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Synthesis, Characterization and Antifungal Studies of Transition Metal Complexes of N-Methyl- and N-Ethylacetoacetanilide Isonicotinylhydrazones

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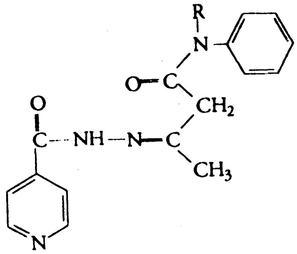
A series of transition metal complexes of N-methyl- and N-ethylacetoacetanilide isonicotinylhydrazones (L^1H_2 and L^2H_2 repectively) have been synthesized. Characterization of these compounds carried out mainly by using elemental analyses, magnetic susceptibility measurements and UV-VIS, IR, ^1H NMR spectral studies. IR spectral studies revealed that the ligands behave as tridendate di- or monoanions and coordinate through the anilide oxygen and isonicotinyl carbonyl oxygen and azomethine nitrogen atoms. Thermogravimetric studies of Mn(II), Co(II), Ni(II) and Cu(II) complexes of N-methylacetoacetanilide (L^1H_2) were also carried out. Antifungal studies of L^2H_2 and Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of both the ligands were also carried out.

INTRODUCTION

The coordination chemistry of aroylhydrazones, particularly that of isonicotinylhydrazones, is fascinating due to their diverse pharmacological applications[1]. These compounds exibit antibacterial, antifungal, antiviral and antitumour activities[2–4].

There are reports on the donor properties of acetoacetanilide isonicotinylhydrazone towards various metal ions[5]. Our own investigations on acetoacetanilide isonicotinylhydrazone and its complexes reveal their antitumour activity[6]. However, their solubilities were found to be very poor. With a view to synthesize more soluble complexes of these compounds, it is found to be worthwhile and interesting to study the donor properties of N-methyl- and N-ethylacetoacetanilide isonicotinylhydrazones (Fig. 1) towards various transition metal ions.



L^1H_2 (R = CH_3)

L^2H_2 (R = C_2H_5)

Fig. 1. Structures of the Ligands

EXPERIMENTAL

Metal salts used were of AnalaR grade. For the preparation of the complexes, except those of Fe(III), Hg(II) and Ag(I), metal acetates were used. The chlorides

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of Fe(III) and Hg(II) and nitrate of Ag(I) were used for the synthesis of complexes. Isonicotinylhydrazide used was of AnalaR grade. The solvents used were of E. Merck reagent grade. N-Methyl- and N-ethylacetoacetanilides were prepared and purified according to the reported procedure[7].

Preparation of N-methyl- and N-ethylacetoacetanilide isonicotinylhydrazone

Sodium N-methylacetoacetanilide (0.1 mol) in ethanol-water mixture (4 : 1, 200 mL) and isonicotinylhydrazide in ethanol (0.1 mol, 200 mL) were mixed and refluxed on a water bath for 3 h. As only a very small amount of the solid product separated from the reaction mixture, the resulting solution after reducing the volume was used as such for the synthesis of the complexes.

Isonicotinylhydrazide in ethanol (0.1 mol, 200 mL) was added to sodium N-ethylacetoacetanilide (0.1 mol) in ethanol-water mixture (4 : 1, 200 mL) and refluxed on a water bath for 3 h. The resulting red solution was evaporated nearly to dryness and extracted with acetone. The red coloured solid product which separated out was filtered off, washed with acetone several times and dried under reduced pressure over anhydrous calcium chloride. The product was recrystallized from ethanol.

Preparation of the complexes

Complexes of N-methylacetoacetanilide isonicotinylhydrazone (L^1H_2): The ethanolic solution of the ligand obtained as per the synthetic procedure mentioned above was used as such for the preparation of the complexes. To this solution (25 mL), the metal salt solution in methanol (0.01 mol, 25 mL) was added and stirred at room temperature for 1 h. In most of the cases, addition of water was necesary for the isolation of the solid complexes. The solid complexes which formed readily was filtered off, washed several times with water and finally with methanol and dried in a desiccator over anhydrous calcium chloride.

Complexes of N-ethylacetoacetanilide isonicotinylhydrazone (L^2H_2): A methanolic solution of the metal acetate (0.005 mol, 25 mL) was added to an ethanolic solution of the ligand (0.05 mol, 25 mL) and the mixture was stirred for 2 h. The solid product which formed readily was filtered off, washed several times with water and finally with methanol. It was dried under reduced pressure over anhydrous calcium chloride.

Analysis of the metal contents in the complexes was performed by standard methods[8]. Carbon, hydrogen and nitrogen were estimated microanalytically on a CHN—O rapid analyzer at CDRI Lucknow. IR spectra (4000–400 cm^{-1}) were recorded on a Shimadzu 8101 FTIR spectrophotometer using KBr discs. ^1H-NMR spectra of the ligand (L^2H_2) and the Zn(II) complexes were carried out on a Varian 300-NMR spectrometer. The magnetic moments were determined on a Gouy-type balance using $Hg[Co(NCS)_4]$ as a calibrant. The electronic spectra were recorded on a Shimadzu 1601A spectrophotometer. Thermograms were recorded on a TGS-I thermobalance with the following operational characteristics: heating rate, 10° per min^{-1}; sample size, 2–10 mg; atmosphere, static air; crucible, platinum.

The fungi were grown on a Sabouraud's glucose agar medium (glucose = 4 g, peptone = 1 g, agar-agar = 2 g and 100 mL distilled water, pH = 5.6). Cup-plate technique was used for detecting antifungal activity[9–11]. The greater diameter shown by the compound than the control (Table-6) indicates their antifungal activity.

RESULTS AND DISCUSSION

Analytical results and magnetic moment values are summarized in Table-1.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE COMPOUNDS

Sl. No.	Empirical formulae of compounds	m.p. (°C) (Colour)	Yield (%)	Found (calcd.) %				μ_{eff} (B.M.)
				M	C	H	N	
1.	$C_{17}H_{18}N_4O_2$ $[L^1H_2]$	>300, (red)	14	–	–	–	–	–
2.	$MnC_{17}H_{22}N_4O_5$ $[MnL^1(H_2O)_3]$	>300 (pale red)	60	13.08 (13.17)	48.40 (48.91)	5.16 (5.32)	13.30 (13.42)	6.05
3.	$Fe_2C_{34}H_{36}N_8O_6Cl_2$ $[FeL^1Cl(H_2O)]_2$*	>300 (brown)	70	13.24 (13.38)	48.82 (48.86)	4.27 (4.34)	13.37 (13.41)	5.00
4.	$CoC_{17}H_{22}N_4O_5$ $[CoL^1(H_2O)_3]$	>300 (brown)	85	13.78 (13.99)	48.35 (48.44)	5.26 (5.27)	12.76 (13.29)	5.02
5.	$NiC_{17}H_{22}N_4O_5$ $[NiL^1(H_2O)_3]$	>300 (yellow)	82	13.88 (13.95)	48.28 (48.47)	5.04 (5.27)	13.27 (13.30)	2.80
6.	$CuC_{17}H_{22}N_4O_5$ $[CuL^1(H_2O)_3]$	>300 (green)	85	14.95 (14.93)	47.87 (47.92)	5.18 (5.21)	13.86 (13.15)	2.12
7.	$ZnC_{17}H_{22}N_4O_5$ $[ZnL^1(H_2O)_3]$	>300 (yellow)	85	15.82 (15.29)	47.68 (47.71)	5.18 (5.19)	13.24 (13.09)	–
8.	$CdC_{17}H_{22}N_4O_5$ $[CdL^1(H_2O)_3]$	>300 (yellow)	88	23.40 (23.68)	42.76 (42.98)	4.62 (4.67)	11.15 (11.80)	–
9.	$HgC_{17}H_{18}N_4O_3$ $[HgL^1(H_2O)]$	255 (orange)	85	38.17 (38.08)	38.07 (38.73)	3.33 (3.44)	10.96 (10.63)	–
10.	$AgC_{17}H_{19}N_4O_3$ $[AgL^1H(H_2O)]$	>300 (brown)	68	24.12 (24.87)	46.86 (46.98)	4.12 (4.88)	12.78 (12.89)	–
11.	$C_{18}H_{20}N_4O_2$ $[L^2H_2]$	>300 (red)	45	–	64.48 (66.66)	5.88 (6.19)	17.40 (17.27)	–
12.	$MnC_{36}H_{38}N_8O_4$ $[Mn(L^2H)_2]$	268 (yellowish brown)	62	7.17 (7.84)	60.68 (61.62)	5.28 (6.19)	15.90 (15.97)	5.69
13.	$Fe_2C_{36}H_{40}N_8O_6Cl_2$ $[FeL^2Cl(H_2O)]_2$**	>300 (brown)	65	12.56 (12.94)	50.10 (50.07)	4.48 (4.65)	12.96 (12.98)	4.85
14..	$CoC_{36}H_{38}N_8O_4$ $[Co(L^2H)_2]$	>300 (brown)	75	8.35 (8.36)	61.08 (61.27)	5.27 (5.41)	15.87 (15.88)	4.68
15.	$NiC_{36}H_{38}N_8O_4$ $[Ni(L^2H)_2]$	>300 (reddish brown)	78	8.10 (8.36)	61.16 (61.29)	5.35 (5.41)	15.87 (15.88)	3.24
16.	$CuC_{18}H_{20}N_4O_5$ $[CuL^2(H_2O)]$	>300 (brown)	80	16.01 (15.74)	53.02 (53.51)	5.05 (4.97)	13.85 (13.87)	2.19
17.	$ZnC_{18}H_{20}N_4O_5$ $[ZnL^2(H_2O)_3]$	>300 (brown)	82	14.46 (14.81)	46.94 (48.92)	5.62 (5.46)	12.68 (12.68)	–
18.	$CdC_{18}H_{20}N_4O_5$ $[CdL^2(H_2O)_3]$	>300 (brown)	82	22.89 (23.01)	44.01 (44.21)	4.73 (4.93)	11.45 (11.46)	–

*Cl = 8.35 (8.49), **Cl = 8.26 (8.22)

The results agree well with the proposed formulae of the ligands and their complexes. The complexes of L^1H_2 correspond to the formulae $[ML^1(H_2O)_3]$, where M = Mn(II) Co(II), Ni(II), Cu(II), Zn(II) or Cd(II); $[FeL^1Cl(H_2O)]_2$ $[HgL^1(H_2O)]$, and $[AgL^1H(H_2O)]$. The complexes of L^2H_2 have the following formulae $[M(L^2H)_2]$, where M = Mn(II), Co(II) or Ni(II); $[ML^2(H_2O)_3]$, where M = Zn(II) or Cd(II), $[FeL^2Cl(H_2O)]_2$ and $[CuL^2(H_2O)]$.

The IR spectra of the ligands (Table-2) show deep broad bands centered around 3450–3200 cm^{-1} region. This may be due to ν(N—H) which is involved in hydrogen bonding[12, 13]. In the spectra of all the complexes, except those of Ag(I) of L^1H_2 and Mn(II), Co(II) and Ni(II) of L^2H_2, this region appears as broad and this may be due to OH stretching bands of coordinated water molecules. The ν(C=O) (anilide) band appears at 1680 and 1685 cm^{-1}, respectively, in the spectra of L^1H_2 and L^2H_2.[14] In the spectra of the Ag(I) complex of L^1H_2 and Mn(II), Co(II) and Ni(II) complexes of L^2H_2, this band shifts to the lower frequency region by a few cm^{-1}. This may be due to the participation of anilide carbonyl oxygen in coordination. In the spectra of all other complexes, this band disappears and a new one appears at *ca.* 1150 cm^{-1}. This may be due to the enolization of —CH_2—C=O to —CH=C—OH and subsequent coordination through deprotonated oxygen.

The strong band at 1650 and 1653 cm^{-1}, in the spectra of L^1H_2 and L^2H_2, respectively, may be assigned to ν(C=O) (isonicotinyl). In the spectra of all the complexes this band disappears and a new band is observed at *ca.* 1250 cm^{-1}. This indicates the enolization of =N—NH—C=O to =N—N=C—OH and subsequent coordination through deprotonated oxygen. The medium band observed at 1610 and a strong one at 1601 cm^{-1} in the spectra of L^1H_2 and L^2H_2, respectively, may be assigned to ν(C=N). In the spectra of all the complexes this band shifts to lower frequency region by a few cm^{-1}, indicating the participation of azomethine nitrogen in coordination. A band observed at 1005 cm^{-1} in the spectra of L^1H_2 and L^2H_2 may be assigned to ν(N—N). In the spectra of all the chelates this band shifts to higher frequency region by a few cm^{-1}. This observation confirms the participation of azomethine nitrogen in coordination. In the spectra of all the complexes of L^1H_2 and Fe(III), Cu(II), Zn(II) and Cd(II) complexes of L^2H_2, the broad bands at *ca.* 3300 cm^{-1}, together with new bands at *ca.* 940, 850 and 660 cm^{-1} may indicate the presence of coordinated water molecule[14]. The nature of metal-ligand bonding is confirmed by the newly formed bands at *ca.* 550 and 430 cm^{-1} in the spectra of the complexes which may be assigned to ν(M—O) and ν(M—N), respectively.

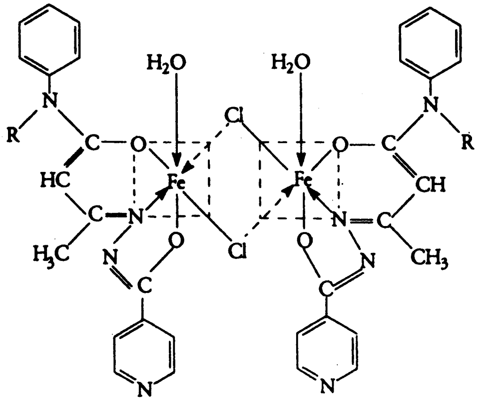
The Mn(II) complexes, $[MnL^1(H_2O)_3]$ and $[Mn(L^2H)_2]$ register magnetic moment values 6.05 and 5.69 B.M., respectively. These values are in accordance with spin free d^5 configuration for Mn(II) ions, in these complexes. The Fe(III) complexes of L^1H_2 and L^2H_2 register magnetic moment values 5.00 and 4.85 B.M., respectively. These value which are low compared to the spin-only value (5.93 B.M.) may be due to binuclear configuration facilitating antiferromagnetic superexchange interaction (Fig. 2)[15, 16]. The Co(II) and Ni(II) complexes show magnetic moment values, which are quite close to the reported values for octahedral complexes. The Cu(II) complexes, $[CuL^1(H_2O)_3]$ and $[CuL^2(H_2O)]$

TABLE-2

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

Compound	ν(N—H) or ν(O—H)	ν(C═O) (Anilide)	ν(C═O) (Isonicotinyl)	ν(C═N)	ν(C—O) (Isonicotinyl)	ν(C—O) (Anilide)	ν(N—N)	ν(M—N)	ν(M—O)
$[L^1H_2]$	3560 b, 3420 b 3180 sh, 3020 w	1680 m	1650 s	1610 m	–	–	1005 m	–	–
$[MnL^1(H_2O)_3]$	3400 b, 3265 m 3080 sh	–	–	1593 s	1296 s	1155 m	1020 m	525 m	430 m
$[FeL^1Cl(H_2O)]_2$	3649 m, 3390 b, 3265 b, 3080 sh	–	–	1593 m	1224 m	1140 s	1024 m	560 w	460 w
$[CoL^1(H_2O)_3]$	3400 b, 3240 b	–	–	1590 s	1232 s	1158 m	1022 w	550 w	430 sh
$[NiL^1(H_2O)_3]$	3649 m, 3400 b	–	–	1590 s	1190 s	1140 s	1026 m	550 w	430 sh
$[CuL^1(H_2O)_3]$	3422 s, 3250 m, 3050 w	–	–	1595 m	1234 s	1157 m	1035 m	540 w	429 m
$[ZnL^1(H_2O)_3]$	3400 b, 3230 b 3067 m	–	–	1593 s	1219 s	1157 s	1025 m	561 m	420 sh
$[CdL^1(H_2O)_3]$	3566 m, 3250 m 3080 b	–	–	1572 m	1217 s	1157 s	1014 s	561 m	421 sh
$[HgL^1(H_2O)]$	3566 m, 3426 m 3388 b	–	–	1590 m	1296 s	1153 s	1012 m	559 m	438 m
$[AgL^1H(H_2O)]$	3410 s, 3320 w	1650 s	–	1560 m	1230 m	1160 m	1028 m	520 m	430 m
$[L^2H_2]$	3450 b, 3060 m	1685 m	1653 m	1601 s	–	–	1005 m	–	–
$[Mn(L^2H)_2]$	3350 m, 3060 w	1640 s	–	1576 m	1277 s	–	1012 m	550 m	432 w
$[FeL^2Cl(H_2O)]_2$	3380 b	–	–	1590 s	1232 s	1155 m	1022 m	510 w	460 m
$[Co(L^2H)_2]$	3400 m, 3060 w	1630 s	–	1589 m	1257 s	–	1022 m	557 m	436 w
$[Ni(L^2H)_2]$	3450 w, 3060 w	1640 s	–	1578 s	1267 m	–	1018 m	520 w	436 w
$[CuL^2(H_2O)]$	3450 b, 3060 m	–	–	1560 m	1250 s	1160 s	1030 m	510 w	420 w
$[ZnL^2(H_2O)_3]$	3400 b, 3080 w	–	–	1561 m	1219 s	1154 s	1030 m	550 m	430 w
$[CdL^2(H_2O)_3]$	3400 b	–	–	1565 m	1219 s	1151 m	1014 m	550 w	430 w

show magnetic moment values 2.12 and 2.19 B.M., respectively, which eliminates the possibility of antiferromagnetic exchange interaction in them.



R = CH_3 or C_2H_5

Fig. 2. Suggested Structures of the Fe(III) Complexes

The electronic spectra (Table-3) of the Mn(II) complexes, $[Mn(L^1(H_2O)_3]$ and $[Mn(L^2H)_2]$ register characteristic weak bands at 22075 and 22172 cm^{-1}, respectively. This band may be assigned[17, 18] to $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ transition of Mn(II) ion in a spin-free d^5 configuration. Generally, Fe(III) complexes register intense bands in the high energy region. In the present investigation, the Fe(III) complexes, $[FeL^1Cl(H_2O)]_2$ and $[FeL^2Cl(H_2O)]_2$ register an intense band at *ca.* 28000 and a broad one at *ca.* 19600 cm^{-1}. These bands may be assigned to $^6A_{1g} \rightarrow {}^4T_{2g}(D)$ and $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ transitions characteristic of an Fe(III) atom in a spin-free d^5 configuration. The Co(II) complexes, $[CoL^1(H_2O)_3]$ and $[Co(L^2H)_2]$ register an intense band at *ca.* 23000–21000, a broad one at *ca.* 18100 and a weak one at *ca.* 9800–9600 cm^{-1}. These bands may be assigned 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 characteristic of an octahedrally coordinated Co(II) ion. The ratio ν_1/ν_3 at (*ca.* 2.2) is in accordance with the expected value for an octahedral Co(II) complex (1.92–2.95). The Ni(II) complexes of L^1H_2 and L^2H_2 register an intense band at *ca.* 24600–23300, a broad one at *ca.* 16800 and a weak one at *ca.* 9900–9700 cm^{-1}. These bands may be assigned, respectively, to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_1)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_3)$ transitions of an octahedral Ni(II) complex. The ratio ν_1/ν_2 (cm^{-1}) of $[NiL^1(H_2O)_3]$ is found to be 1.46, which is lower than the value expected for a regular octahedral Ni(II) complex (1.71) and hence a distorted octahedral geometry may be assigned to this complex. The ν_1/ν_2 ratio for

$[Ni(L^2H)_2]$ indicates its octahedral structure. The Cu(II) complexes, $[CuL^1(H_2O)_3]$ and $[CuL^2(H_2O)]$ register broad bands at *ca.* 22200 and 14200 cm^{-1}. These bands may be assigned to $^3B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ or $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions of square-planar/distorted octahedral Cu(II) complex.

TABLE-3
EELECTRONIC SPECTRAL BANDS AND THEIR ASSIGNMENTS[a]
OF THE COMPLEXES

Complex	Bands (cm^{-1})	Assignments
$[MnL^1(H_2O)_3]$	22075	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$
$[FeL^1Cl(H_2O)]_2$	28248 br	$^6A_{1g} \rightarrow {}^4T_{2g}(D)$
	19646 br	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$
$[CoL^1(H_2O)_3]$	21511	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	18181 w	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
	9615 br	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
$[NiL^1(H_2O)_3]$	24691	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
	16863	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
	9708 br	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
$[CuL^1(H_2O)_3]$	22222	$^2B_{1g} \rightarrow {}^2E_g$
	14285	$^2B_{1g} \rightarrow {}^2A_{1g}$
$[Mn(L^2H)_2]$	22172	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$
$[FeL^2Cl(H_2O)_2]$	27932 br	$^6A_{1g} \rightarrow {}^4T_{2g}(D)$
	19729 br	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$
$[Co(L^2H)_2]$	23809	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$
	18050 w	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
	9891 br	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
$[Ni(L^2H)_2]$	23255	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
	12987	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
	9891 br	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
$[CuL^2(H_2O)]$	23474 br	$^2B_{1g} \rightarrow {}^2E_g$
	14184 br	$^2B_{1g} \rightarrow {}^2B_{2g}$

br = broad, w = weak

The ^1H-NMR (Table-4) of the Zn(II) complex of L^1H_2, recorded in DMSO show a singlet at 8.80–8.45 ppm, which may be assigned to α-protons of pyridine ring[19, 20]. The multiplet observed at 7.91–7.45 ppm may be assigned to β-protons of pyridine ring and protons of anilide ring. A small multiplet observed at 5.20 ppm may be assigned to α-CH proton formed during coordination with the metal ion. The signals observed at 3.21, 2.85 and 1.85 ppm may be assigned to protons of N—CH_3, coordinated water and ω-CH_3 protons, respectively.

TABLE-4
SIGNIFICANT ^{1}H-NMR SPECTRAL ASSIGNMENTS^a OF L^2H_2 AND THE Zn(II) COMPLEXES OF L^1H_2 AND L^2H_2

Compound	δ (ppm)	Proton
$[ZnL^1(H_2O)_3]$	8.80–8.45 (s)	α-Protons of pyridine ring
	7.91–7.45 (m)	Anilide ring proton and β-protons of pyridine ring
	5.20 (s)	α-CH
	3.21 (s)	N—CH_3
	2.85 (s)	Coordinated water
	1.85 (s)	ω-CH_3
L^2H_2	8.70 (s)	NH
	8.64–8.44 (s)	α-Protons of pyridine ring
	7.84–7.67 (m)	Anilide ring proton and β-protons of pyridine ring
	3.50–3.25 (s)	N-Ethyl CH_2
	3.17 (s)	α-CH_2
	1.60 (s)	ω-CH_3
	1.12 (t)	N-Ethyl CH_3
$[ZnL^2(H_2O)_3]$	8.66–8.46 (s)	α-Protons of pyridine ring
	7.90–7.70 (m)	β-Protons of pyridine ring and protons of anilide ring
	5.65 (s)	α-CH
	3.19–3.12 (q)	N-Ethyl CH_2
	1.57 (s)	ω-CH_3
	1.28–1.23 (t)	N-Ethyl CH_3

^{a}s = singlet, m = multiplet, t = triplet, q = quartet

In the spectrum of L^2H_2 recorded in DMSO, a singlet observed at 8.70 ppm may be assigned to NH. The singlet observed at 8.64–8.44 ppm might be assigned to α-protons of pyridine ring. The multiplet observed at 7.84–7.67 ppm may be assigned to β-protons of pyridine ring and proton of anilide ring. The signals observed at 3.17, 1.60 and 1.12 ppm may be assigned to α-CH_2, ω-CH_3 and N-ethyl CH_3 protons, respectively. The signal due to N-ethyl CH_2 proton may be merged in the intense signal observed at 3.50–3.25 ppm.

In the spectrum of the Zn(II) complex of L^2H_2 recorded in $CDCl_3$, the peak observed at 8.70 ppm in ligand spectrum disappears. This may be due to the enolization of =N—NH—C=O to =N—N=C—OH during complex formation. The singlet observed at 8.66–8.46 ppm may be assigned to α-protons of pyridine ring. The multiplet observed at 7.90–7.70 ppm may be assigned to β-protons of pyridine ring and protons of anilide ring. A small singlet observed at 5.65 ppm may be assigned to α-CH proton formed by the enolization of —CH_2—C=O to —CH=C—OH during coordination. A quartet at 3.19–3.12, a singlet observed at 1.57 and a triplet at 1.28–1.23 ppm may be assigned to N-ethyl CH_2, ω-CH_3 and N-ethyl CH_3 protons, respectively.

Thermogravimetric studies (Table-5) of Mn(II), Co(II), Ni(II) and Cu(II) complexes of L^1H_2 were also carried out[21]. The thermograms of these complexes reveal several interesting features. In the case of the Mn(II) complex, loss of two water molecules alone occurs in the temperature range of 125–210°C, which reveals their coordinated nature. In the second stage, the decomposition of monohydrate complex, $[MnL^1(H_2O)]$ occurs in the temperature range 250–450°C leading to the formation of MnO_2. In the case of the Co(II) and Ni(II) complexes, the decomposition starts at about 110°C and a weight loss of *ca.* 8.5% (corresponding to the loss of two molecules of water) is noticed between 110–120°C. The third water molecule is lost at 120–190 and 120–250°C for these complexes as indicated by the inflections in their thermograms. The analysis of thermograms together with infrared spectral studies indicates that all the three water molecules are coordinated to the central metal ions. The complexes then decompose forming their oxides, Co_3O_4 and NiO, in the temperature range of 310–490 and 290–550°C, respectively. The Cu(II) complexes have two staged decomposition patterns. The first stage occurs in the temperature range of 110–210°C, with the loss of three coordinated water molecules. The second stage of decomposition leads to the formation of CuO in the temperature range of 210–350°C.

TABLE-5

THERMAL ANALYSIS DATA OF THE COMPLEXES OF L^1H_2

Compound	Decomp. stage	Decomp. temp. range (°C)	T.G.	Mass-loss % from independent pyrolysis	Theroctical	Decomposition pattern
$[MnL^1(H_2O)_3]$	1	125–210	8.5	–	8.63	$[MnL^1(H_2O)_3] \rightarrow MnL^1(H_2O)$
	2	250–450	79.0	79.24	79.16	$[MnL^1(H_2O)_3] \rightarrow MnO$
$[CoL^1(H_2O)_3]$	1	110–120	8.0	–	8.55	$[CoL^1(H_2O)_3] \rightarrow CoL^1(H_2O)$
	2	120–190	12.5	–	12.83	$[CoL^1(H_2O)_3] \rightarrow CoL^1$
	3	310–490	80.0	80.24	80.76	$[CoL^1(H_2O)_3] \rightarrow Co_3O_4$
$[NiL^1(H_2O)_3]$	1	110–120	8.5	–	8.56	$[NiL^1(H_2O)_3] \rightarrow NiL^1(H_2O)$
	2	120–250	13.0	–	12.95	$[NiL^1(H_2O)_3] \rightarrow NiL^1$
	3	290–550	82.0	82.40	82.09	$[NiL^1(H_2O)_3] \rightarrow NiO$
$[CuL^1(H_2O)_3]$	1	110–210	12.0	–	12.69	$[CuL^1(H_2O)_3] \rightarrow CuL^1$
	2	210–350	81.0	81.28	81.32	$[CuL^1(H_2O)_3] \rightarrow CuO$

Our results of investigation on the antifungal activity revealed that the Co(II) and Ni(II) complexes exhibit higher activity than the Mn(II) complexes. Compared to the ligand L^2H_2, its complexes exhibit greater activity. Probably this may be due to the greater lipophilic nature of the complexes.

Based on the above observations, the Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of L^1H_2 and Mn(II), Co(II), Ni(II), Zn(II) and Cd(II) complexes of L^2H_2 exhibit octahedral or distorted octahedral geometry. The Hg(II) and Ag(I) complexes of L^1H_2 may be tetrahedral and the Cu(II) complex of L^2H_2 may be planar. Both the Fe(III) complexes are found to have 6-coordinate binuclear structure.

TABLE-6

ANTIFUNGAL ACTIVITY SHOWN BY THE METAL COMPLEXES OF L^1H_2 AND L^2H_2

Compound	Diameter of zone of inhibition (mm)			
	Aspergillus niger	*Penicillium* species	*Candida albicans*	*Trichosporon* species
DMSO	10	10	14	10
$[MnL^1(H_2O)_3]$	20	25	20	12
$[CoL^1(H_2O)_3]$	28	30	25	18
$[NiL^1(H_2O)_3]$	35	30	25	14
$[CuL^1(H_2O)_3]$	28	25	22	12
L^2H_2	12	13	14	12
$[Mn(L^2H)_2]$	20	28	28	22
$[Co(L^2H)_2]$	25	28	30	25
$[Ni(L^2H)_2]$	24	30	35	25
$[CuL^2(H_2O)]$	30	24	30	22
$[ZnL^2(H_2O)_3]$	24	28	30	20

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