexes on the mycelial growth of *Phytophthora capsici*

Conc. of sample	Ligand	Sample				
		Complex	Complex			Control
			Co(II)	Ni(II)	Cu(II)	
25ppm	Diameter mm	32	32.2	30.2	28.8	34
	% of inhibition	5.88	5.29	11.2	15.3	
50ppm	Diameter mm	30.8	30.9	28.4	23.6	34
	% of inhibition	9.41	9.12	16.5	30.6	
75 ppm	Diameter mm	28.2	25.8	22.9	12.8	34
	% of inhibition	17.1	24.1	32.6	62.4	
100ppm	Diameter mm	18.6	15.8	12.6	10.1	34
	% of inhibition	45.3	53.5	62.9	70.3	

TABLE 7: The inhibitory effects of the ligand and its metal complexes on the sporangial production of *Phytophthora capsici*

Conc. of sample	Ligand	Sample				
		Complex	Complex			Control
			Co(II)	Ni(II)	Cu(II)	
25ppm	No of sporangia per field	56	52	49	45	64
	% of inhibition	12.5	18.8	23.4	29.7	
50ppm	No of sporangia per field	51	48	42	36	64
	% Of inhibition	20.3	25	34.4	43.7	
75ppm	No of sporangia per field	44	34	28	17	64
	% Of inhibition	31.2	46.8	56.2	73.4	
100ppm	No of sporangia per field	34	19	19	12	64
	% Of inhibition	46.8	70.3	70.3	81.2	

zoosporangial production and zoospore release. The data of inhibitory effects of the ligand and the complexes on various stages of the growth of *Phytophthora capsici* are given in TABLES 6-9. Figure 9 gives graphical comparison of inhibitory effects of ligand and complexes on mycelial growth

The higher activities of the metal complexes in comparison to the free metal ions may be due to the increased lipophilicity that enhances the penetration of the complexes into lipid membranes and blocks the metal binding sites in the enzymes of the organisms.^[56] These complexes may also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism^[33]. Furthermore,

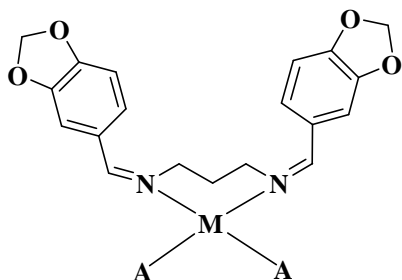
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TABLE 8: The inhibitory effect of the ligand and its metal complexes on the sporangial release of *Phytophthora capsici*

Conc. of sample	Sample	Complex				Control
		Ligand	Co(II)	Ni(II)	Cu(II)	
25ppm	% of zoospore release	38.4	30.2	25.2	20.2	51.4
	% of inhibition	25.3	41.2	51.0	60.7	
50ppm	% of zoospore release	25.1	20.6	15.6	11.6	51.4
	% of inhibition	51.2	59.9	69.6	77.4	
75ppm	% of zoospore release	18.6	9.4	6.6	0	51.4
	% of inhibition	63.8	81.7	87.2	100	
100ppm	% of zoospore release	10.8	2.2	0	0	51.4
	% of inhibition	79.0	95.7	100	100	

TABLE 9: The inhibitory effect of ligand and its metal complexes on the zoospore germination of *Phytophthora capsici*

Conc. of sample	Sample	Complex				Control
		Ligand	Co(II)	Ni(II)	Cu(II)	
25ppm	% Of zoospore germination	43.8	48.6	32.2	28.4	68.6
	% Of inhibition	36.2	29.2	53.1	58.6	
50ppm	% Of zoospore germination	37.8	42.2	24.6	14.0	68.6
	% Of inhibition	44.9	38.5	64.1	79.6	
75ppm	% Of zoospore germination	29.2	27.6	15.2	6.2	68.6
	% Of inhibition	57.4	59.8	77.8	91.0	
100ppm	% Of zoospore germination	19.4	8.6	7.6	2.2	68.6
	% Of inhibition	71.7	87.5	88.9	96.8	



Where M = Ni(II) and A = CH_3COO^- or ClO_4^-
or M = Cu(II) and A = ClO_4^-

Figure 9 : Structure suggested for $[\text{NiL}(\text{OOC}-\text{CH}_3)_2]$, $[\text{NiL}(\text{ClO}_4)_2]$ and $[\text{CuL}(\text{ClO}_4)_2]$

the mode of action of the compounds may involve the formation of a hydrogen bond through the azomethine group with the active centres of cell constituents, resulting in the interference with normal cell division process^[57]. The observation that not only the Cu(II) complex of the Schiff bases, but the Co(II) and Ni(II) complexes also showed sufficient antifungal activity may open

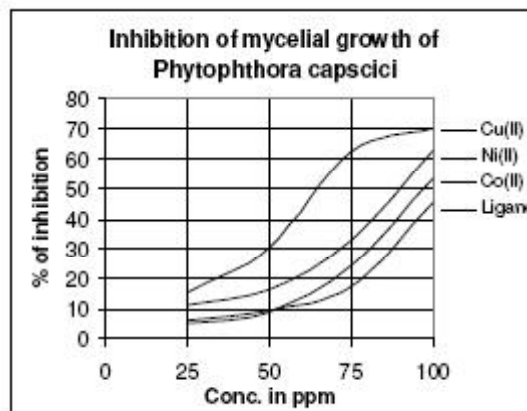


Figure 10 : Graphical comparison of inhibitory effects of ligand and complexes on mycelial growth

up new avenues in the quest for tackling the problem of foot-rot disease in black pepper.

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