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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
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Synthesis, Characterization, Thermal Decomposition and Antifungal Studies of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) Complexes of N,N′-bis[1,3-benzodioxol-5ylmethylene]ethane-1, 2-diamine

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Synthesis, Characterization, Thermal Decomposition and Antifungal Studies of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) Complexes of N,N′-bis[1,3-benzodioxol-5-ylmethylene]ethane-1, 2-diamine

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A bidentate/tetradentate Schiff base namely, N,N′-bis[1,3-benzodioxol-5-ylmethylene] ethane-1,2-diamine was synthesized by condensing piperonaldehyde (3,4-dioxymethylenebenzaldehyde) with ethylenediamine. Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of this chelating/bridging ligand were synthesized using acetates, chlorides, bromides, nitrates and perchlorates of these metals. The ligand and the complexes were characterized by elemental analysis, ^{1}H NMR, 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 analyzed and the kinetic parameters for the different stages of decompositions were determined. The antifungal activities of the ligand and some of its complexes against *Phytophthora capsici* were tested in carrot agar medium.

Keywords antifungal activity, diamine, piperonal, Schiff base, thermal decomposition, transition metal complexes

INTRODUCTION

Schiff base derivatives and their transition metal complexes, known from the 19th century, have made considerable contributions to the advances in coordination chemistry[1,2] and have found a broad-spectrum of applications in very diverse fields such as biochemical,[3] analytical,[4] catalytic,[5] therapeutic[6] and biomimetic[7] activities. These applications include their uses as MRI contrast agents,[8] biological markers,[9] antitumor agents,[10] etc. In addition, the capacity of Schiff bases to form stable complexes with transition metal ions[2,11,12] has inspired attention to such compounds so that extensive research effort is being devoted to the synthesis of new Schiff base complexes of transition metal ions. 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 analytical,[13–15] industrial,[16] clinical[17] and biochemical[18,19] areas, and they possess considerable physiological activities.[20,21] Piperonaldehyde and a few Schiff bases derived from it are also having noteworthy biological and antimicrobial activities.[22–24] 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 ethylenediamine and its transition metal complexes were synthesized and characterized. The ligand named as N,N′-bis[1,3-benzodioxol-5-ylmethylene]ethane-1,2-diamine (L), (Figure 1) has 4 potential donor sites, two nitrogen atoms as azomethine groups and two oxygen atoms as two dioxymethylene groups. Complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) were synthesized using acetates, chlorides, bromides, nitrates and perchlorates of these metals. Investigations on thermal decomposition behaviur and antifungal activities of some of these complexes were also done.

EXPERIMENTAL

Materials and Measurements

All chemicals used in the present work viz, piperonaldehyde, ethylenediamine, 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.[25] ^{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

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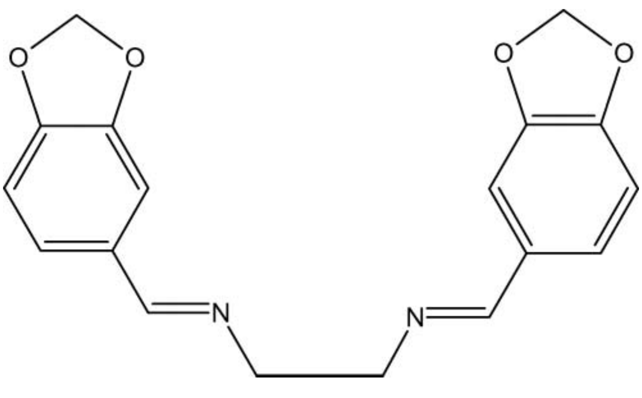


FIG. 1. N,N′-bis[1,3-benzodioxol-5-ylmethylene] ethane-1,2-diamine.

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 behaviors of complexes were monitored using a Perkin Elmer TGA-7 Analyzer.

Synthesis of the Ligand and Complexes

Ethylenediamine (20mmol, 120 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 recrystallyzing from ethanol (yield = 635 mg, 88%).

Complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with this ligand were synthesized 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. In the case of Co(II), solutions of the salts and ligand in acetone were used. Metal acetates were dissolved in methanol-water or acetone-water mixture and added to refluxing solutions of the ligand in methanol or acetone. Several complexes, especially those with 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 diethylether 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 $CaCl_2$.

Biological Assay

The antifungal activities of the ligand, its Mn(II), Co(II), Ni(II) and Cu(II) complexes were tested on the four stages of the growth of *Phytophthora capscici*, the pathogen that 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

Characterization of Ligand

In this paper we designed and synthesized a bidentate/tetradentate Schiff base ligand N,N′-bis[1,3-benzodioxol-5-ylmethylene]ethane-1,2-diamine (L) as shown in the scheme (Figure 2).

The ^1H NMR spectrum of the ligand has been recorded in DMSO-d_6 at room temperature. The spectrum of the ligand showed strong signal at 8.21 ppm, due to the azomethine protons. The spectrum also showed several signals in the range 7.50 to 6.84 ppm, assigned to the different types of aromatic protons on the piperonal moieties in the molecule. The signals at 5.96 ppm and in the range 3.86–3.84 ppm were assigned to the methylenic protons of the dioxymethyene groups on the piperonal moieties and of the ethylenediamine group in the molecule. The IR spectrum of the ligand showed bands at 3050 and 2905 cm^{-1} assigned to the C—H stretching of aromatic and methylene groups, respectively. The bands present at 1639 and 1255 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 873 and 817 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[27] was present at 926 cm^{-1}. The absence of the characteristic stretching frequency

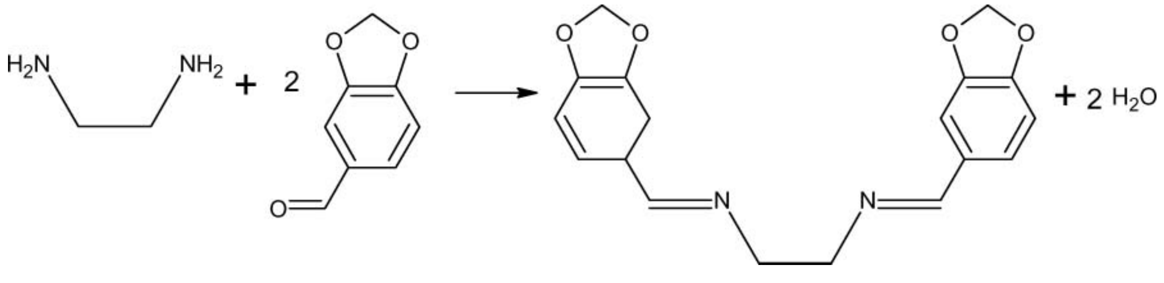


FIG. 2. Scheme for reaction between ethane-1,2-diamine and piperonaldehyde.

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 $C_{18}H_{16}O_4N_2$and the structure given in Figure 1.

Formulae and General Properties of Complexes

The reaction of the ligand (L) with different salts of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions in appropriate molar ratios gave different types of metal complexes of the given formulae, as evidenced by the micro-analytical and spectral data. The reaction of acetates, chlorides and bromides of Cr(III) and Fe(III) and acetates and chlorides of Mn(II), 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. The acetates of all the metal ions used here, yielded hydroxo complexes. The reactions are represented by the following schemes.

$2MA_3 + L + 2H_2O \rightarrow [M_2LA_6(H_2O)_2]$,

where M = Cr(III) or Fe(III) and $A^- = OH^-$, Cl^- or Br^-

$2M(AcO)_3 + L + 8H_2O \rightarrow [M_2L(OH)_6(H_2O)_2] + 6AcOH$

where M = Cr(III) or Fe(III) and $AcO^- = CH_3COO^-$

$MA_3 + L + H_2O \rightarrow MLA_3(H_2O)]$,

where M = Cr(III) or Fe(III) and $A^- = NO_3^-$ or ClO_4^-

$2MCl_2 + L + 2H_2O \rightarrow [M_2LCl_4(H_2O)_2]$,

where M = Mn(II), Ni(II) or Cu(II) and $A^- = Cl^-$

$2Mn(AcO)_2 + L + 6H_2O \rightarrow [Mn_2L(OH)_4(H_2O)_2] + 4AcOH$

where $AcO^- = CH_3COO^-$

$MA_2 + L + 2\,H_2O \rightarrow [MLA_2(H_2O)_2]$,

where M = Mn(II) and $A^- = Br^-$ or ClO_4^-

or M = Co(II) and $A^- = Br^-$, NO_3^- or ClO_4^-

or M = Ni(II) and $A^- = Br^-$ or ClO_4^-

or M = Cu(II) and $A^- = Br^-$

$M(NO_3)_2 + L + 4\,H_2O \rightarrow [ML(H_2O)_4](NO_3)_2$,

where M = Mn(II) or Cu(II)

$2CoCl_2 + L \rightarrow [Co_2LCl_4]$,

$2\,M(AcO)_2 + L + 4\,H_2O \rightarrow [M_2L(OH)_4] + 4AcOH$

where M = Co(II), Ni(II) or Cu(II) and $AcO^- = CH_3COO^-$

$MA_2 + L + 2\,H_2O \rightarrow [ML(H_2O)_2]\,A_2$,

where M = Ni(II) and $A^- = NO_3^-$

or M = Cu(II) and $A^- = ClO_4^-$

The colors, magnetic susceptibilities and molar conductivities and melting points of the complexes are listed in Table 1 and the micro-analytical data in Tables 2 and 3. 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 most of the complexes behaved as nonelectrolytes[28], indicating the coordinated nature of the anions. The data also indicated that the nitrato complexes of Mn(II) and Ni(II) and the nitrato and perchlorato complexes of Cu(II) behaved as 1:2 electrolytes.[28]

IR Spectra of Complexes

Tables 4, 5 and 6 lists the most important IR spectral bands of the 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 1639 cm^{-1} present in the spectrum of the free ligand, new bands appeared in the ranges of 1600–1583, 1619–1595, 1600–1595, 1626–1595, 1633–1624 and 1624–1564 cm^{-1} in the Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) complexes, respectively, and were assigned to the coordinated azomethine groups.[29,30,31]

The characteristic absorption frequency of the dioxymethylyne 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. But in a few cases, either this band was absent or significantly shifted to lower frequency region. The hydroxo and chloro complexes of Mn(II), the chloro complexes of Ni(II) and Cu(II) (No.7, 8, 23 and 28) showed significant shift or absence of this band. Hence, it could be reasonably assumed that one of the oxygen atoms of the dioxymethylene groups had been coordinated in them.[27]

The IR spectra of all the complexes revealed new bands at 678–440 and 525–412 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 due to the coordination of the oxygen atoms of the dioxymethylene groups. In the chloro complex of Co(II) (No. 18), ν (M–O) band could not be identified, indicating the absence of Co-O bond. The inclusion of water molecules in the coordination sphere of the metal complexes, except for hydroxo and chloro complexes of Co(II) and hydroxo complexes of Ni(II) and Cu(II) (Nos. 17, 18, 22 and 23) was supported by the appearance of broad bands in the range 3440–3286 and medium or weak bands at 962–956 and 631–638 cm^{-1}, owing to ν(OH), $\rho K_{rock}(H_2O)$ and $\rho_{wagg}(H_2O)$, respectively of coordinated water molecules.[31,32]

Coordination of Anions

The acetato ligand may coordinate to a metal center in either a monodentate, bidentate or bridging manner. The $\nu_a(CO_2)$ and $\nu_s(CO_2)$ bands of the free acetate ions are around 1560 and 1416 cm^{-1}, respectively. In monodentate coordination $\nu_a(CO_2)$ is found at higher energy than 1560 cm^{-1} and $\nu_s(CO_2)$ is lower than 1416 cm^{-1}. As a result, the separation between the $\nu(CO_2)$ bands is much larger in monodentate complexes than the free ion. The opposite trend is observed in bidentate acetato coordination; the separation between $\nu(CO_2)$ bands is smaller than

TABLE 1
Formulae and general properties of ligand and complexes

No.	Compound	Color	Yield %	M.P °C	μ_{eff} B.M.	Λ_m ohm^{-1} cm^2 mol^{-1}
1	$C_{18}H_{16}O_4N_2$ (L)	Colorless	88	166		
2	$[Cr_2L(OH)_6(H_2O)_2]$	Brown	65	254	3.49	28.46
3	$[Cr_2LCl_6(H_2O)_2]$	Green	67	243	3.24	—
4	$[Cr_2LBr_6(H_2O)_2]$	Greenish yellow	62	222	3.52	28.43
5	$[CrL(NO_3)_3((H_2O)]$	Green	88	304	3.82	56.25
6	$[CrL(ClO_4)_3(H_2O)_{]}$	Green	87	326	3.91	14.82
7	$[Mn_2L(OH)_4(H_2O)_2]$	Yellowish brown	71	238	4.92	21.4
8	$[Mn_2LCl_4(H_2O)_2]$	Yellowish brown	68	247	4.72	12.24
9	$[MnLBr_2(H_2O)_2]$	Yellowish brown	82	280	5.91	42.8
10	$[MnL(H_2O)_4](NO_3)_2$	Yellowish brown	79	>300	6.10	148.42
11	$[MnL(ClO_4)_2(H_2O)_2]$	Yellowish brown	76	>300	6.20	41.6
12	$[Fe_2L(OH)_6(H_2O)_2]$	Orange	67	264	4.56	23.92
13	$[Fe_2LCl_6(H_2O)_2]$	Orange	63	248	5.02	16.32
14	$[Fe_2LBr_6(H_2O)_2]$	Orange	64	290	4.92	24.63
15	$[FeL(NO_3)_3((H_2O)]$	Orange	82	260	6.12	49.45
16	$[FeL(ClO_4)_3(H_2O)]$	Orange	79	256	5.94	51.82
17	$[Co_2L(OH)_4]$	Greenish blue	61	275	3.31	—
18	$[Co_2LCl_4]$	Bright green	64	283	3.42	11.51
19	$[CoLBr_2(H_2O)_2]$	Orange	67	235	4.84	42.47
20	$[CoL(NO_3)_2(H_2O)_2]$	Orange brown	82	>300	5.02	31.83
21	$[CoL(ClO_4)_2(H_2O)_2]$	Orange	79	>300	5.19	36.59
22	$[Ni_2L(OH)_4]$	Grey	59	285	D	28.21
23	$[Ni_2LCl_4(H_2O)_2]$	Greenish yellow	63	292	2.45	14.69
24	$[NiLBr_2(H_2O)_2]$	Green	73	285	3.35	31.21
25	$[NiL(H_2O)_2]\ (NO_3)_2$	Brown	75	>300	D	137.44
26	$[NiL(ClO4)_2(H_2O)_2]$	Green	72	>300	3.42	26.68
27	$[Cu_2L(OH)_4]$	Brown	63	>300	1.37	—
28	$[Cu_2LCl_4(H_2O)_2]$	Blue	61	>300	1.45	13.1
29	$[CuLBr_2(H_2O)_2]$	Green	58	284	2.10	38.06
30	$[CuL(H_2O)_4](NO_3)_2$	Bluish green	69	>300	1.98	162.23
31	$[CuL(H_2O)_2](ClO_4)_2$	Brown	71	>300	1.90	138.45

for the free ion. For bridging acetate, however, the two $\nu(CO_2)$ bands are close to the free ion.[34,36,37] But in the spectra of complexes synthesised using metal acetates, the characteristic frequencies of either free or coordinated acetate ions could not be identified.[33,37] The strong absorption bands present at 3420, 3381, 3430, 3257, 3417 and 3390 cm^{-1} in the spectra of the hydroxo complexes of Cr(III), Mn(II), Fe(III), Ni(II),Co(II) and Cu(II), respectively, were assigned to the ν(O—H) of the hydroxo groups,[33,38] which were coordinated to the metal ions. Elemental analyses data and conductance values of these complexes also supported the assumption.

The IR spectra of nitrato complexes of Mn(II), Ni(II) and Cu(II) (No. 10, 25 and 30) showed sharp bands at 1384, 1385 and 1384 cm^{-1}, respectively, which corresponded to the $\nu NO_{(asy)}$ of free nitrate ion.[31,38,39] The conductance values of these complexes confirmed the presence free nitrate ions. But in the IR spectra of nitrato complexes of Cr(III), Fe(III) and Co(II) such bands were absent and new bands appeared in the ranges 1449–1445, 1361–1326 and 1041–1036 cm^{-1}, assigned to νNO_3^- of unidentate nitrate ions.[31,39] The non-conducting nature of these complexes confirmed the presence of coordinated nitrate ions in them.

The IR spectra of perchlorato complexes of Cr(III), Mn(II), Fe(III), Co(II) and Ni(II) (No. 6,11,16,21 and 26) showed bands in the ranges 1117–1120, 1038–1043 and 934–938 cm^{-1} indicating the presence of monodentatively coordinated perchlorate ion of C_{3v} symmetry.[31,40] The spectrum of Cu(II) perchlorato complex (No.31) showed a strong band at 1112 and a week band at 981 cm^{-1} assigned to the triply degenerate ν(ClO)(asy) and to the symmetry forbidden ν(ClO)(sy) of the free perchlorate ion, which further confirmed its conductance value.[35,41]

TABLE 2
Micro-analytical data of ligand, Cr(III), Mn(II) and Fe(III) complexes

	Found (calculated) %				
Compound	Metal	C	H	N	Anion
$C_{18}H_{16}O_4N_2$ (L)		66.74 (66.67)	4.94 (4.93)	8.61 (8.64)	
$[Cr_2L(OH)_6(H_2O)_2]$	19.23 (18.37)	37.64 (38.16)	4.67 (4.59)	4.72 (4.95)	
$[Cr_2LCl_6(H_2O)_2]$	16.12 (15.36)	30.85 (31.91)	2.74 (2.95)	4.01 (4.14)	32.6 (31.46)
$[Cr_2LBr_6(H_2O)_2]$	11.83 (11.02)	21.84 (22.88)	2.04 (2.12)	2.84 (2.97)	52.14 (50.85)
$[CrL(NO_3)_3((H_2O)]$	9.12 (8.97)	36.34 (37.24)	2.98 (3.10)	11.7 (12.07)	
$[CrL(ClO_4)_3(H_2O)]$	7.86 (7.51)	30.5 (31.19)	2.46 (2.60)	3.96 (4.04)	43.91 (43.11)
$[Mn_2L(OH)_4(H_2O)_2]$	21.12 (20.45)	39.43 (40.15)	4.32 (4.46)	5.1 (5.20)	
$[Mn_2LCl_4(H_2O)_2]$	18.21 (17.97)	34.93 (35.29)	3.14 (3.27)	4.35 (4.58)	23.62 (23.20)
$[MnLBr_2(H_2O)_2]$	9.12 (9.57)	38.13 (37.57)	3.52 (3.48)	4.93 (4.87)	27.15 (27.83)
$[MnL(H_2O)_4](NO_3)_2$	9.08 (9.57)	38.2 (37.57)	4.42 (4.17)	9.54 (9.74)	
$[MnL(ClO_4)_2(H_2O)_2]$	8.74 (8.96)	36.11 (35.18)	3.31 (3.26)	4.72 (4.56)	31.93 (32.41)
$[Fe_2L(OH)_6(H_2O)_2]$	20.34 (19.51)	36.81 (37.63)	4.38 (4.53)	4.59 (4.88)	
$[Fe_2LCl_6(H_2O)_2]$	17.12 (16.35)	30.86 (31.53)	2.81 (2.92)	3.92 (4.10)	43.67 (42.86)
$[Fe_2LBr_6(H_2O)_2]$	12.2 (11.76)	21.9 (22.69)	2.0 (2.10)	2.81 (2.94)	51.9 (50.42)
$[FeL(NO_3)_3((H_2O)]$	10.1 (9.59)	36.1 (36.99)	2.96 (3.08)	11.2 (11.99)	
$[FeL(ClO_4)_3(H_2O)]$	8.46 (8.04)	30.1 (31.01)	2.43 (2.58)	3.87 (4.02)	43.6 (42.86)

Magnetic- and Electronic Spectral Studies

The solid-state electronic spectra of the complexes were recorded by the procedure recommended by Venenzi.[42] Tables 7 and 8 list important electronic spectral bands of the complexes and their assignments.

Cr(III) Complexes

In the spectra of all the Cr(III) complexes, two peaks were identified in the ranges 582–542 and 442–384 nm and were assigned to the $^4A_2g \rightarrow {}^4T_{1g}(P)$ and the $^4A_2g \rightarrow {}^4T_{2g}$ transitions in an octahedral geometry.[43,44] The Cr(III) complexes,

TABLE 3
Micro-analytical data of ligand, Co(II), Ni(II) and Cu(II) complexes

	Found (calculated) %				
Compound	Metal	C	H	N	Anion
$[Co_2L(OH)_4]$	23.83 (23.14)	41.77 (42.35)	3.78 (3.92)	5.22 (5.49)	
$[Co_2LCl_4]$	21.82 (20.20)	35.48 (36.97)	2.61 (2.74)	4.63 (4.80)	25.1 (24.32)
$[CoLBr_2(H_2O)_2]$	11.01 (10.19)	36.67 (37.31)	3.32 (3.45)	4.72 (4.84)	28.3 (27.63)
$[CoL(NO_3)_2(H_2O)_2]$	11.64 (10.87)	38.39 (39.78)	3.43 (3.68)	9.97 (10.31)	
$[CoL(ClO_4)_2(H_2O)_2]$	8.93 (9.55)	35.22 (34.95)	3.36 (3.24)	4.62 (4.53)	31.48 (32.20)
$[Ni_2L(OH)_4]$	23.75 (23.05)	41.87 (42.40)	3.73 (3.93)	5.13 (5.50)	
$[Ni_2LCl_4(H_2O)_2]$	19.32 (18.95)	33.96 (34.87)	3.13 (3.23)	4.43 (4.52)	23.71 (22.93)
$[NiLBr_2(H_2O)_2]$	10.91 (10.14)	38.42 (37.33)	3.24 (3.46)	4.71 (4.84)	29.01 (27.65)
$[NiL(H_2O)_2]\ (NO_3)_2$	11.72 (10.82)	38.66 (39.81)	3.53 (3.69)	11.1 (10.32)	
$[NiL(ClO4)_2(H_2O)_2]$	9.92 (9.50)	33.89 (34.97)	3.13 (3.24)	4.36 (4.53)	33.43 (32.22)
$[Cu_2L(OH)_4]$	25.19 (24.47)	40.89 (41.62)	3.71 (3.85)	5.17 (5.40)	
$[Cu_2LCl_4(H_2O)_2]$	21.13 (20.19)	33.53 (34.34)	2.95 (3.18)	4.38 (4.45)	23.37 (22.58)
$[CuLBr_2(H_2O)_2]$	11.21 (10.88)	35.99 (37.02)	3.24 (3.43)	4.69 (4.80)	29.1 (27.42)
$[CuL(H_2O)_4](NO_3)_2$	11.32 (10.88)	36.2 (37.01)	3.92 (4.11)	9.12 (9.60)	
$[CuL(H_2O)_2](ClO_4)_2$	10.80 (10.20)	33.84 (34.70)	3.11 (3.21)	4.28 (4.50)	32.61 (31.97)

TABLE 4
Significant IR spectral bands of ligand and Cr(III) and Mn(II) complexes

		Assignments and band frequencies* (cm^{-1})									
		νO–H (coordinated	(coordinated water)			νNO_3^-					
No.	Compound	H_2O or OH^-)	ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)	νC=N	νNO(asy) (free NO_3^-)	νNO_3^- (coordinated)	νClO_4^- (coordinated)	δ O–CH_2–O	ν M-N	ν M-O
1	$C_{18}H_{16}O_4N_2$ (L)				1639 s				926 m		
2	$[Cr_2L(OH)_6(H_2O)_2]$	3420 s 3345 b	963 w	630 w	1583 m				926 m	522 m	432 m
3	$[Cr_2LCl_6(H_2O)_2]$	3424 b	961 m	637w	1598 s				929 m	537w	443w
4	$[Cr_2LBr_6(H_2O)_2]$	3423 b	958 m	632w	1600 m				928 m	551 m	436w
5	$[CrL(NO_3)_3((H_2O)]$	3286 b	964 m	633 w	1593 m		1447 mw 1361 W 1034 sh		927 m	519 w	446 m
6	$[CrL(ClO_4)_3(H_2O)]$	3433 b	956 m	638 w	1597 m			1117 m 1038 m 934 w	928 m	544 w	417 m
7	$[Mn_2L(OH)_4(H_2O)_2]$	3381s 3296 b	958 w	632w	1597 m				—	621 w	519 m
8	$[Mn_2LCl_4(H_2O)_2]$	3410 b	958 m	635 w	1619 m				—	605 w	506 w
9	$[MnLBr_2(H_2O)_2]$	3398 b			1594 s				927 m	625 m	514w
10	$[MnL(H_2O)_4](NO_3)_2$	3402 b	962 m	633 w	1600 m	1384 s			926 m	616 m	504m
11	$[MnL(ClO_4)_2(H_2O)_2]$	3433 b	960 m	636 w	1595 s			1118 m 1042 w 941 w	926 m	631 m	525 m

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

TABLE 5
Significant IR spectral bands of ligand and Fe(III) and Co(II) complexes

		Assignments and band frequencies* (cm^{-1})									
		νO–H (coordinated H_2O or OH^-)	(coordinated water)			νNO_3^-					
No.	Compound		ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)	νC=N	νNO(asy) (free NO_3^-)	νNO_3^- (coordinated)	νClO_4^- (coordinated)	δ O–CH_2–O	νM-N	νM-O
12	$[Fe_2L(OH)_6(H_2O)_2]$	3430s 3284 b	957 w	631 w	1595 m				926 m	605 w	490 m
13	$[Fe_2LCl_6(H_2O)_2]$	3370 b	957 m	636 w	1600 m				926 m	678 w	420 w
14	$[Fe_2LBr_6(H_2O)_2]$	3430 b	955 w	633 w	1598 m				927 m	627 m	482 m
15	$[FeL(NO_3)_3((H_2O)]$	3434 b	959 m	636 w	1596 m		1445 m 1348 m 1036 sh		928 m	620 m	452 m
16	$[FeL(ClO_4)_3(H_2O)]$	3440 b	962 m	633 w	1598 m			1117 m 1040 m 934 w	928 m	630 w	438 m
17	$[Co_2L(OH)_4]$	3257 s			1590 s				926 m		
18	$[Co_2LCl_4]$	-			1626 m				926 m	522 m	432 m
19	$[CoLBr_2(H_2O)_2]$	3412 b	957 m	636 w	1587 m				929 m	537 w	443 w
20	$[CoL(NO_3)_2(H_2O)_2]$	3413 b	961 m	634 w	1597 m		1449 m 1326 m 1041 w		928 m	551 m	436 w
21	$[CoL(ClO_4)_2(H_2O)_2]$	3428 b	959 m	637 w	1595 s			1117 m 1038 m 934 w	927 m	519 w	446 m

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

TABLE 6
Significant IR spectral bands of ligand and Ni(II) and Cu(II) complexes

		Assignments and band frequencies* (cm^{-1})									
			(coordinated water)				νClO_4^-				
No.	Compound	νO–H (coordinated H_2O or OH^-)	ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)	νC=N	νNO_3^- νNO(asy) (free NO_3^-)	νClO(asy) νClO(sy) (free ClO_4^-)	νClO_4^- (coordinated)	δ O–CH_2–O	νM-N	νM-O
22	$[Ni_2L(OH)_4]$	3417 s			1626 s				928 m	544 w	417 m
23	$[Ni_2LCl_4(H_2O)_2]$	3415 b	959 m	635 w	1624 m				—	621 w	519 m
24	$[NiLBr_2(H_2O)_2]$	3386 b			1626 s				—	605 w	506 w
25	$[NiL(H_2O)_2]\ (NO_3)_2$	3390 b	962 m	633 w	1631 m	1385 s			927 m	625 m	514 w
26	$[NiL(ClO4)_2(H_2O)_2]$	3382 b	960 m	636 w	1633 s			1118 m 1042 w 941 w	926 m	616 m	504 m
27	$[Cu_2L(OH)_4]$	3390 s			1595 s				926 m	631 m	525 m
28	$[Cu_2LCl_4(H_2O)_2]$	3348 b	958 m	636 w	1569 s				926 m	605 w	490 m
29	$[CuLBr_2(H_2O)_2]$	3324 b	956 m	631 w	1564 s				926 m	678 w	420 w
30	$[CuL(H_2O)_4](NO_3)_2$	3417 b	961 m	634 w	1624 s	1385 s			927 m	627 m	482 m
31	$[CuL(H_2O)_2](ClO_4)_2$	3302 b	960 m	633 w	1585 m		1112 s 981 w		928 m	620 m	452 m

*s-strong, m-medium, w-weak, b-broad, sh-shoulder.

TABLE 7
Electronic spectral bands of Cr(III), Mn(II) and Fe(III) complexes and their assignments

No.	Compound	Bands (nm)	Assignment	Geometry
2	$[Cr_2L(OH)_6(H_2O)_2]$	542 442	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral
3	$[Cr_2LCl_6(H_2O)_2]$	582 384	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral
4	$[Cr_2LBr_6(H_2O)_2]$	552 401	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral
5	$[CrL(NO_3)_3((H_2O)]$	563 412	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral
6	$[CrL(ClO_4)_3(H_2O)]$	558 418	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral
7	$[Mn_2L(OH)_4(H_2O)_2]$	393 w	$^6A_1g(F) \rightarrow {}^4T_{2g}(G)$	Octahedral
8	$[Mn_2LCl_4(H_2O)_2]$	398 w	$^6A_1g(F) \rightarrow {}^4T_{2g}(G)$	Octahedral
9	$[MnLBr_2(H_2O)_2]$	402 w	$^6A_1g(F) \rightarrow {}^4T_{2g}(G)$	Octahedral
10	$[MnL(H_2O)_4](NO_3)_2$	369 w	$^6A_1g(F) \rightarrow {}^4T_{2g}(G)$	Octahedral
11	$[MnL(ClO4)_2(H_2O)_2]$	384 w	$^6A_1g(F) \rightarrow {}^4T_{2g}(G)$	Octahedral
12	$[Fe_2L(OH)_6(H_2O)_2]$	492 398	$^6A_{1g} \rightarrow {}^4T_{2g}$ CT	Octahedral
13	$[Fe_2LCl_6(H_2O)_2]$	512 402	$^6A_{1g} \rightarrow {}^4T_{2g}$ CT	Octahedral
14	$[Fe_2LBr_6(H_2O)_2]$	502 399	$^6A_{1g} \rightarrow {}^4T_{2g}$ CT	Octahedral
15	$[FeL(NO_3)_3((H_2O)]$	488 401	$^6A_{1g} \rightarrow {}^4T_{2g}$ CT	Octahedral
16	$[FeL(ClO_4)_3(H_2O)]$	505 399	$^6A_{1g} \rightarrow {}^4T_{2g}$ CT	Octahedral

having d^3 configuration, with a ground term $^3A_{2g}$ are expected to show magnetic moments very close to the spin-only value.[45] In the present investigation the hydroxo, chloro and bromo complexes of Cr(III) showed slightly lower values of magnetic moments viz. 3.24, 3.49 and 3.52 B.M., respectively, indicating some sort of molecular association that could lead to magnetic exchange interaction through a bridging ligand.[46,47] The nitrato and perchlorato complexes showed magnetic moments of 3.82 and 3.91 B.M., respectively, indicating sufficient magnetic dilution.[45,48]

Mn(II) Complexes

The electronic spectra of the Mn(II) complexes showed a number of weak bands around 400 nm which were assigned to the spin- and parity forbidden $^6A_1g(F) \rightarrow {}^4T_{2g}(G)$ transitions in an octahedral field.[49,50] The bromo, nitrato and perchlorato complexes of Mn(II) showed magnetic moments in the range 5.91 to 6.20 B.M. which was consistent with the spin-only value for high-spin octahedral geometry.[49,51] The hydroxo and chloro complexes showed magnetic moments of 4.72 and 4.92 B.M., respectively, indicating probable bimetallic nature and the consequent antiferromagnetic coupling[49,52]

Fe(III) Complexes

The complexes of Fe(III) were orange in color and gave weak bands in the range 400–500 nm, assigned to the spin- and parity forbidden $^6A_{1g} \rightarrow {}^4T_{2g}$ transitions of Fe(III) ion in an octahedral field.[53,54] In the present investigation, the nitrato and perchlorato complexes of Fe(III) showed magnetic moments of 6.12 and 5.94 B.M., respectively, indicating high-spin octahedral symmetry.[45,55] The hydroxo, chloro and bromo complexes showed lower values of magnetic moments of 5.02, 4.56 and 4.92 B.M., respectively, indicating probable bimetallic nature with bridging ligands.[45,56]

Co(II) Complexes

The hydroxo and chloro complexes of Co(II) were having bright greenish-blue color and their spectra showed bands at 1641–1627, 652–673 and 514–501 nm assigned, respectively, to the $^4A_2(F) \rightarrow {}^4T_2(F)$, $^4A_2(F) \rightarrow {}^4T_1(F)$ and $^4A_2(F) \rightarrow$

TABLE 8
Electronic spectral bands of Co(II), NI(II) and Cu(II) complexes and their assignments

No.	Complex	Bands (nm)	Assignment	Geometry
17	$[Co_2L(OH)_4]$	1641	${}^4A_2(F) \rightarrow {}^4T_2(F)$	Tetrahedral
		652	${}^4A_2(F) \rightarrow {}^4T_1(F)$	
		514	${}^4A_2(F) \rightarrow {}^4T_1(P)$	
18	$[Co_2LCl_4]$	1627	${}^4A_2(F) \rightarrow {}^4T_2(F)$	Tetrahedral
		673	${}^4A_2(F) \rightarrow {}^4T_1(F)$	
		501	${}^4A_2(F) \rightarrow {}^4T_1(P)$	
19	$[CoLBr_2(H2O)_2]$	1015	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	Octahedral
		622	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
		478	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
20	$[CoL(NO_3)_2(H2O)_2]$	1115	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	Octahedral
		678	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
		409	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
21	$[CoL(ClO_4)_2(H2O)_2]$	1098	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	Octahedral
		589	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
		423	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
22	$[Ni_2L(OH_4]$	610	${}^1A_{1g} \rightarrow {}^1B_{1g}$	Square-planar
		413	${}^1A_{1g} \rightarrow {}^1E_g$	
23	$[Ni_2LCl_4(H_2O)_2]$	1140	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	Octahedral
		700	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
		410	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
24	$[NiLBr_2(H_2O)_2]$	1148	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	Octahedral
		710	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
		389	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
25	$[NiL(H_2O)_2]\ (NO_3)_2$	548	${}^1A_{1g} \rightarrow {}^1B_{1g}$	Square-planar
		394	${}^1A_{1g} \rightarrow {}^1E_g$	
26	$[NiL(ClO_4)_2(H_2O)_2]$	1152	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	Octahedral
		726	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
		398	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
27	$[Cu_2L(OH)_4]$	790	${}^2B_{1g} \rightarrow {}^2A_{1g}$	Square-planar
		468	CT	
28	$[Cu_2LCl_4(H_2O)_2]$	694 b	${}^2E_g \rightarrow {}^2T_{2g}$	Distorted octahedral
29	$[CuLBr_2(H_2O)_2]$	730 b	${}^2E_g \rightarrow {}^2T_{2g}$	Distorted octahedral
30	$[CuL(H_2O)_4](NO_3)_2$	655 b	${}^2E_g \rightarrow {}^2T_{2g}$	Distorted octahedral
31	$[CuL(H_2O)_2](ClO4)_2$	810	${}^2B_{1g} \rightarrow {}^2A_{1g}$	Square-planar
		442	CT	

${}^4T_1(P)$ transitions in a tetrahedral geometry.[57,58] The spectra of the bromo, nitrato and perchlorato complexes showed bands in the ranges 1115–1018, 678–589 and 478–404 nm assigned, respectively, to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions.[53,55] The hydroxo and chloro complexes of Co(II) showed magnetic moments of 3.31, 3.42 B.M., respectively, indicating tetrahedral geometries without any orbital contribution.[59,60] The slightly lower values indicated bimetallic nature and the resulting anti-ferromagnetic coupling in them.[57,61] The bromo, nitro and perchlorato complexes showed magnetic moments in the range 4.84–5.19 B.M., which corresponded to those of high-spin octahedral geometry with sufficient magnetic diluion.[53,55]

Ni(II) Complexes

The electronic spectra of chloro, bromo and perchlorato complexes of Ni(II) showed bands in the ranges 1152–1140, 726–700 and 410–394 nm and 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 octahedral geometry.[53,62] Moreover, the ratios of wave numbers of the transitions assigned as ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ were found to be in the

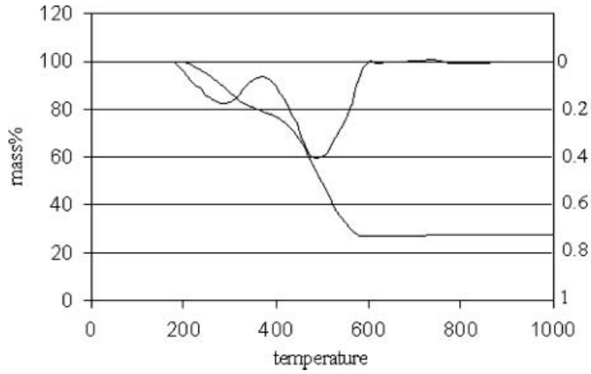


FIG. 3. TG-DTG traces of [Co_2LCl_4].

range 1.6 to 1.8, a distinctive feature of octahedral geometries. The spectra of the hydroxo and nitrato complexes of Ni(II) showed bands at 610 and 548 nm assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions and at 413 and 394 nm assigned to $^1A_{1g} \rightarrow {}^1E_g$ transitions in square planar geometry.[32,63] These Ni(II) complexes were found to be diamagnetic, supporting their square-planar geometries.[32,63] The chloro complex showed a low magnetic moment of 2.45 B.M., which could be due to its bimetallic nature and the subsequent antiferromagnetic coupling.[45,64] But the greenish-yellow color of the complex and its electronic spectrum indicated an octahedral geometry. The bromo and the perchlorato complexes showed the magnetic moments of 3.35 and 3.28 B.M., respectively, indicating octahedral geometry without any orbital contribution[53,65]

Cu(II) Complexes

The chloro, bromo and nitrato complexes of Cu(II), presently investigated, were greenish-blue in color and their electronic spectra showed bands at 694, 730 and 655 nm, respectively, assigned to the $^2E \rightarrow {}^2T_2$ transitions in a distorted octahedral geometry.[62,66] The spectra of hydroxo and perchlorato complexes of Cu(II), showed bands at 790 and 810 nm, respectively, which were assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions in square-planar geometry.[32,53,63] The hydroxo and chloro complexes of Cu(II) showed magnetic moments of 1.37 and 1.45 B.M.,

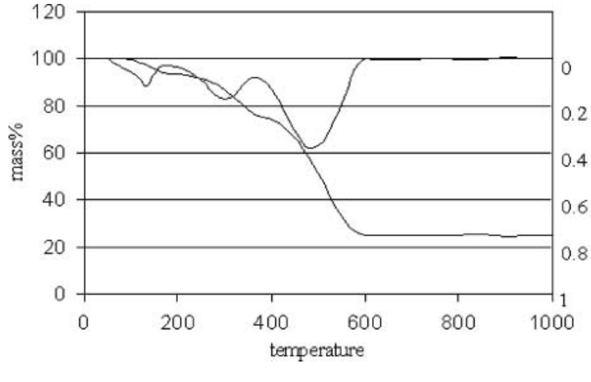


FIG. 4. TG-DTG traces of [$Ni_2LCl_4(H_2O)_2$].

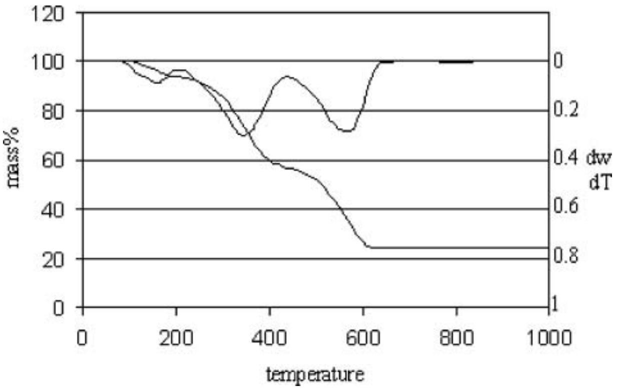
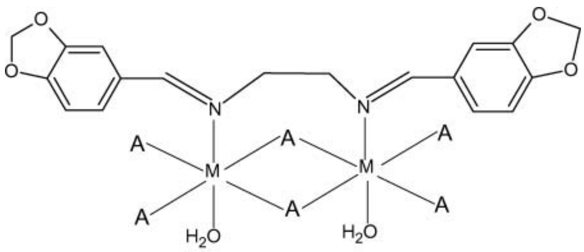
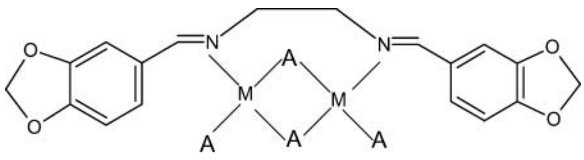


FIG. 5. TG-DTG traces of [$Cu_2LCl_4(H_2O)_2$].



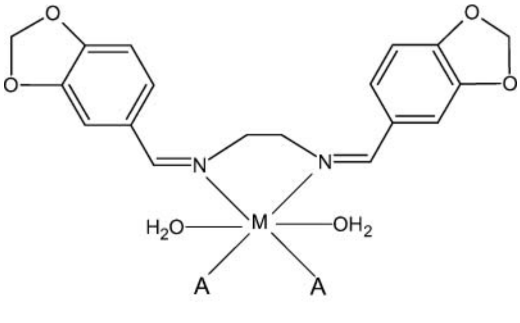
where M = Cr(III) or Fe(III) and A = OH^-, Cl^- or Br^-

FIG. 6. Structure suggested for [$Cr_2L(OH)_6(H_2O)_2$], [$Cr_2LCl_6(H_2O)_2$], [$Cr_2LBr_6(H_2O)_2$], [$Fe_2L(OH)_6(H_2O)_2$], [$Fe_2LCl_6(H_2O)_2$] and [$Fe_2LBr_6(H_2O)_2$].



where M= Ni (II) or Cu (II) and A = OH^-

FIG. 7. Structure suggested for [$Ni_2L(OH)_4$] and [$Cu_2L(OH)_4$].



where M = Mn(II) and A = Br^- or ClO_4^-
or M= Co (II) and A = Br^-, NO_3^- or ClO_4^-
or M= Ni(II) and A = Br^- or ClO_4^-
or M = Cu (II) and A = Br^-

FIG. 8. Structure suggested for [$MnL(Br)_2(H_2O)_2$], [$MnL(ClO_4)_2(H_2O)_2$], [$CoL(Br)_2(H_2O)_2$], [$CoL(ClO_4)_2(H_2O)_2$], [$CoL(NO_3)_2(H_2O)_2$], [$NiL(ClO_4)_2(H_2O)_2$] [$NiL(Br)_2(H_2O)_2$] and [$CuL(Br)_2(H_2O)_2$].

TABLE 9
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	
$[Co_2LCl_4]$	I	220–380	290	21.3	20.7		Loss of 1 piperonal moiety
	II	380–580	490	51.4	51.8		Loss of rest of the ligand, 4 Cl^- ions & subsequent formation of metal oxide
	Total			72.7	72.5	71.9	$Co_2LCl_4 \rightarrow 2/3Co_3O_4$
$[Ni_2LCl_4(H_2O)_2]$	I	110–180	135	6	5.8		Loss of $2H_2O$
	II	180–400 (220–400)*	310	19.8	19.5		Loss of 1 piperonal moiety
	III	400–600	500	48.8	50.6		Loss of remaining ligand , $4Cl^-$ ions & formation of metal oxide
	Total			75.6	74.9	75.5	$Ni_2LCl_42H_2O \rightarrow 2\ NiO$
$[Cu_2LCl_4(H_2O)_2]$	I	110–200	160	5.9	5.7		Loss of $2H_2O$
	II	200–460 (240–460)*	350	38.1	38.4		Loss of 2piperonal moieties
	III	460–620	560	31.2	32.2		Loss of remaining ligand, $4Cl^-$ ions & formation of metal oxide
	Total			75.2	76.3	74.7	$Cu_2LCl_42H_2O \rightarrow 2\ CuO$

*Temperature range of significant mass-loss in the stage

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 a bridging ligand.[45,53] The bromo, nitrato and perchlorato complexes were found to have magnetic moments in the range 1.90 to 2.10 B.M., indicating sufficient magnetic dilution.[45,53]

Thermogravimetric Analysis

Thermograms of three complexes, viz, $[Co_2LCl_4]$, $[Ni_2LCl_4(H_2O)_2]$ and $[Cu_2LCl_4(H_2O)_2]$, were analyzed. The Co(II) complex gave Co_3O_4 and the Ni(II) and Cu(II) complexes gave NiO and CuO, respectively, as the end products at temperatures around 600°C and the decomposition patterns were in good agreement with the suggested formulae. The Ni(II) and Cu(II) complexes underwent dehydration reactions around 150°C, losing two molecules of water, thus confirming the presence of coordinated water molecules in them. However, the Co(II) complex did not show any mass-loss in this range and were stable up to ~220°C, thus indicating the absence of water molecules in them. 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

TABLE 10
Kinetic parameters for the decomposition of Co(II), Ni(II) and Cu(II) complexes

Complex	Stage	E_a kJ/mol	A s^{-1}	ΔS^* J/K/mol	ΔH^* kJ/mol	ΔG^* kJ/mol	γ	n
$[Co_2LCl_4]$	I	57.50	5.13×10^2	−198.31	52.81	164.47	−0.9926566	1
	II	114.59	1.60×10^5	−153.09	108.25	225.06	−0.9941095	1
$[Ni_2LCl_4(H_2O)_2]$	I	68.98	3.01×10^6	−123.51	65.59	115.98	−0.9997576	1
	II	59.82	4.50×10^2	−199.68	54.98	171.38	−0.9997821	1
	III	116.13	1.50×10^5	−153.76	109.70	228.56	−0.9948807	1
$[Cu_2LCl_4(H_2O)_2]$	I	67.51	8.83×10^5	−131.99	64.74	108.69	−0.9951084	1
	II	60.17	2.58×10^2	−204.86	54.99	182.62	−0.9972724	1
	III	149.94	9.26×10^6	−120.07	143.01	243.04	−0.9986331	1

TABLE 11
The inhibitory effects of the ligand and its metal complexes on the mycelial growth of *Phytophthora capsici*

Conc. of sample		Sample					
			Complex				
		Ligand	Mn(II)	Co(II)	Ni(II)	Cu(II)	Control
25 ppm	Diameter mm	31.2	32.6	31.6	28.3	22.8	34
	% of inhibition	8.24	4.12	7.06	16.8	32.9	
50 ppm	Diameter mm	29	30.4	29.2	22.6	12.9	34
	% of inhibition	14.7	10.6	14.1	33.5	62.1	
75 ppm	Diameter mm	23.2	26.9	20.3	17.2	7.5	34
	% of inhibition	31.8	20.9	40.3	49.4	77.9	
100 ppm	Diameter mm	14.2	23.2	10.3	9.2	5.8	34
	% of inhibition	58.2	31.8	69.7	72.9	82.9	

have also been calculated using the relations, ΔH^*- 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.[67] Figures 3, 4 and 5 give the TG-DTG traces of the complexes. Table 9 gives the different stages of decomposition and Table 10 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 6, 7 and 8.

Anti Fungal Studies

Black pepper or *Piper nigram 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 loss 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 percent.[68–70] The ligand and the Mn(II) Co(II), Ni(II) and Cu(II) hydroxo complexes 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. The Ni(II) and Co(II) complexes followed it. The data of inhibitory effects of the ligand and the complexes on various stages of the growth of *Phytophthora capsici* are given in Tables 11–14. Figure 9 gives graphical comparison of inhibitory effects of ligand and complexes on mycelial growth. Mn(II) complex was found to be

TABLE 12
The inhibitory effects of the ligand and its metal complexes on the sporangial production of *Phytophthora capsici*

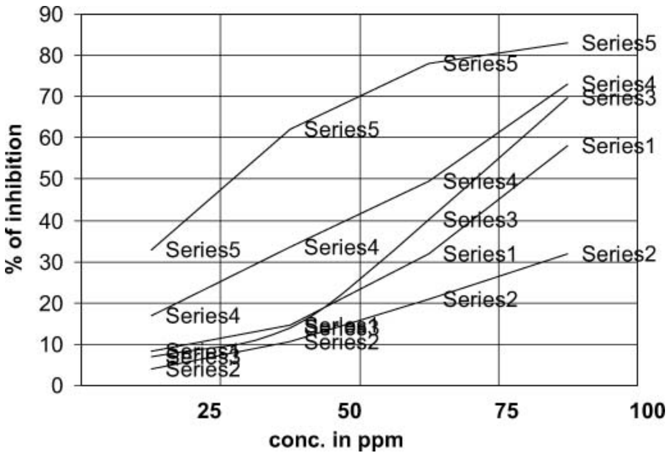
		Sample				
			Complex			
Conc. of		Ligand	Co(II)	Ni(II)	Cu(II)	Control
25 ppm	no of sporangia per field	52	49	46.6	43.2	64
	% of inhibition	18.8	23.4	27.2	32.5	
50 ppm	no of sporangia per field	48.4	44.8	38.8	33.8	64
	% of inhibition	24.4	30	39.4	47.2	
75 ppm	no of sporangia per field	41	32.4	26.2	15.6	64
	% of inhibition	35.9	49.4	59.1	75.6	
100 ppm	no of sporangia per field	31.4	17.4	18	11	64
	% of inhibition	50.9	72.8	71.9	82.8	

TABLE 13
The inhibitory effect of the ligand and its metal complexes on the sporangial release of *Phytophthora capsici*

		Sample				
			Complex			
Conc. of		Ligand	Co(II)	Ni(II)	Cu(II)	Control
25 ppm	% of zoospore release	36.4	28	23	19	51.4
	% of inhibition	29.2	45.5	55.3	63.0	
50 ppm	% of zoospore release	23.2	19	14	11	51.4
	% of inhibition	54.9	63	72.8	78.6	
75 ppm	% of zoospore release	17.4	8.6	5.8	0	51.4
	% of inhibition	66.1	83.3	88.7	100	
100 ppm	% of zoospore release	9.8	1.8	0	0	51.4
	% of inhibition	80.9	96.5	100	100	

TABLE 14
The inhibitory effect of ligand and its metal complexes on the zoospore germination of *Phytophthora capsici*

		Sample				
			Complex			
Conc. of		*Ligand*	Co(II)	Ni(II)	Cu(II)	Control
25 ppm	% of zoospore germination	41.8	46.3	30.2	26.8	68.6
	% of inhibition	39.1	32.5	56	60.9	
50 ppm	% of zoospore germination	36	40.2	23.4	13.2	68.6
	% of inhibition	47.5	41.4	65.9	80.8	
75 ppm	% of zoospore germination	28	26.2	14.2	5.8	68.6
	% of inhibition	59.2	61.8	79.3	91.5	
100 ppm	% of zoospore germination	18.6	7.8	6.8	1.8	68.6
	% of inhibition	72.9	88.6	90.2	97.4	



Series 1 – ligand, series 2, 3, 4 & 5 – Mn(II), Co(II), Ni(II) and Cu(II) complex.

FIG. 9. Gaphical representation of inhibitory effects of the ligand and complexes on the mycelial growth of *Phytophthora capsici*.

less effective than the ligand in inhibiting the mycelial growth and therefore, was not screened for the other stages of growth.

From the data it was clear that most of these complexes and the ligand were inhibitory to all the four stages in the growth of *Phytophthora capsici.* But the metal complexes were generally found to show more antifungal activity than the parent ligand in all four stages of investigation. The acetates of Cu(II), Co(II), Ni(II) and Mn(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.[71] Among the four stages, the inhibition was more pronounced in zoosporangial production and zoospore release. The complex of Cu(II) was found to be more effective than the complexes of other metal ions in retarding the growth of *Phytophthora capsici* at various stages. The Ni(II) and Co(II) complexes followed it.

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.[72] 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.[32] Furthermore, the mode of action of the compounds may involve the formation of a hydrogen bond through the azomethine group with the active centers of cell constituents, resulting in the interference with normal cell division process.[73] 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 up new avenues in the quest for tackling the problem of foot-rot disease in black pepper.

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