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SYNTHESIS AND CHARACTERIZATION OF METAL COMPLEXES OF *N*-METHYL- AND *N*-ETHYLACETOACETANILIDE SEMICARBAZONES

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ABSTRACT

Fourteen new metal complexes of *N*-methyl- (H_2L) and *N*-ethylacetoacetanilide (H_2L') semicarbazones, having the general formulae $[M(LH)_2]$, $[ML/L'(H_2O)]$, $[ML/L'(H_2O)_3]$, and $[FeLCI(H_2O)_2]$, where $M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)$ or $Hg(II)$, LH = tridentate monoanion of H_2L and L/L' = tridentate dianion of H_2L or H_2L' , were synthesized. Characterization of these compounds was mainly done by chemical analyses, molar conductance, magnetic susceptibility and electronic, infrared and 1H NMR spectral studies. Thermogravimetric studies of $Mn(II)$, $Co(II)$, $Ni(II)$, and $Cu(II)$ complexes of *N*-methylacetoacetanilide semicarbazone were also carried out.

Key Words: *N*-methyl- and *N*-ethylacetoacetanilide semicarbazones; Synthesis; Characterization; Thermogravimetric studies

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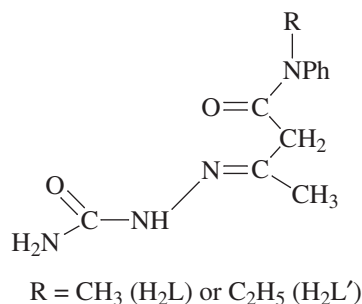


Figure 1. Suggested structure of the ligands.

INTRODUCTION

Compounds having $>C=N-N<$ groups were found to exhibit immense physiological and analytical applications. Semicarbazones, typical members of this class, can act as ligands towards various metal ions. They usually act as chelating ligands towards transition metal ions by bonding through oxygen and hydrazinic nitrogen atoms (1), although in a few cases they are reported to behave as monodentate ligands. In continuation of our investigations on the donor properties of semicarbazones and thiosemicarbazones of β -ketoderivatives (2,3), it was found to be worthwhile and interesting to synthesize and characterize metal complexes of semicarbazones of *N*-substituted acetoacetanilides. We describe here the synthesis and characterization of several typical transition metal complexes of semicarbazones of *N*-methyl- (H_2L) and *N*-ethylacetoacetanilide (H_2L') (Fig. 1).

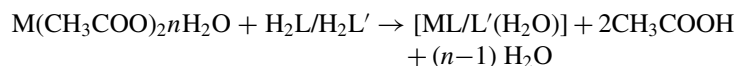
RESULTS AND DISCUSSION

The ligands of the present investigation exist mainly in the keto form. This is established from the IR and 1H NMR spectral studies. The ligands show bands in the regions 3400–3000, 1700–1640, and 1610–1590 cm^{-1} , which are assigned, respectively, to N–H, C=O and C=N stretching vibrations. In the spectra of the complexes, broadening of the bands in N–H region is noticed. The C=O band either shifts to lower frequency or disappears during complex formation. The C=N stretching band is also found to be lowered in the spectra of the complexes. The 1H NMR spectra of the ligands show peaks due to CH_2 and NH protons, eliminating the possibility of their enol structures.



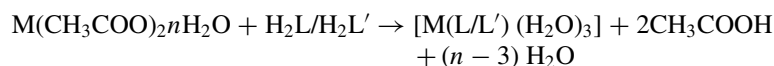
Formulae and General Properties of the Complexes

Formation of the complexes can be represented by the following equations:



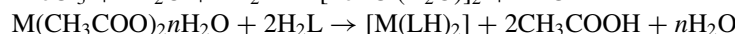
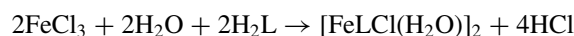
L = tridentate dianion of H_2L , M = Zn(II)

L' = tridentate dianion of $\text{H}_2\text{L}'$, M = Zn(II) or Cd(II)



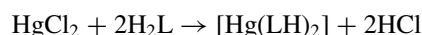
M = Co(II) or Ni(II) for L

M = Mn(II), Co(II), Ni(II) or Cu(II) for L'



M = Mn(II), Cu(II) or Cd(II)

LH = tridentate monoanion of H_2L



Except for the Fe(III) and Ni(II) complexes of *N*-methylacetoacetanilide semicarbazone, all the others were found to be pale coloured, nonhygroscopic air- and photostable. The Fe(III) and Ni(II) complexes of the *N*-methyl derivative were found to be deliquescent. Generally, the complexes were found to be soluble in ethanol, methanol, and DMSO. However, the solubility of the Zn(II) and Cd(II) complexes are very poor. The electrical conductance of the complexes measured in DMSO and the calculated molar conductance values indicate their nonelectrolytic nature. The analytical data (Table 1) of the H_2L complexes correspond to the formulae $[\text{M}(\text{LH})_2]$, where M = Mn(II), Cu(II), Cd(II) or Hg(II); $[\text{ML}(\text{H}_2\text{O})_3]$, where M = Co(II) or Ni(II); $[\text{ZnL}(\text{H}_2\text{O})]$ and $[\text{FeLCl}(\text{H}_2\text{O})]_2$. The complexes of $\text{H}_2\text{L}'$ have the formulae $[\text{ML}'(\text{H}_2\text{O})_3]$, where M = Mn(II), Co(II), Ni(II) or Cu(II) and $[\text{ML}'(\text{H}_2\text{O})]$, where M = Zn(II) or Cd(II).

Magnetic Behaviour

The magnetic moment (Table 1) of $[\text{Mn}(\text{LH})_2]$ (6.14 B.M.) which is close to the spin-only value (5.92 B.M.) indicates its octahedral geometry (4). The low value of the magnetic moment of $[\text{MnL}'(\text{H}_2\text{O})_3]$ (4.54 B.M.) may be due to its distorted octahedral geometry (5). The Fe(III) complex of H_2L shows a magnetic moment value of 4.96 B.M., which is found to be lower than the spin-only value



Table 1. Analytical and Physical Data of the Compounds

Sl. No.	Complex	Empirical Formulae	Formula Weight	Colour	Decomp. Temp. °C	Yield (%)	Found (Calculated) %			
							M	C	H	N
(1)	H ₂ L	C ₁₂ H ₁₆ N ₄ O ₂	248.13	White	183	70	—	58.10 (58.03)	6.15 (6.49)	22.32 (22.57)
(2)	[Mn(LH) ₂]	MnC ₂₄ H ₃₀ N ₈ O ₈	549.18	Pale yellow	296	55	10.10 (10.00)	51.89 (52.44)	5.20 (5.50)	20.32 (20.50)
(3)	[Fe ₂ Cl(H ₂ O)] ₂ ^a	Fe ₂ C ₂₄ H ₃₂ N ₈ O ₆ Cl ₂	710.87	Dark brown	162	62	15.26 (15.71)	40.24 (40.51)	4.48 (4.54)	15.25 (15.75)
(4)	[CoL(H ₂ O) ₃]	CoC ₁₂ H ₂₀ N ₄ O ₅	359.09	Pale pink	>300	65	15.86 (16.41)	40.20 (40.10)	5.38 (5.61)	15.38 (15.59)
(5)	[NiL(H ₂ O) ₃]	NiC ₁₂ H ₂₀ N ₄ O ₅	358.87	Pale green	>300	60	16.28 (16.35)	39.89 (40.12)	5.40 (5.62)	15.42 (15.60)
(6)	[Cu(LH) ₂]	CuC ₂₄ H ₃₀ N ₈ O ₄	557.79	Olive green	256	65	10.80 (11.39)	51.58 (51.63)	5.48 (5.78)	20.20 (20.07)
(7)	[ZnL(H ₂ O)]	ZnC ₁₂ H ₁₆ N ₄ O ₃	329.52	White	179	65	19.40 (19.84)	43.86 (43.70)	4.82 (4.89)	16.94 (16.99)
(8)	[Cd(LH) ₂]	CdC ₂₄ H ₃₀ N ₈ O ₄	606.64	White	>300	62	18.44 (18.53)	46.60 (46.49)	5.15 (4.98)	18.28 (18.46)
(9)	[Hg(LH) ₂]	HgC ₂₄ H ₃₀ N ₈ O ₄	694.83	Pale rose	172	61	28.60 (28.86)	40.84 (41.44)	4.42 (4.35)	15.98 (16.11)
(10)	H ₂ L'	C ₁₃ H ₁₈ N ₄ O ₂	262.14	White	171	60	—	59.32 (59.50)	6.94 (6.92)	21.40 (21.36)
(11)	[MnL'(H ₂ O) ₃]	MnC ₁₃ H ₂₂ N ₄ O ₅	369.12	Pale yellow	>300	52	14.88 (15.06)	41.76 (42.26)	5.68 (6.00)	15.10 (15.17)
(12)	[CoL'(H ₂ O) ₃]	CoC ₁₃ H ₂₂ N ₄ O ₅	373.11	Pale pink	>300	58	15.86 (15.79)	41.42 (41.81)	5.40 (5.94)	15.14 (15.01)
(13)	[NiL'(H ₂ O) ₃]	NiC ₁₃ H ₂₂ N ₄ O ₅	372.89	Pale green	>300	55	15.41 (15.74)	41.42 (41.83)	5.90 (5.95)	15.15 (15.02)
(14)	[CuL'(H ₂ O) ₃]	CuC ₁₃ H ₂₂ N ₄ O ₅	377.72	Olive green	195	62	16.57 (16.82)	41.46 (41.30)	5.82 (5.87)	14.87 (14.82)
(15)	[ZnL'(H ₂ O)]	ZnC ₁₃ H ₁₈ N ₄ O ₃	343.53	Pale yellow	>300	62	18.60 (19.03)	45.02 (45.41)	5.10 (5.28)	16.32 (16.30)
(16)	[CdL'(H ₂ O)]	CdC ₁₃ H ₁₈ N ₄ O ₃	390.54	Pale yellow	120	65	29.00 (28.78)	39.52 (39.94)	4.66 (4.64)	14.12 (14.33)

^aCl = 9.89 (9.98).

(5.90 B.M.). This may be due to its binuclear configuration, facilitating antiferromagnetic exchange interaction (6). The μ_{eff} values of 5.00 and 4.83 B.M. for the Co(II) complexes together with their pale-pink colour indicate their octahedral structure. The Ni(II) complexes, $[\text{NiL}(\text{H}_2\text{O})_3]$ and $[\text{NiL}'(\text{H}_2\text{O})_3]$, register magnetic moment values at 2.71 and 2.53 B.M., respectively. Their pale-green colour and the magnetic moment values indicate octahedral geometry around the Ni(II) ion. The Cu(II) complexes, $[\text{Cu}(\text{LH})_2]$ and $[\text{CuL}'(\text{H}_2\text{O})_3]$, register magnetic moments at 2.15 and 2.17 B.M., respectively, which indicate the absence of antiferromagnetic exchange interaction in them.

Electronic Spectra

The important electronic spectral bands of the Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) complexes and their assignments are given in the Table 2. The Mn(II) complex of H_2L do not register any characteristic band in the visible region.

Table 2. Electronic Spectral Data of the Complexes and Assignments^a

Compound	Bands (cm^{-1})	Assignments	Geometry
$[\text{FeLCl}(\text{H}_2\text{O})_2]$	26109 22026 br	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{D})$ ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$	Octahedral binucleated
$[\text{CoL}(\text{H}_2\text{O})_3]$	22222 18181 br 9551 w	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$	Distorted octahedral
$[\text{NiL}(\text{H}_2\text{O})_3]$	25000 15673 br 9756 w	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$	Distorted octahedral
$[\text{Cu}(\text{LH})_2]$	20876 br 11037 br	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ ${}^2\text{B}_{1g} \rightarrow {}^4\text{A}_{1g}$	Octahedral
$[\text{Mn}(\text{L}'\text{H})_2]$	28818 22935	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{D})$ ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$	Octahedral
$[\text{CoL}'(\text{H}_2\text{O})_3]$	21598 17889 br 9587 w	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$	Distorted octahedral
$[\text{NiL}'(\text{H}_2\text{O})_3]$	24691 16000 br 9881 w	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$	Distorted octahedral
$[\text{CuL}'(\text{H}_2\text{O})_3]$	23529 15600 br	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ ${}^2\text{B}_{1g} \rightarrow {}^4\text{A}_{1g}$	Distorted octahedral

^abr = broad, w = weak.



Whereas, the Mn(II) complex of H_2L' registers a series of weak bands stretching over the whole UV-Visible region of the spectrum. The most prominent ones observed at 28,818 and 22,935 cm^{-1} may be assigned, respectively, to ${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ transitions which are characteristic of an octahedral Mn(II) complex (7,8). The Fe(III) complex of H_2L registers bands at 26,109 and 22,026 cm^{-1} . These may be assigned, respectively, to ${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ transitions of an Fe(III) ion in a spin-free d^5 configuration. The Co(II) complexes register a band $\sim 22,000$, a broad one $\sim 18,000$ and a weak one ~ 9700 cm^{-1} . These may be assigned, respectively, to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions of an octahedrally coordinated Co(II) ion. The complexes of Ni(II), viz., $[NiL(H_2O)_3]$ and $[NiL'(H_2O)_3]$, register an intense band at $\sim 25,000$, a broad one at $\sim 16,000$ and a weak one at ~ 9800 cm^{-1} . These may assigned, respectively, to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transitions of 6-coordinated octahedral Ni(II) ion. $[Cu(LH)_2]$ registers bands at 20,876 and 11,037 cm^{-1} , whereas $[CuL'(H_2O)_3]$ registers bands at 23,529 and 15,600 cm^{-1} . These are characteristic of an octahedral or distorted octahedral geometry around the Cu(II) ion.

Infrared Spectra

The important IR spectral bands and their tentative assignments are given in Table 3. The bands around 3500 cm^{-1} in the spectra of the ligands may be assigned to asymmetric and symmetric stretching modes of NH_2 and NH groups. In the spectra of the Fe(III), Co(II), and Ni(II) complexes of H_2L and all the complexes of H_2L' , this region appears as broad and this may be due to the stretching modes of coordinated water molecule (9).

The $\nu(C=O)$ (anilide) band appears at 1670 and 1692 cm^{-1} in the spectra of H_2L and H_2L' , respectively (10). In the spectra of the Mn(II), Cu(II), Cd(II), and Hg(II) complexes of H_2L , this band shifts to lower frequency by a few cm^{-1} , indicating the participation of the anilide carbonyl oxygen in coordination. In the spectra of all the other complexes i.e., those of Fe(III), Co(II), Ni(II), and Zn(II) with H_2L , and all the complexes of H_2L' this band disappears and a new band is observed at ~ 1190 cm^{-1} . This may be due to the enolization of $-CH_2-C=O$ to $-CH=C-OH$ and subsequent coordination through the deprotonated oxygen.

The $\nu(C=O)$ (semicarbazide) band appears at 1645 and 1651 cm^{-1} in the spectra of H_2L and H_2L' , respectively. In the spectra of all the complexes this band is absent and a new band appears in the 1110–1140 cm^{-1} region. This may be due to the enolization of $=N-NH-C=O$ to $=N-N=C-OH$ during complex formation.

The $\nu(C=N)$ band appears at 1605 and 1593 cm^{-1} in the spectra of H_2L and H_2L' , respectively. In the spectra of all the complexes, this band shifts to lower frequency indicating the participation of the azomethine nitrogen in coordination.



METAL COMPLEXES OF SEMICARBAZONES

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Table 3. Significant IR Spectral Bands (cm^{-1}) of the Compounds and Their Assignments^a

Sl. No.	Compound	$\nu(\text{N-H})$	$\nu(\text{C=O})$ (Anilide)	$\nu(\text{C=O})$ (Semicarbazide)	$\nu(\text{C=N})$ (Anilide)	$\nu(\text{C-O})$ (Semicarbazide)	$\nu(\text{C-O})$ (Anilide)	$\nu(\text{C-O})$ (Semicarbazide)	$\nu(\text{N-N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
(1)	H ₂ L	3520 m, 3300 m, 3185 m, 3050 sh	1670 s	1645 s	1605 m	—	—	—	1010	—	—
(2)	[Mn(LH) ₂]	3339 s, 3169 w	1640 s	—	1578 m	—	1134 s	1022 s	530 m	466 m	466 m
(3)	[FeLCl(H ₂ O)] ₂	3420 b	—	—	1586 m	1173 s	1128 s	1020 s	549 m	480 m	480 m
(4)	[CoL(H ₂ O) ₃]	3420 sh, 3240 w, 3180 w	—	—	1598 s	1220 s	1132 s	1020 s	560 m	430 w	430 w
(5)	[NiL(H ₂ O) ₃]	3480 w, 3350 w, 3240 w	—	—	1574 s	1194 s	1134 s	1034 s	530 s	450 m	450 m
(6)	[Cu(LH) ₂]	3350 w, 3195 m	1650 s	—	1550 m	—	1105 s	1015 s	490 m	428 w	428 w
(7)	[ZnL(H ₂ O)]	3566 m, 3350 m, 3200 w, 3140 w	—	—	1580 m	1180 s	1143 s	1020 m	520 m	440 m	440 m
(8)	[Cd(LH) ₂]	3566 m, 3308 m, 3160 w	1646 s	—	1576 s	—	1128 s	1028 s	530 m	457 m	457 m
(9)	[Hg(LH) ₂]	3640 w, 3400 m, 3200 w, 3180 sh	1655 s	—	1566 m	—	1119 s	1020 s	549m	480 m	480 m
(10)	H ₂ L'	3449 s, 3289 m, 3180 m, 3080 sh	1692s	1651 s	1593 s	—	—	—	1005 s	—	—
(11)	[MnL'(H ₂ O) ₃]	3640–3050 b	—	—	1576 m	1196 m	1117 s	1034 s	559 s	467 m	467 m
(12)	[CoL'(H ₂ O) ₃]	3650–3000 b	—	—	1560 s	1196 s	1132 s	1026 s	525 m	460 m	460 m
(13)	[NiL'(H ₂ O) ₃]	3650–3000 b	—	—	1570 s	1192 s	1136 s	1030 s	530 m	450 m	450 m
(14)	[CuL'(H ₂ O) ₃]	3600–3000 b	—	—	1573 s	1170 s	1111 m	1030 m	505 s	490 s	490 s
(15)	[ZnL'(H ₂ O)]	3600–3000 b	—	—	1578 s	1181 s	1134 m	1031 m	572 s	465 m	465 m
(16)	[CdL'(H ₂ O)]	3600–3000 b	—	—	1570 s	1192 m	1134 m	1024 m	520 m	462 m	462 m

^as = strong, m = medium, b = broad, w = weak, sh = shoulder.

The $\nu(\text{N-N})$ band of the free ligands (at 1010 and 1005 cm^{-1} for H_2L and $\text{H}_2\text{L}'$, respectively) undergoes a marked shift to higher frequency upon complex formation. This observation is also an indication of the participation of the azomethine nitrogen in coordination. The broad bands at $\sim 3500 \text{ cm}^{-1}$ together with medium ones at $\sim 870\text{--}950$ and $\sim 660 \text{ cm}^{-1}$ in the spectra of the Fe(III) , Co(II) , Ni(II) , and Zn(II) complexes of H_2L and all the complexes of $\text{H}_2\text{L}'$ may be assigned, respectively, to stretching, rocking and wagging modes of coordinated water molecules. The bands due to M-N and M-O stretching frequencies appear, respectively, at ~ 530 and $\sim 450 \text{ cm}^{-1}$ in the spectra of all the complexes.

^1H NMR Spectra

H_2L and Its Zn(II) Complex

The spectrum of the ligand, recorded in CDCl_3 (Table 4) shows a singlet at 7.92 and a doublet at 7.23–7.17 ppm. These may be assigned to NH and NH_2 protons, respectively. The symmetrical multiplet observed at 7.48–7.31 ppm may be assigned to aromatic protons. The singlets observed at 3.28, 3.08, and 1.83 ppm may be assigned to N-CH_3 , $\alpha\text{-CH}_2$, and $\omega\text{-CH}_3$ protons, respectively.

In the spectrum of the Zn(II) complex recorded in CDCl_3 , the NH proton signal is not observed. It is a clear evidence for the enolization of $=\text{N-NH-C=O}$ to $=\text{N-N=C-OH}$ during complex formation. The peaks due to aromatic, NH_2 , N-CH_3 , coordinated water, and $\omega\text{-CH}_3$ protons are observed at 7.48–7.33 (m), 7.23–7.17 (d), 3.29 (s), 3.00 (s), and 1.82 (s) ppm, respectively. The signal due to $\alpha\text{-CH}_2$ protons, which is observed as a singlet at 3.09 ppm in the ligand spectrum, is shifted to 7.65 ppm. This may be due to the enolization of $-\text{CH}_2\text{-C=O}$ to $-\text{CH=C-OH}$ during complex formation.

$\text{H}_2\text{L}'$ and Its Zn(II) Complex

The ligand spectrum, recorded in CDCl_3 shows a singlet at 7.95 and a doublet at 7.20–7.16 ppm. These peaks may be due to NH and NH_2 protons, respectively. The symmetrical multiplet at 7.47–7.33 ppm may be assigned to aromatic protons. The quartet at 3.79–3.72 and triplet at 1.15–1.10 ppm are due to *N*-ethyl CH_2 and *N*-ethyl CH_3 protons, respectively. The singlets observed at 3.02 and 1.81 ppm may be due to $\alpha\text{-CH}_2$ and $\omega\text{-CH}_3$ protons, respectively.

In the spectrum of the Zn(II) complex recorded in DMSO, the absence of a peak at 7.95 ppm is a clear evidence for the enolization of $=\text{N-NH-C=O}$ to $=\text{N-N=C-OH}$ during complex formation. A multiplet observed in the region 7.54–7.26, a doublet at 7.20–7.17, a quartet at 3.61–3.53, a singlet at 2.07, and a triplet at 1.16–1.12 ppm may be assigned to aromatic, NH_2 , *N*-ethyl CH_2 ,



Table 4. Significant ^1H NMR Spectral Assignments of H_2L and $\text{H}_2\text{L}'$ and Their $\text{Zn}(\text{II})$ Complexes^a

Compound	δ (ppm)	Proton
(H_2L)	7.92 (1H, s)	NH
	7.48–7.31 (5H, m)	Aromatic
	7.23–7.17 (2H, 6.78 Hz)	NH_2
	3.28 (3H, s)	$\text{N}-\text{CH}_3$
	3.08 (2H, s)	$\alpha-\text{CH}_2$
	1.83 (3H, s)	$\omega-\text{CH}_3$
$[\text{ZnL}(\text{H}_2\text{O})]$	7.48–7.33 (5H, m)	Aromatic
	7.23–7.17 (2H, 6.96 Hz)	NH_2
	7.65 (1H, s)	$\alpha-\text{CH}$
	3.28 (3H, s)	$\text{N}-\text{CH}_3$
	3.00 (2H, s)	Coordinated water
	1.82 (3H, s)	$\alpha-\text{CH}_3$
$(\text{H}_2\text{L}')$	7.95	NH
	7.47–7.33 (5H, m)	Aromatic
	7.20–7.16 (2H, d, 6.78 Hz)	NH_2
	3.79–3.72 (2H, q, 7.14 Hz)	<i>N</i> -ethyl CH_2
	3.02 (2H, s)	$\alpha-\text{CH}_2$
	1.81 (3H, s)	$\omega-\text{CH}_3$
$[\text{ZnL}'(\text{H}_2\text{O})]$	1.15–1.10 (3H, t, 7.14 Hz)	<i>N</i> -ethyl CH_3
	11.18 (1H, s)	Hydrogen bonded NH
	7.54–7.26 (5H, m)	Aromatic
	7.20–7.17 (2H, d, 7.31 Hz)	NH_2
	3.61–3.53 (2H, q, 6.96 Hz)	<i>N</i> -ethyl CH_2
	2.69 (2H, s)	Coordinated water
	2.07 (3H, s)	$\omega-\text{CH}_3$
	1.16–1.12 (3H, t, 6.96 Hz)	<i>N</i> -ethyl CH_3

^as = singlet, m = multiplet, d = doublet, t = triplet, q = quartet.

$\omega-\text{CH}_3$, and *N*-ethyl CH_3 protons, respectively. The new peaks observed at 5.54 and 2.69 ppm may be assigned to $\alpha-\text{CH}$, formed as a result of enolization of $-\text{CH}_2-\text{C}=\text{O}$ to $-\text{CH}=\text{C}-\text{OH}$, and protons of coordinated water molecule, respectively.

Thermal Decomposition Studies

The thermal analysis data of the complexes of H_2L are summarized in Table 5. The $\text{Mn}(\text{II})$ complex follows a two-step degradation pattern. In the first step, loss of a ligand molecule takes place and the second stage of decomposition



Table 5. Thermal Analysis Data of the Complexes of H_2L

Compound	Decomposition Stage	Decomposition Temp. range ($^{\circ}C$)	Mass-loss % from			Reaction
			TG	Independent Pyrolysis	Theoretical	
$[Mn(LH)_2]$	1	110–280	45	–	45.18	$[Mn(LH)_2] \rightarrow Mn(LH)$
	2	270–350	83.5	84	84.17	$[Mn(LH)_2] \rightarrow MnO_2$
$[CoL(H_2O)_3]$	1	130–180	15	–	15.05	$[CoL(H_2O)_3] \rightarrow CoL$
	2	220–280	34	–	34.55	$[CoL(H_2O)_3] \rightarrow Co(L)_{0.5}$
	3	280–420	78	77.8	77.65	$[CoL(H_2O)_3] \rightarrow Co_3O_4$
$[NiL(H_2O)_3]$	1	110–175	16	–	15.06	$[NiL(H_2O)_3] \rightarrow NiL$
	2	250–400	80	79	79.19	$[NiL(H_2O)_3] \rightarrow NiO$
$[Cu(LH)_2]$	1	180–320	85	85	85.74	$[Cu(LH)_2] \rightarrow CuO$

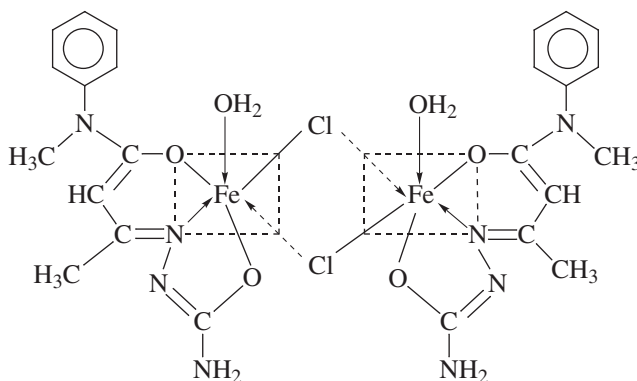


Figure 2. Structure of Fe(III) complex of H_2L .

leads to the formation of MnO_2 . The Co(II) complex follows a three-staged decomposition pattern. In the first stage, the loss of 3 water molecules takes place in the temperature range of 130–180°C, indicating their coordinated nature. In the second stage, the loss of half of the ligand molecule occurs. The third stage of decomposition leads to the formation of Co_3O_4 .

The Ni(II) complex follows a two-step decomposition. In the first step, the loss of the three coordinated water molecules occurs in the temperature range of 110–175°C. The second stage of decomposition leads to the formation of NiO. In the case of the Cu(II) complex, only a single stage of decomposition occurs leading to the formation of CuO.

The analytical and physico-chemical studies show that the Mn(II) and Cu(II) complex of H_2L has octahedral geometry. The Co(II) and Ni(II) complexes of H_2L and the Mn(II), Co(II), Ni(II), and Cu(II) complexes of H_2L' are found to have distorted-octahedral geometry. The Fe(III) complex of H_2L is found to be 6-coordinate dimeric with a chloro bridged distorted octahedral structure (Fig. 2). The Zn(II) complexes and the Cd(II) complex of H_2L' are 4-coordinate, whereas the Cd(II) and Hg(II) complexes of H_2L are 6-coordinate.

EXPERIMENTAL

All the chemicals used in the present investigation were of BDH AnalaR quality. The N-substituted acetoacetanilides were prepared by the reported methods (11).



Preparation of *N*-Substituted Acetoacetanilides

N-methyl- and *N*-ethylacetoacetanilides were obtained as their sodium derivatives. *N*-alkylaniline (0.1 mol) and ethylacetoacetate (11.4 mL, 0.1 mol) were taken in a round-bottomed flask and refluxed on a sand bath at the boiling temperature for 15 min. The oily product was cooled and treated with 2N NaOH (200 mL). The white product that formed was filtered, washed successively with diethyl ether and petroleum ether (60–80°C). The product was recrystallised from ethanol and dried in a desiccator under reduced pressure over anhydrous calcium chloride. Sodium *N*-methylacetoacetanilide: yield, 14.98 g (70%); m.p. 85°C, sodium *N*-ethylacetoacetanilide: yield, 14.62 g (65%); m.p. 180°C. These sodium derivatives were used for the preparation of the ligands.

Preparation of the Ligands

The semicarbazide (0.55 g, 0.05 mol) in the minimum amount of water was added to sodium *N*-methyl- or *N*-ethylacetoacetanilide (0.05 mol) in ethanol-water (2:1 in the case of *N*-methyl acetoacetanilide and 4:1 in the case of *N*-ethylacetoacetanilide) (150 mL) with stirring. The reaction mixture was kept stirring for 2 h and allowed to stand for one day at room temperature. The white crystalline product formed was filtered, washed several times with water, and dried in a desiccator over anhydrous calcium chloride. The product was recrystallised from methanol.

Preparation of the Complexes

A methanolic solution (20 mL) of metal acetate (0.005 mol) was added to an ethanolic solution (20 mL) of H_2L or H_2L' (0.005 mol) and the mixture was refluxed for 2 h on a water bath. The solution was cooled and evaporated at room temperature to reduce the volume to 20 mL. The solid complex that formed was filtered off, washed several times with water and finally with methanol. It was dried under reduced pressure over anhydrous calcium chloride. In the case of the Mn(II), Cu(II), Cd(II), and Hg(II) complexes of H_2L a 1:2 molar ratio of metal to ligand was maintained for better yields.

Analytical Methods

The complexes were analysed for their metal contents by standard methods. Chlorine was determined by Volhard's method after sodium carbonate fusion



and dissolving in dilute nitric acid (12). Carbon, hydrogen and nitrogen were determined by microanalysis using a Hitachi CHN-O rapid analyser. The molar conductances of the complexes were determined using 10^{-3} M solutions in DMSO at $28 \pm 3^\circ\text{C}$ on a direct-reading 305 Systronic conductivity bridge and a dip-type cell (cell constant = 1.083) calibrated with AnalaR potassium chloride. The magnetic susceptibilities were determined at room temperature by the Gouy method using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as a calibrant and diamagnetic corrections were made using Pascal constants (13). The electronic spectra of the compounds were recorded on a Shimadzu UV-Vis-1601 spectrophotometer using the Nujol mull technique (14). The IR spectra were recorded using KBr discs on a 8101 Shimadzu FTIR spectrophotometer. The ^1H NMR spectra of the ligands and the Zn(II) complexes were recorded in CDCl_3 or $\text{DMSO}-d_6$ on a Varian 300 NMR spectrometer. Thermal analyses were carried out on a TGS-I Perkin Elmer thermobalance with the following operational characteristics: heating rate, $10^\circ \text{ min}^{-1}$; sample size, 2–10 mg; atmosphere, static air; crucible, platinum.

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