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Synthesis, Characterization and Antifungal Studies of Metal Complexes of Benzoyl- and Salicylylhydrazones of N-Methylacetoacetanilide

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Complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with benzoylhydrazone, L^1H_2 and salicylylhydrazone, L^2H_3 of N-methylacetoacetanilide have been prepared and characterized. The IR spectral studies indicate that the ligands act either as bidendate donors coordinating through aroyl oxygen and azomethine nitrogen atoms or as tridentate donors coordinating through aroyl- and anilide oxygen and azomethine nitrogen atoms. Antifungal studies of Mn(II), Co(II), Ni(II) and Cu(II) complexes with four selected fungal strains were also carried out.

INTRODUCTION

The coordination chemistry of hydrazone and related ligands has been extensively investigated. They find application in various fields, such as in medicine, as insecticides, fungicides, bactericides, plasticizers and stabilizers for polymers[1–4]. They act as multidentate ligands towards metal ions forming coloured and stable chelates. Literature survey revealed that most of the work on metal complexes of hydrazone has been centered around those derived from simple aldehydes and ketones and much less work has been reported on those of β-ketoanilides[5]. Since there is no report on hydrazones of N-substituted acetoacetanilides, it is considered worth while and interesting to study the donor properties of those ligands derived by the condensation of N-methylacetoacetanilides with benzoylhydrazine, L^1H_2 and salicylylhydrazine, L^2H_3 (Fig. 1) towards several typical transition metal ions.

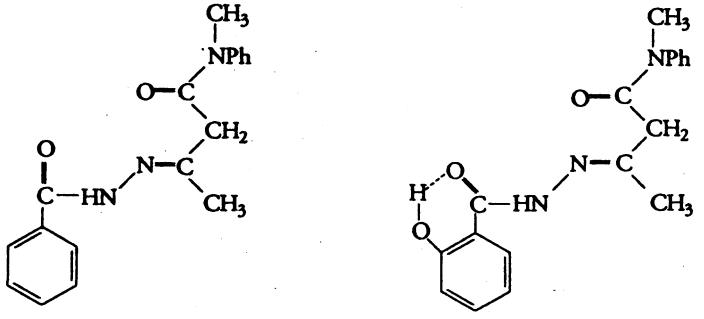

Fig. 1. Structures of the Ligands (a) L^1H_2 and (b) L^2H_3

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EXPERIMENTAL

The metal salts used were of BDH 'AnalaR' grade. Mainly acetates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) and chloride of Hg(II) were used for the synthesis of the complexes. N-methylacetoacetanilide benzoylhydrazine and salicylylhydrazine were prepared and purified by reported methods[6]. The solvents and other reagents used were of E. Merk grade. Commercially available ethanol was purified by standard method[7].

Preparation of N-methylacetoacetanilide benzoyl- or salicylylhydrazones and their complexes

The ligands were prepared by refluxing respective hydrazine (0.1 mol, 250 mL) in ethanol with sodium N-methylacetoacetanilide (0.1 mol) in a 4 : 1 ethanol-water mixture (25 mL), on a water bath, for about 3 h. As only a very small amount of solid products separated out from the reaction mixtures in both the cases, the resulting solutions, after reducing the volume were used as such for the preparation of the complexes. To this solution (25 mL), the metal salt in methanol (0.01 mol) was added and stirred for 1 h. In most of the cases, addition of water was necessary for the isolation of solid complexes. The complexes formed were filtered off, washed with water and finally with methanol and dried in a desiccator over anhydrous calcium chloride. In the case of Mn(II) and Cd(II) complexes of benzoylhydrazone and Mn(II), Co(II), Ni(II) and Cd(II) complexes of salicylylhydrazone a 1 : 2 ratio of metal to ligand gave better yields.

Analysis for the metal contents of the complexes were performed by standard methods[8]. Carbon, hydrogen and nitrogen were determined on a CHN—O rapid analyser. IR spectra (4000–400 cm^{-1} using KBr pellet) were recorded on an FTIR-8101 Shimadzu spectrophotometer. The ^{1}H-NMR spectra of the Zn(II) complexes were recorded on a Varian 300-NMR spectrometer. The magnetic moments were determined on a Gouy-type balance using $Hg[Co(CNS)_4]$ as calibrant and the magnetic moments were calculated after applying diamagnetic corrections using Pascal constants[9]. The electronic spectra were taken on a UV-1601 Shimadzu spectrophotometer, using Nujol mull technique[10]. The thermogravimetric curves of the complexes were obtained on a Perkin-Elmer TGS-I thermobalance with following operational characteristics: heating rate, 10° min^{-1}; sample size, 2–10 mg; atmosphere, static air; and crucible, platinum.

Antifungal activity

The fungal strains used were *Aspergillus niger, Candida albicans, Trihosporon* species and *Penicillium* species. The cultures were maintained on Sabouraud's glucose agar stants. Cup-plate technique[11] was used for the detection of antifungal activity. Suspension of spores of *Aspergillus niger, Penicillium* species and *Trichosporon* species were prepared in normal saline (0.9%). In the case of *Candida albicans*, the suspension was made using cells from the slope of the sabouraud's agar. About 25 mL of Sabouraud's glucose agar media (peptone = 1 g, D-glucose = 4 g, agar-agar = 2 g, distilled water = 100 mL; pH has been adjusted to 5.7 using 10% HCl, autoclaving at 15 lb pressure for 15 min) was

poured into petri-plates (9 cm) and allowed to cool. To this solid agar media, the suspension of the fungal strain in normal saline was added. After swirling the plate properly, for the uniform distribution of the spores on the surface, excess suspension was decanted. Plates were allowed to dry in an incubator at 37°C for 1 h. Using an agar punch, wells of 10 mm diameter were made on these plates. In each well 200 μL (1000 ppm) of the compound in DMSO was added. Each plate has a well for the control, *i.e.*, in which the solvent DMSO alone is poured. The wells were properly labeled for each sample and the plates were prepared in triplicate and incubated at room temperature for 4–5 days. The antifungal activity was detected by measuring the diameter of the inhibition zone around each well. The results presented in Table-6.

RESULTS AND DISCUSSION

The analytical data and magnetic moments of the complexes are summarized in Table-1. The results of elemental analysis are in good agreement with the proposed formulae of the complexes.

Due to the poor yield of the ligands, the complexes were synthesized directly using the concentrated reaction mixture obtained during the synthesis of the respective ligand. However, a little of the samples of the ligands obtained during the synthesis were used for recording their infrared spectra. Significant infrared bands of the ligands and the complexes are assigned in Table-2.

(a) L^1H_2 and its metal complexes

The IR spectrum of L^1H_2 and its metal complexes (Table-2) show characteristic bands in the 3600–2700 cm^{-1} region. These may be assigned to the symmetric and asymmetric stretching bands of NH group[12]. The ligand spectrum shows a strong band at 1667 cm^{-1}. This may be assigned to ν(C=O) (anilide)[13, 14]. In the spectra of the complexes of Mn(II) and Cd(II), there is no change in the position of this band, indicating the non-participation of this C=O group in coordination. In the spectra of the complexes of Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) this band disappears and a new band is found *ca.* 1170 cm^{-1}. This may be due to the enolization of —CH_2—C=O to —CH=C—OH and subsequent coordination through deprotonated oxygen. A very strong band at 1632 cm^{-1} in the spectrum of the ligand may be assigned to ν(C=O) (aroyl). In the spectra of all the complexes this band disappears and a new band is observed *ca.* 1250 cm^{-1}. This may be due to the enolization of =N—NH—C=O to =N—N=C—OH and subsequent coordination through deprotonated oxygen.

A strong band at 1592 cm^{-1} in the spectrum of the ligand may be assigned to ν(C=N). In the spectra of all the complexes this band is found to be shifted to lower frequency by *ca.* 40 cm^{-1}. This may be due to the participation of azomethine nitrogen in coordination. The amide II and III bands are found *ca.* 1500 cm^{-1}. The ν(N—N) band in the ligand spectrum occurs at 1015 cm^{-1}, whereas in the spectra of all the complexes this band suffers a shift to higher frequency region indicating the participation of azomethine nitrogen in coordina-

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES

Sl. No.	Empirical formulae Compounds	m.p. (°C) Colour	Yield (%)	Found (Calcd.), %				μ_{eff} (B.M.)
				M	C	H	N	
1.	(L^1H_2)	–	14	–	–	–	–	–
	$C_{18}H_{19}N_3O_2$	pale pink						
2.	$[Mn(L^1H)_2(H_2O)_2]$	> 300	55	7.98	60.70	5.47	11.40	5.45
	$MnC_{36}H_{40}N_6O_6$	pale brown		(7.77)	(61.08)	(5.70)	(11.87)	
3.	$[CoL^1(H_2O)_3]$	> 300	80	13.86	51.98	5.37	10.35	5.16
	$CoC_{18}H_{23}N_3O_5$	brown		(14.03)	(51.41)	(5.52)	(9.99)	
4.	$[NiL^1(H_2O)_3]$	> 300	85	13.72	51.01	5.27	9.76	2.97
	$NiC_{18}H_{23}N_3O_5$	yellowish brown		(13.90)	(51.44)	(5.52)	(10.00)	
5.	$[CuL^1(H_2O)]$	292	82	16.41	54.96	4.40	10.57	2.04
	$CuC_{18}H_{19}N_3O_3$	green		(16.35)	(55.57)	(4.92)	(10.80)	
6.	$[ZnL^1(H_2O)]$	> 300	85	16.65	55.08	4.47	10.28	–
	$ZnC_{18}H_{19}N_3O_3$	pale yellow		(16.74)	(55.30)	(4.90)	(10.75)	
7.	$[Cd(L^1H_2)_2]$	162	85	15.05	58.70	4.96	11.36	–
	$CdC_{36}H_{36}N_6O_4$	yellow		(15.42)	(59.28)	(4.98)	(11.53)	
8.	$[HgL^1(H_2O)]$	192	85	38.01	41.52	3.77	7.91	–
	$HgC_{18}H_{19}N_3O_3$	yellowish orange		(38.15)	(41.08)	(3.64)	(7.99)	
9.	(L^2H_3)	–	12	–	–	–	–	–
	$C_{18}H_{19}N_3O_3$	red						
10.	$[Mn(L^2H_2)_2]$	> 300	60	7.65	61.37	5.42	11.60	6.31
	$MnC_{36}H_{36}N_6O_6$	Yellow		(7.81)	(61.43)	(5.16)	(11.94)	
11.	$[Co(L^2H_2)_2]$	> 300	90	8.67	60.87	5.26	11.82	5.13
	$CoC_{36}H_{36}N_6O_6$	brown		(8.33)	(61.08)	(5.13)	(11.88)	
12.	$[Ni(L^2H_2)_2]$	> 300	90	8.82	61.08	5.05	11.42	3.03
	$NiC_{36}H_{36}N_6O_6$	yellowish brown		(8.30)	(61.10)	(5.13)	(11.88)	
13.	$[Cu(L^2H)(H_2O)]$	> 300	92	15.32	53.28	4.71	9.71	2.91
	$CuC_{18}H_{19}N_3O_4$	green		(15.70)	(53.37)	(4.73)	(10.37)	
14.	$[Zn(L^2H)(H_2O)_3]$	> 300	88	14.18	48.37	5.30	9.32	–
	$ZnC_{18}H_{23}N_3O_6$	yellow		(14.77)	(48.80)	(5.23)	(9.49)	
15.	$[Cd(L^2H_2)_2]$	> 300	88	14.68	56.72	4.72	11.10	–
	$CdC_{36}H_{36}N_6O_6$	yellow		(14.77)	(56.79)	(4.77)	(11.04)	
16.	$[Hg(L^2H)(H_2O)_3]$	> 300	89	34.76	37.50	4.10	7.28	–
	$HgC_{18}H_{23}N_3O_6$	yellow		(34.72)	(37.38)	(4.01)	(7.26)	

*Cl = 8.25(8.20)

TABLE-2
SIGNIFICANT INFRARED SPECTRAL BANDS (cm^{-1}) OF L^1H_2 AND L^2H_3 AND THEIR METAL COMPLEXES

Compound	ν(N—H) or ν(O—H)	ν(C=O) (Anilide)	ν(C=O) (Aroyl)	ν(C=N)	ν(C—O) (Aroyl)	ν(C—O) (Anilide)	ν(N—N)	ν(M—N)	ν(M—O)
(L^1H_2)	3450sh, 3190m, 3306m	1667s	1632s	1592s	–	–	1015m	–	–
[$Mn(L^1H_2)_2(H_2O)_2$]	3420m, 3180m, 3060m	1667s	–	1554m	1288s	–	1026m	525m	440s
[$CoL^1(H_2O)_3$]	3650m, 3567m, 3410m, 3090sh	–	–	1541s	1230s	1170s	1025s	545m	450m
[$NiL^1(H_2O)_3$]	3460m, 3320m, 3960sh	–	–	1560s	1257m	1146s	1026m	550m	430m
[$CuL^1(H_2O)$]	3420m, 3340m, 3180sh, 3050sh	–	–	1558s	1240s	1185m	1026m	530m	450m
[$ZnL^1(H_2O)$]	3450m, 3230w, 3190sh, 3063sh	–	–	1541m	1288s	1174s	1026m	517m	445m
[$Cd(L^1H_2)_2$]	3420m, 3140w, 3050sh	1667s	–	1543s	1220m	–	1024m	561m	440m
[$HgL^1(H_2O)$]	3590m, 3350sh,	–	–	1562m	1279s	1155s	1028m	557m	440m
(L^2H_3)	3500–2700b	1650s	1636s	1593s	–	–	1010m	–	–
[$Mn(L^2H_2)_2$]	3520m, 3040sh	1600s	–	1565s	1252s	–	1034m	532m	428m
[$Co(L^2H_2)_2$]	3390b, 3180m	1620s	–	1560s	1250s	–	1028m	520m	430m
[$Ni(L^2H_2)_2$]	3400b	1607s	–	1560s	1255s	–	1032w	557m	430m
$Cu(L^2H)(H_2O)$	3620w, 3335b,	–	–	1571s	1254m	1157s	1043m	558m	457m
[$Zn(L^2H)(H_2O)_3$]	3600m, 3450b, 3200b	–	–	1571s	1254m	1157s	1043m	558m	457m
[$Cd(L^2H_2)_2$]	3649m, 3400m 3300m, 3080sh	1620s	–	1571s	1252s	–	1026m	580m	430w
[$Hg(L^2H)(H_2O)_3$]	3640m, 3320b	–	–	1569s	1254m	1149s	1024m	559m	440w

s = strong, m = medium, b = broad, sh = shoulder, w = weak

tion. The broad band at *ca.* 3500 cm^{-1} in the spectra of the complexes together with the bands *ca.* 900 and *ca.* 660 cm^{-1}, are respectively due to stretching, rocking and wagging modes of coordinated water molecules[15]. The ν(M—N) and ν(M—O) bands are observed, respectively, *ca.* 540 and *ca.* 450 cm^{-1} in the spectra of all the complexes.

(b) L^2H_3 and its metal complexes

The ligand spectrum (Table-2) shows a broad region between 3500–2700 cm^{-1}. However, there are no characteristic OH or NH stretching bands in this broad region. This indicates the presence of hydrogen bonding in the ligand molecule. The probable hydrogen bonded structure of the ligand is as in Fig. 1 (b).

The bands of strong intensity at 1650 and 1636 cm^{-1}, found in the spectrum of the ligand may be assigned to ν(C=O) (anilide) and ν(C=O) (aroyl). The shift of ν(C=O) (aroyl) to lower frequency region may be due to intramolecular hydrogen bonding. In the spectra of the complexes of Mn(II), Co(II), Ni(II) and Cd(II), the ν(C=O) (anilide) is found to be lowered by *ca.* 30–50 cm^{-1}. This indicates the participation of anilide carbonyl oxygen in coordination. However, in the spectra of the complexes of Cu(II), Zn(II) and Hg(II), this band disappears and a new band is observed *ca.* 1150 cm^{-1}. This may be due to the enolization of anilide carbonyl oxygen and subsequent coordination through deprotonated oxygen. In the spectrum of the ligand, the phenolic ν(C—O) band is observed at 1319 cm^{-1}. In the spectra of all the complexes no change in the position of this band is noticed. This suggests the non-participation of phenolic oxygen in coordination.

The medium band observed at 1593 cm^{-1} in the ligand spectrum may be assigned to ν(C=N). In the spectra of all the complexes, a downward shift is noticed for this band. This may be due to the participation of azomethine nitrogen in coordination. The ν(N—N) band is observed at 1010 cm^{-1} in the ligand spectrum. In the spectra of all the complexes, this band is found to be shifted to higher frequency regions, suggesting the participation of azomethine nitrogen in coordination. The broad bands of medium intensity observed *ca.* 3550 cm^{-1} in the spectra of most of the complexes together with the bands at 940–850 and *ca.* 650 cm^{-1} suggest the coordinated nature of water molecule in these complexes. Further evidence for the metal ligand bonding is given by the ν(M—N) and ν(M—O) bands observed in the spectra of the complexes at *ca.* 540 and *ca.* 450 cm^{-1}, respectively.

The magnetic moments (Table-1) of $[Mn(L^1H)_2(H_2O)_2]$ and $[Mn(L^2H_2)_2]$ are found to be 5.45 and 6.31 B.M., respectively. These values suggest octahedral or distorted octahedral geometry for these complexes[16]. The Co(II) and Ni(II) complexes show magnetic moment values in accordance with their octahedral geometry. The magnetic moment values, 2.04 and 2.19 B.M. observed, respectively, for $[CuL^1(H_2O)]$ and $[Cu(L^2H)(H_2O)]$ indicate the absence of antiferromagnetic exchange interaction in them.

The electronic spectra of the Mn(II) complexes (Table-3) $[Mn(L^1H)_2(H_2O)_2]$ and $[Mn(L^2H_2)_2]$, show a series of very weak band stretching throughout the green and blue portion of the visible spectrum extending into the ultraviolet region[17,18]. The bands observed at 426 and 451 nm may be assigned to $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ transition of typical octahedral Mn(II) complex. The Co(II) complexes, $[CoL^1(H_2O)_3]$ and $[Co(L^2H_2)_2]$ register an intense band *ca* 450, a broad one *ca*. 560 and a weak one *ca*. 1050 nm. These may be assigned respectively to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_1)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_3)$ transitions of a typical octahedrally coordinated Co(II) ion. The ratio, ν_3/ν_1 *ca*. 2.2 is in accordance with the expected value for an octahedral Co(II) complex (1.92–2.95). The yellowish-brown coloured Ni(II) complexes, $[NiL^1(H_2O)_3]$ and $[Ni(L^2H_2)_2]$ register an intense band *ca*. 400, a broad one *ca*. 650 and a weak one *ca*. 1020 nm. These may be respectively due to the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_1)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_3)$ transitions of an octahedral Ni(II) complex. The ratio, ν_2/ν_1 for a typical octahedral Ni(II) complex is *ca*. 1.7. However, slightly low value noticed in the case of $[NiL^1(H_2O)_3]$ indicates its distorted octahedral geometry. Both the Cu(II) complexes, $[CuL^1(H_2O)]$ and $[Cu(L^2H)(H_2O)]$ register two broad bands *ca*. 450 and *ca*. 700 nm. These may be respectively due to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions of square-planar Cu(II) complex.

TABLE-3
ELECTRONIC SPECTRAL DATA OF THE COMPLEXES

Complex	Bands (cm^{-1})	signments
$[Mn(L^1H)_2(H_2O)_2]$	23474	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$
$[CoL^1(H_2O)_3]$	21276br	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_1)$
	17857	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$
	9756w	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_3)$
$[NiL^1(H_2O)_3]$	24813	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_1)$
	18518br	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$
	9900w	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_3)$
$[CuL^1(H_2O)]$	22222	$^2B_{1g} \rightarrow {}^2E_g$
	15313br	$^2B_{1g} \rightarrow {}^2A_{1g}$
$[Mn(L^2H_2)_2]$	22172	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$
$[Co(L^2H_2)_2]$	21978	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_1)$
	16666br	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$
	9587w	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_3)$
$[(Ni(L^2H_2)_2]$	24390	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_1)$
	14085br	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$
	9708w	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_3)$
$[Cu(L^2H)(H_2O)]$	23529	$^2B_{1g} \rightarrow {}^2E_g$
	14285br	$^2B_{1g} \rightarrow {}^2A_{1g}$

As the ligands could not be isolated in pure state, the ^{1}H-NMR spectra of the Zn(II) complexes alone were taken. The spectrum of the Zn(II) complex of

benzoylhydrazone was recorded in $CDCl_3$, while that of salicylylhydrazone in DMSO-d_6.

The spectrum of $[ZnL^1(H_2O)]$ (Table-4) shows a multiplet at 8.31–7.16 ppm and this may be assigned to aromatic protons. A small singlet at 5.80 ppm may be assigned to α-CH proton, formed by the enolization of —CH_2—C=O to —CH=C—OH during complex formation. A singlet observed at 3.32, a broad peak observed at 2.83–2.73 and one at 1.95 ppm may be assigned to protons of N—CH_3, coordinated water molecule and ω-CH_3, respectively.

TABLE-4
SIGNIFICANT ^{1}H-NMR SPECTRA OF Zn(II) COMPLEXES OF L^1H_2 AND L^2H_3

Compounds	δ (ppm)	Proton
$[ZnL(H_2O)]$	8.31–7.16m	Aromatic
	5.80s	α-CH
	3.32s	N-CH_3
	2.83–2.73b	Coordinated water
	1.95s	ω-CH_3
$[Zn(LH)(H_2O)_3]$	13.79s	Phenolic hydrogen bonded OH
	7.89–6.83m	Aromatic
	5.25s	α-CH
	3.21s	N-CH_3
	2.80s	Coordinated water
	2.10s	ω-CH_3

m = multiplet, s = singlet, b = broad

In the spectrum of $[Zn(L^2H)(H_2O)_3]$ (Table-4) a singlet observed at 13.79 ppm may be assigned to hydrogen bonded phenolic OH. A multiplet observed at 7.89–6.83 ppm may be assigned to aromatic protons. A small singlet observed at 5.25 ppm may be assigned to α-CH proton formed during the formation of the complex, by the enolization of —CH_2—C=O to —CH=C—OH. The singlets observed at 3.21 and 2.10 ppm may be assigned to N-CH_3 and ω-CH_3 protons, respectively. The singlet observed at 2.80 ppm may be assigned to protons of coordinated water molecules.

The thermogravimetric studies of Mn(II), Co(II), Ni(II) and Cu(II) complexes of L^1H_2 and L^2H_3 (Table-5) were also carried out. The Mn(II) complex of L^1H_2 follows a three-staged decomposition pattern. In the first stage, the loss of two water molecules takes place around 140–220°C, indicating their coordinated nature[19]. In the second stage, the loss of a ligand molecule occurs. The third stage of decomposition leads to the formation of MnO_2. The Co(II) complex follows a two staged decomposition pattern. In the first stage, at a temperature range of 125–210°C, the loss of two coordinated water molecules takes place. In the second stage, the anhydrous complex decomposes gradually to form Co_3O_4. The

Mn(II) and Co(II) complexes of salicylylhydrazone have a single staged decomposition in the temperature range of 110–390 and 150–410°C, respectively. A two-staged decomposition occurs in the case of the Ni(II) complex of L^1H_2, in the temperature ranges 116–200 and 280–440°C. In the first stage, loss of three coordinated water molecules occurs and the second stage of decomposition leads

TABLE-5
THERMAL ANALYSES DATA OF Mn(II), Co(II), Ni(II) AND Cu(II) COMPLEXES OF L^1H_2 AND L^2H_3

Compound	Decomp. stage	Decomp. temp. range (°C)	Mass-loss % from			Decomposition pattern
			TG	Independent pyrolysis	Theoretical	
$[Mn(L^1H)_2(H_2O)_2]$	1	140–220	5.50	–	5.10	$[Mn(L^1H)_2(H_2O)_2] \rightarrow Mn(L^1H_2)_2$
	2	240–320	44.00	–	43.71	$[Mn(L^1H)_2(H_2O)_2] \rightarrow Mn(L^1H_2)$
	3	320–480	87.00	87.84	87.71	$[Mn(L^1H)_2(H_2O)_2] \rightarrow MnO_2$
$[CoL^1(H_2O)_3]$	1	125–210	12.50	–	12.86	$[CoL^1(H_2O)_3] \rightarrow CoL^1$
	2	280–440	81.00	80.67	80.89	$[CoL^1(H_2O)_3] \rightarrow Co_3O_4$
$[NiL^1(H_2O)_3]$	1	116–200	12.00	–	12.87	$[NiL^1(H_2O)_3] \rightarrow NiL^1$
	2	280–440	82.00	82.47	82.21	$[NiL^1(H_2O)_3] \rightarrow NiO$
$[CuL^1(H_2O)]$	1	120–200	12.50	–	12.72	$[CuL^1(H_2O)] \rightarrow CuL^1$
	2	220–340	85.00	85.24	85.04	$[CuL^1(H_2O)] \rightarrow CuO$
$[Mn(L^2H_2)_2]$	1	110–390	88.00	88.19	87.60	$[Mn(L^2H_2)_2] \rightarrow MnO_2$
$[Co(L^2H_2)_2]$	1	150–410	88.50	88.00	88.66	$[Co(L^2H_2)_2] \rightarrow Co_3O_4$
$[Ni(L^2H_2)_2]$	1	135–310	22.00	–	21.86	$[Ni(L^2H_2)_2] \rightarrow Ni(L^2H)(LH)_{0.5}$
	2	310–410	89.50	89.00	89.24	$[Ni(L^2H_2)_2] \rightarrow NiO$
$[Cu(L^2H)(H_2O)]$	1	125–240	4.00	–	4.45	$[Cu(L^2H)(H_2O)] \rightarrow CuL^2H$
	2	250–390	80.40	80.24	80.35	$[Cu(L^2H)(H_2O)] \rightarrow CuO$

to the formation of NiO. The Ni(II) complex of L^2H_3 also follows a two-staged decomposition pattern. In the first stage, the loss of half of a ligand molecule occurs in the temperature range, 135–310°C. In the second stage, the formation of NiO occurs in the temperature range 310–410°C. The Cu(II) complexes of L^1H_2 and L^2H_3 follow a two-staged decomposition pattern. The loss of water molecule occurs in the temperature ranges 120–200 and 125–240°C, respectively. This indicates the coordinated nature of water in these complexes. The second stage leads to the formation of CuO in the temperature ranges 220–340 and 250–390°C, respectively, for $[CuL^1(H_2O)]$ and $[Cu(L^2H)(H_2O)]$.

Preliminary studies of antifungal activity revealed that the complexes showed activity against all the fungal strains (Table-6). Another significant observation is that Co(II) and Ni(II) complexes exhibited greater activity compared to Mn(II) and Cu(II) complexes. The identification of actual mechanism of antifungal activity shown by these compounds needs further study. However, this may be due to the destruction of the fungal cell wall by these compounds, thus leading to their death.

TABLE-6
ANTIFUNGAL ACTIVITY SHOWN BY THE METAL COMPLEXES FOR L^1H_2 AND L^2H_3

Compounds	Diameter of zone of inhibition (mm)			
	Aspergillus niger	*Penicillium* species	*Candida albicans*	*Trichosporon* species
DMSO	10	10	14	10
$[Mn(L^1H)_2(H_2O)_2]$	20	22	18	22
$[CoL^1(H_2O)_3]$	26	23	17	30
$[NiL^1(H_2O)_3]$	27	25	20	30
$[CuL^1(H_2O)]$	20	23	17	25
$[Mn(L^2H_2)_2]$	20	20	18	20
$[Co(L^2H_2)_2]$	22	25	19	30
$[Ni(L^2H_2)_2]$	22	25	18	25
$[Cu(L^2H)(H_2O)]$	12	20	16	22

On the basis of the above observations, the Mn(II), Co(II), Ni(II) and Zn(II) complexes of both the ligands and Cd(II) and Hg(II) complexes of salicylylhydrazone are found to have 6-coordinate octahedral or distorted octahedral geometry. The others, *i.e.*, Cu(II), Zn(II), Cd(II) and Hg(II) complexes of benzoylhydrazone and Cu(II) complex of salicylylhydrazone are 4-coordinate, of which the two Cu(II) complexes may be square-planar and the others may be tetrahedral in geometry.

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