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Synthesis, Characterization and Thermal Studies of Thiosemicarbazones of N-methyl- and N-ethylacetoacetanilide

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**SYNTHESIS, CHARACTERIZATION AND THERMAL STUDIES OF
THIOSEMICARBAZONES OF N-METHYL- AND
N-ETHYLACETOACETANILIDE**

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ABSTRACT

Fourteen new complexes of several typical transition metal ions with two multidentate ligands, thiosemicarbazones of N-methyl- and N-ethylacetoacetanilide, have been synthesized. These complexes have the general formulae $[MX_3]$, $[MY_2]$, $[MY]$, $[MZ(H_2O)_3]$, $[MZ(OH)(H_2O)]_2$ or $[MZ(H_2O)]$, where $M = Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II)$ or $Ag(I)$ and $X =$ bidentate monoanion, $Y =$ tridentate monoanion and $Z =$ tridentate dianion of the ligands. They have been characterized by elemental analyses, molar conductance and magnetic susceptibility measurements as well as electronic, infrared and 1H NMR spectral studies and thermogravimetric studies.

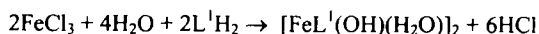
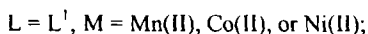
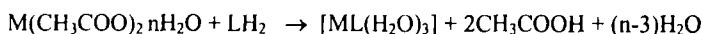
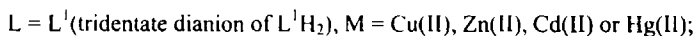
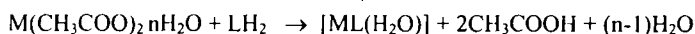
INTRODUCTION

Detailed investigations of the coordination chemistry of amides and anilides are fascinating in view of their similarity to peptides and proteins, which are essential

constituents of life. As ligands, β -diketoanilides have not received the kind of attention that they really deserve. Detailed investigation on synthetic, structural and biological aspects of metal complexes of thiosemicarbazone derived from β -diketones and related compounds are rare¹⁻³. Our earlier investigations on acetoacetanilide thiosemicarbazones and their metal complexes show that they possess antitumour activity⁴. Hence, in a programme to investigate the donor properties of Schiff bases of substituted acetoacetanilides, the synthesis and characterization of thiosemicarbazones of N-methyl- and N-ethylacetoacetanilide, L^1H_2 and L^2H_2 , respectively, (Fig. 1) and their complexes with several typical transition metal ions are presented here.

RESULTS AND DISCUSSION

All the complexes are coloured, non-hygroscopic, air- and photostable. Generally, they are soluble in ethanol, methanol and DMSO. The electrical conductance measured in DMSO and the calculated molar conductance values indicate that they are non-electrolytes. The analytical data of the L^1H_2 complexes (Table I) indicate the following stoichiometries, $[ML^1(H_2O)_3]$, where $M = Mn(II), Co(II)$ or $Ni(II)$; $[ML^1(H_2O)]$, where $M = Cu(II), Zn(II), Cd(II)$ or $Hg(II)$; $[FeL^1(OH)(H_2O)_2]$ and $[Ag(L^1H)]$, where $L^1 =$ tridentate dianion and $L^1H =$ tridentate monoanion of the ligand L^1H_2 . The analytical data (Table I) of the L^2H_2 complexes correspond to the formulae $[Fe(L^2H)_3]$; $[Co(L^2H)_2]$; $[ML^2(H_2O)_3]$, where $M = Ni(II)$ or $Cu(II)$ and $[Zn L^2(H_2O)]$, where $L^2H =$ bidentate- or tridentate monoanion and $L^2 =$ tridentate dianion of the ligand L^2H_2 . The formation of the complexes may be represented by the following equations:



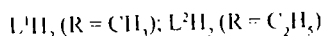
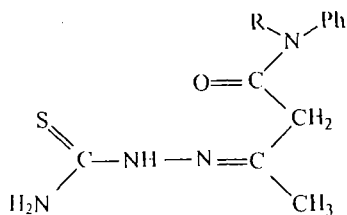
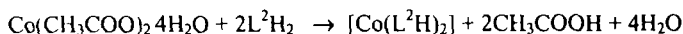
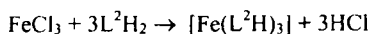
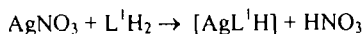


Fig. 1. Structures of the Ligands



Magnetic Behaviour

The magnetic moments (Table I) of the Mn(II), Co(II) and Ni(II) complexes are found in the range as expected for octahedral complexes. Both Fe(III) complexes register magnetic moment values which are lower than the spin-only value expected for a high-spin d^5 state. The appreciably low value (3.86 B.M.) in the case of $[FeL^1(OH)(H_2O)_2]$ may be due to its binuclear configuration facilitating antiferromagnetic exchange interaction⁵. However, the slightly lower value (4.87 B.M.) of $[Fe(L^2H)_3]$ may be due to its distorted-octahedral geometry. The Cu(II) complexes, $[CuL^1H_2O]$ and $[CuL^2(H_2O)_3]$, register magnetic moments of 1.73 and 2.12 B.M., respectively. This is diagnostic of a d^9 system with one unpaired electron and without any antiferromagnetic exchange interaction⁶.

Electronic Spectra

The electronic spectral bands of the complexes and their probable assignments are given in the Table II. The Fe(III) complexes register bands at $\sim 28,700$ and $\sim 20,000$ cm^{-1} . These may be assigned, respectively, to ${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ transitions of a high-spin d^5 Fe(III) complex⁷. The Co(II) complexes register an intense

TABLE I
Colour, Analytical Data, Yields and Magnetic Moments of the Compounds

Sl. No	Compound	Empirical Formula & Molecular weight	Colour	Decomp. Temp. °C	Yield %	M	C	H	N	S	μ_{eff}
(1)	$\text{L} \cdot \text{H}_2$	$\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_8$ 264.13	Pale yellow	152	52	--	54.20 (54.51)	5.90 (6.11)	21.05 (21.20)	12.08 (12.11)	--
(2)	$[\text{MnL}^1(\text{H}_2\text{O})_3]$	$\text{MnC}_{12}\text{H}_{30}\text{N}_4\text{O}_{15}$ 371.10	Cream	195	48	15.00 (14.80)	38.30 (38.80)	5.29 (5.43)	15.10 (15.09)	8.43 (8.62)	5.61
(3)	$[\text{FeL}^1(\text{OH}(\text{H}_2\text{O}))_2]$	$\text{Fe}_2\text{C}_{24}\text{H}_{34}\text{N}_8\text{O}_{25}$ 705.98	Brown	180	55	15.45 (15.82)	40.24 (40.79)	4.64 (4.85)	15.46 (15.86)	8.96 (9.06)	3.86
(4)	$[\text{CoL}^1(\text{H}_2\text{O})_3]$	$\text{CoC}_{12}\text{H}_{20}\text{N}_4\text{O}_4\text{S}$ 375.09	Brown	225	80	16.04 (15.71)	37.94 (38.39)	5.10 (5.37)	14.43 (14.93)	8.28 (8.53)	4.75
(5)	$[\text{NiL}^1(\text{H}_2\text{O})_3]$	$\text{NiC}_{12}\text{H}_{20}\text{N}_4\text{O}_4\text{S}$ 374.87	Pale green	275	80	16.20 (15.66)	38.08 (38.41)	5.24 (5.38)	14.41 (14.94)	8.49 (8.54)	3.24
(6)	$[\text{CuL}^1(\text{H}_2\text{O})]$	$\text{CuC}_{12}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$ 343.67	Olive green	182	75	18.01 (18.49)	41.89 (41.90)	4.40 (4.69)	16.24 (16.29)	9.28 (9.31)	1.73
(7)	$[\text{ZnL}^1(\text{H}_2\text{O})]$	$\text{ZnC}_{12}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$ 345.49	White	220	75	18.64 (18.92)	40.94 (41.64)	4.42 (4.66)	16.34 (16.21)	9.18 (9.26)	--
(8)	$[\text{CdL}^1(\text{H}_2\text{O})]$	$\text{CdC}_{12}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$ 392.53	Pale yellow	215	72	28.44 (28.63)	36.24 (36.68)	4.04 (4.10)	14.20 (14.26)	8.02 (8.15)	--
(9)	$[\text{HgL}^1(\text{H}_2\text{O})]$	$\text{HgC}_{12}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$ 480.17	Pale ash	194	78	41.24 (41.73)	29.30 (29.99)	3.28 (3.35)	11.24 (11.64)	6.28 (6.65)	--
(10)	$[\text{Ag}(\text{L}^1\text{H})]$	$\text{AgC}_{12}\text{H}_{15}\text{N}_4\text{O}_8$ 400.12	Pale ash	160	55	29.04 (29.10)	38.78 (38.80)	4.02 (4.07)	15.14 (15.08)	8.62 (8.62)	--
(11)	$\text{L} \cdot \text{H}_2$	$\text{C}_{13}\text{H}_{18}\text{N}_4\text{O}_8$ 278.14	Pale yellow	176	45	--	55.92 (56.08)	6.46 (6.52)	20.24 (20.13)	11.46 (11.50)	--
(12)	$[\text{FeL}^2(\text{H})_3]$	$\text{FeC}_{39}\text{H}_{51}\text{N}_{12}\text{O}_{51}\text{S}_5$ 887.25	Brown	160	70	6.22 (6.29)	52.68 (52.75)	5.68 (5.79)	18.72 (18.93)	10.47 (10.82)	4.87
(13)	$[\text{CoL}^2(\text{H}_2)]$	$\text{CoC}_{24}\text{H}_{34}\text{N}_8\text{O}_2$ 613.20	Brown	250	85	9.64 (9.61)	50.71 (50.88)	5.62 (5.59)	18.14 (18.26)	10.43 (10.44)	4.77
(14)	$[\text{NiL}^2(\text{H}_2\text{O})_3]$	$\text{NiC}_{13}\text{H}_{21}\text{N}_4\text{O}_4\text{S}$ 388.88	Greenish brown	300	82	14.60 (15.09)	38.40 (40.11)	5.76 (5.70)	14.28 (14.39)	16.27 (16.45)	2.88
(15)	$[\text{CuL}^2(\text{H}_2\text{O})_3]$	$\text{CuC}_{13}\text{H}_{21}\text{N}_4\text{O}_4\text{S}$ 393.72	Pale brown	187	80	15.76 (16.14)	39.46 (39.62)	5.34 (5.63)	14.66 (14.22)	8.16 (8.13)	2.12
(16)	$[\text{ZnL}^2\text{H}_2\text{O}]$	$\text{ZnC}_{13}\text{H}_{18}\text{N}_4\text{O}_8\text{S}$ 359.52	Pale brown	296	70	18.98 (18.18)	43.14 (43.26)	5.14 (5.03)	15.46 (15.53)	8.68 (8.87)	--

TABLE II

Electronic Spectral Data of Complexes and Assignments^a

Sl. No	Complex	Bands cm ⁻¹	Assignment	Geometry
(3)	[FeL ^I (OH)(H ₂ O)] ₂	28653 20000	⁶ A _{1g} → ⁴ T _{2g} (D) ⁶ A _{1g} → ⁴ T _{2g} (G)	Distorted-octahedral
(4)	[CoL ^I (H ₂ O) ₃]	24875 16000 br 9615 w	⁴ T _{1g} (F)→ ⁴ T _{1g} (P) ⁴ T _{1g} (F)→ ⁴ A _{2g} (F) ⁴ T _{1g} (F)→ ⁴ T _{2g} (F)	Distorted-octahedral
(5)	[NiL ^I (H ₂ O) ₃]	25316 15873 br 9775 w	³ A _{2g} (F)→ ³ T _{1g} (P) ³ A _{2g} (F)→ ³ T _{1g} (F) ³ A _{2g} (F)→ ³ T _{2g} (F)	Distorted-octahedral
(6)	[CuL ^I (H ₂ O)]	23980 17482 br	² B _{1g} → ² B _{2g} ² B _{1g} → ² A _{1g}	Square-planar
(12)	[Fe(L ² H) ₃]	28735 19723 br	⁶ A _{1g} → ⁴ T _{2g} (D) ⁶ A _{1g} → ⁴ T _{2g} (G)	Distorted-octahedral
(13)	[Co(L ² H) ₂]	20202 17094 br 9708 w	⁴ T _{1g} (F)→ ⁴ T _{1g} (P) ⁴ T _{1g} (F)→ ⁴ A _{2g} (F) ⁴ T _{1g} (F)→ ⁴ T _{2g} (F)	Octahedral
(14)	[NiL ² (H ₂ O) ₃]	24390 15625 br 9689 w	³ A _{2g} (F)→ ³ T _{1g} (P) ³ A _{2g} (F)→ ³ T _{1g} (F) ³ A _{2g} (F)→ ³ T _{2g} (F)	Distorted-octahedral
(15)	[CuL ² (H ₂ O) ₃]	24330 15220 br	² B _{1g} → ² E _g ² B _{1g} → ² A _{1g}	Distorted-octahedral

^a br = broad, w = weak.

band at ~24,000-20,000, a broad one at ~17,100 – 16,000 and a weak one at ~9,700 cm⁻¹. These may be assigned, respectively, to ⁴T_{1g}(F)→⁴T_{1g}(P), ⁴T_{1g}(F)→⁴A_{2g}(F) and ⁴T_{1g}(F)→⁴T_{2g}(F) transitions of an octahedral Co(II) complex. The Ni(II) complexes register a band at ~25,000, a broad one at ~15,700 and a weak one at ~9,700 cm⁻¹. These may be assigned, respectively, to ³A_{2g}(F)→³T_{1g}(P), ³A_{2g}(F)→³T_{1g}(F) and ³A_{2g}(F)→³T_{2g}(F) transitions of a 6-coordinated octahedral Ni(II) ion. The Cu(II) complexes investigated here register bands at ~24,000 and ~17,000-15,000 cm⁻¹. These

may be assigned, respectively, to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ or ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions of a square-planar or distorted-octahedral Cu(II) complex.

Infrared Spectra

The important infrared spectral bands of the ligands and their complexes are given in the Tables III and IV. The bands observed at $\sim 3300\text{ cm}^{-1}$ may be assigned to NH and NH_2 stretching. In the spectra of the ligands, the absence of bands at 2500 cm^{-1} indicate their thio-keto nature in the solid state⁸. The $\nu(\text{C=O})$ (anilide) is observed at 1700 cm^{-1} in the spectrum of L^1H_2 and at 1650 cm^{-1} in the L^2H_2 spectrum. In the spectra of the complexes, except those of $[\text{Ag}(\text{L}^1\text{H})]$, $[\text{Fe}(\text{L}^2\text{H})_3]$ and $[\text{Co}(\text{L}^2\text{H})_2]$, the $\nu(\text{C=O})$ bands disappear and at the same time new bands are observed at $\sim 1180\text{ cm}^{-1}$. This may be due to the enolization of $-\text{CH}_2-\text{C=O}$ to $-\text{CH=C-OH}$ and subsequent coordination through a deprotonated oxygen. In the spectra of the Ag(I) and Co(II) complexes mentioned above, a shift of this band to lower frequency region by 70 cm^{-1} and 50 cm^{-1} , respectively, are observed, indicating the coordination of this carbonyl oxygen without enolization. In the spectrum of $[\text{Fe}(\text{L}^2\text{H})_3]$, the $\nu(\text{C=O})$ band has no change, indicating the non-participation of this carbonyl oxygen in coordination.

The $\nu(\text{C=N})$ bands are observed at 1590 and 1610 cm^{-1} in the spectra of L^1H_2 and L^2H_2 , respectively. In the spectra of all the complexes, a shift of this band to lower frequency by $\sim 5 - 50\text{ cm}^{-1}$ is observed. This indicates the participation of the azomethine nitrogen atom in coordination. The $\nu(\text{C=S})$ bands are observed as strong absorptions at 1095 and 1082 cm^{-1} in the spectra of L^1H_2 and L^2H_2 , respectively. These bands undergo considerable change during complex formation. In the spectra of all the complexes, this band disappears and a new band appears at $700-820\text{ cm}^{-1}$. This may be assigned to $\nu(\text{C-S})$ [with a little contribution from $\nu(\text{C=N})$] which arises as a result of enolization of the $-\text{NH-C=S}$ group in the ligand to $-\text{N=C-SH}$ in the presence of metal ions. Subsequent coordination of the metal ion through the deprotonated sulphur may take place. The presence of coordinated water molecules in some of the complexes is indicated by the presence of new bands around 900 and 650 cm^{-1} . Newly formed bands at ~ 550 and $\sim 430\text{ cm}^{-1}$ in the spectra of the complexes may be assigned⁹ to $\nu(\text{M-N})$ and $\nu(\text{M-O})$, respectively.

TABLE III
Significant Infrared Spectral Bands* (cm⁻¹) of L'H₂ and its Components.

Sl No	Compound	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C=S})$	$\nu(\text{C-O})$	$\nu(\text{N-N})$	$\nu(\text{C-S})^+$ $\pi(\text{C-N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
(1)	L'H ₂	3422 m, 3350 m, 3220 m, 3480 w, 3660 m	1700 m	1590 m	1095 s	--	995 m	--	--	--
(2)	[MnL'(H ₂ O) ₃]	3260 m, 3216 w, 3100 w	--	1540 m	--	1185 m	1016 m	768 m	550 m	448 m
(3)	[FeL'(OH)(H ₂ O)] ₂	3568 m, 3524 m, 3439 b, 3367 m	--	1563 m	--	1178 s	1022 m	821 m	517 w	460 w
(4)	[CoL'(H ₂ O) ₃]	3440 b, 3140 m	--	1580 m	--	1190 s	1015 s	810 m	560 sh	430 m
(5)	[NiL'(H ₂ O) ₃]	3420 sh, 3390 m, 3110 m, 3050 sh	--	1570 m	--	1187 s	1041 s	750 m	530 m	430 m
(6)	[CuL'(H ₂ O)]	3420 sh, 3300 m, 3180 m	--	1570 m	--	1190 s	1015 m	820 m	580 m	430 w
(7)	[ZnL'(H ₂ O)]	3450 w, 3300 b	--	1577 m	--	1175 s	1024 m	762 m	561 s	425 w
(8)	[Cd L'(H ₂ O)]	3450 w, 3300 b	--	1575 m	--	1192 s	1013 m	810 s	567 w	460 sh
(9)	[HgL'(H ₂ O)]	3400 m, 3290 b, 3190 w, 3020 w	--	1549 s	--	1177 s	1030 m	787 s	524 s	409 m
(10)	[Ag(L'H)]	3410 m, 3330 w, 3120 w, 3080 m	1630s	1570 m	--	--	1024 m	790 s	560 s	416 m

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

TABLE IV
Significant Infrared Spectral Bands^a (cm⁻¹) of EacTCH₂ and its Components

Sl No	Compound	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C=S})$	$\nu(\text{C-O})$	$\nu(\text{N-N})$	$\nu(\text{C-S})+\pi(\text{C-N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
11	L ² H ₂	3430 m, 3280 w 3210 m, 3175 m, 3080 sh	1650 s	1610 s	1082 s	--	1003 s	--	--	--
12	[Fe(L ² H) ₃]	3426 s, 3269 m, 3208 w, 3190 w	1650 s	1595 s	--	--	1024 m	812 s	515 m	--
13	[Co(L ² H) ₂]	3300 b, 3180 b, 3080 sh	1630 s	1557 s	--	--	1020 m	868 s	518 m	430 m
14	[NiL ² (H ₂ O) ₃]	3650-3000 b	--	1590 s	--	1180 s	1020 s	860 m	520 m	430 w
15	[CuL ² (H ₂ O) ₃]	3420 m, 3293 s, 3177 s	--	1593 s	--	1185 s	1007 s	835 s	540 m	435 m
16	[ZnL ² H ₂ O]	3600-3000 b	--	1605 s	--	1192 s	1011 s	837s	515 m	425 m

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

TABLE V

Significant ^1H NMR Spectral Assignments^a of L^1H_2 , L^2H_2 and their $\text{Zn}(\text{II})$ Complexes

Compound	δ (ppm)	Proton
L^1H_2	8.62 (^1H , s)	NH
	7.46 (^5H , m)	Aromatic
	7.18 (^2H , s)	NH_2
	3.27 (^3H , s)	N- CH_3
	3.05 (^2H , s)	α - CH_2
	1.86 (^3H , s)	ω - CH_3
$[\text{ZnL}^1(\text{H}_2\text{O})]$	7.30 (^5H , m)	Aromatic
	6.61 (^2H , d, $J = 15$ Hz)	NH_2
	5.12 (^1H , s)	α -CH
	3.32 (^3H , s)	N- CH_3
	2.65 (^2H , s)	Coordinated water
	1.95 (^3H , s)	ω - CH_3
L^2H_2	8.54 (^1H , s)	NH
	7.42 (^5H , m)	Aromatic
	7.16 (^2H , d, $J = 6.59$ Hz)	NH_2
	3.77 (^2H , q, $J = 7$ Hz)	N-ethyl CH_2
	3.07 (^2H , s)	α - CH_2
	1.90 (^3H , s)	ω - CH_3
	1.12 (^3H , t, $J = 7$ Hz)	N-ethyl CH_3
$[\text{ZnL}^2(\text{H}_2\text{O})]$	7.40 (^5H , m)	Aromatic & NH_2
	4.49 (^1H , s)	α -CH
	3.66 (^2H , q, $J = 7$ Hz)	N-ethyl CH_2
	2.80 (^2H , s)	Coordinated water
	1.91 (^3H , s)	ω - CH_3
	1.14 (^3H , t, $J = 7$ Hz)	N-ethyl CH_3

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

^1H NMR Spectra

The ^1H NMR spectra of L^1H_2 and its $\text{Zn}(\text{II})$ complex were recorded in DMSO. The ligand spectrum shows singlets (Table V) at 8.62 and 7.18 ppm. These peaks are assigned to NH and NH_2 protons, respectively¹⁰. The multiplet observed at 7.46 ppm are in the range expected for aromatic protons. The singlets observed at 3.27, 3.05 and

1.86 ppm may be assigned to N-CH₃, α-CH₂ and ω-CH₃ protons, respectively. In the spectrum of the Zn(II) complex the most important observation is the disappearance of the signal due to the NH proton, which is an indication of the enolization of =N-NH-C=S to =N-N=C-SH during complex formation. The resonances observed at 7.30, 6.61, 3.32, 2.65 and 1.95 ppm may be assigned to aromatic, NH₂, N-CH₃, coordinated water and ω-CH₃ proton, respectively. The peak due to α-CH₂ protons is not observed in the spectrum of the Zn(II) complex. However, a new peak observed at 5.12 ppm in the spectrum of the complex may be assigned to the α-CH proton formed by the enolization of -CH₂-C=O to -CH=C-OH during coordination with the metal ion.

The ¹H NMR spectrum of L²H₂ shows a singlet (Table V) at 8.54 and a doublet at 7.16 ppm. These peaks may be assigned to NH and NH₂ protons, respectively. The symmetrical multiplet observed at 7.42 ppm are assigned to aromatic protons. A quartet observed at 3.77 and a triplet at 1.12 ppm may be assigned, respectively, to N-ethyl CH₂ and N-ethyl CH₃ protons. A singlet observed at 3.07 and 1.90 may be assigned, respectively, to α-CH₂ and ω-CH₃ protons. In the spectrum of the Zn(II) complex, the peak due to the NH proton disappears. This may be due to the enolization of =N-NH-C=S to =N-N=C-SH during complex formation. The multiplet observed at 7.40 ppm may be due to aromatic protons. The peaks due to NH₂ protons might have been merged in the aromatic region. The peaks observed at 3.66, 1.91 and 1.14 ppm may be due to N-ethyl CH₂, ω-CH₃ and N-ethyl CH₃ protons, respectively. The new peaks observed at 4.49 and 2.80 ppm may be assigned to α-CH formed due to enolization of -CH₂-C=O to -CH=C-OH and the coordinated water, respectively.

Thermal Decomposition Studies

The thermal analyses data of the Mn(II), Co(II), and Cu(II) complexes of L¹H₂ are summarized in Table VI. The composition of the intermediates and final products are fixed by the observed mass loss in the TG and independent pyrolysis experiments as well as by chemical analyses. The salient features of the thermal analyses of the complexes are as follows.

The Mn(II) complex follows a three-step decomposition pattern. In the first stage, the loss of three water molecules takes place at a temperature above 120° C,

TABLE VI
Thermal Analysis Data of Complexes of L'H₂

Compound	Decomposition		Mass loss % from			Decomposition pattern
	Stage	Temp. range	TG	Independent pyrolysis	Calcd.	
[MnL'(H ₂ O) ₃]	1	110-180	14	--	14.56	[MnL'(H ₂ O) ₃] → MnL
	2	190-420	64.50	--	64.42	[MnL'(H ₂ O) ₃] → Mn(L) _{0.5}
	3	460-670	76	76.43	76.58	[MnL'(H ₂ O) ₃] → MnO ₂
[CoL'(H ₂ O) ₃]	1	110-180	14	--	14.40	[CoL'(H ₂ O) ₃] → CoL
	2	180-660	78	78.50	78.61	[CoL'(H ₂ O) ₃] → Co ₃ O ₄
[CuL'(H ₂ O)]	1	110-170	5	--	5.24	[CuL'(H ₂ O)] → CuL
	2	200-500	57	--	57.24	[CuL'(H ₂ O)] → Cu(L) _{0.75}
	3	640-790	77	76.40	76.86	[CuL'(H ₂ O)] → CuO

indicating their coordinated nature. In the second stage, loss of half of the ligand molecule occurs. The third stage of decomposition leads to the formation of MnO_2 . The cobalt (II) complex follows a two-stage decomposition pattern. In the first step, loss of three water molecules occurs and the second step of decomposition leads to the formation of Co_3O_4 . The Cu(II) complex follows a three-stage decomposition. In the first stage, the loss of one molecule of water takes place. In the second stage three fourth of a ligand molecule is lost and the third step of decomposition leads to the formation of CuO .

On the basis of the above observations the complexes of Mn(II), Co(II) and Ni(II) are very likely 6-coordinate with octahedral or distorted-octahedral geometry. The Cu(II) complex of N-methylacetoacetanilide thiosemicarbazone (L^1H_2) is very likely 4-coordinate square-planar, whereas that of the N-ethyl derivative (L^2H_2) is 6-coordinate distorted-octahedral. All of the Zn(II), Cd(II) and Hg(II) complexes synthesized here are 4-coordinate and, therefore, may be tetrahedral in geometry (Fig. 2). The Ag(I) complex is 3-coordinate likely with trigonal-planar geometry. The Fe(III) complex of N-methylacetoacetanilide thiosemicarbazone (L^1H_2) is proposed to be 6-coordinate dimeric with a hydroxo bridged structure. However, the attempts for molecular weight determination failed due to the lack of sufficient solubility of this complex in common solvents at low temperature and also due to its immiscibility with molten camphor, diphenyl, etc. Hence we do not have a simple means for ascertaining its dimeric structure. The Fe (III) complex of N-ethyl derivative (L^2H_2) is proposed to be 6-coordinate with a distorted-octahedral geometry (Fig. 3).

EXPERIMENTAL

All chemicals used in the present investigation were of BDH AnalaR quality. The sodium derivatives of N-substituted acetoacetanilides were prepared by the reported methods¹¹.

Preparation of L^1H_2 and L^2H_2

Thiosemicarbazide in ethanol (0.05 mol, 150 mL) was added to sodium N-methyl or N-ethylacetoacetanilide (0.05 mol) in ethanol-water (2:1 in the case of N-

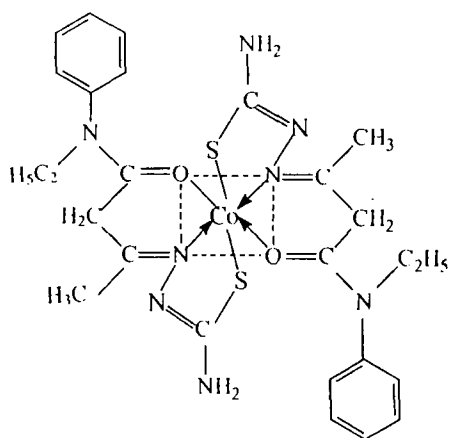
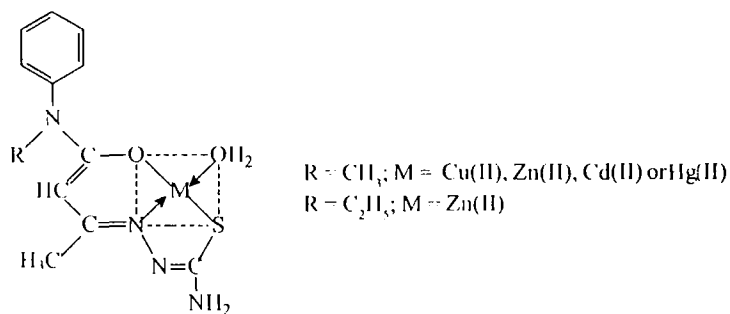
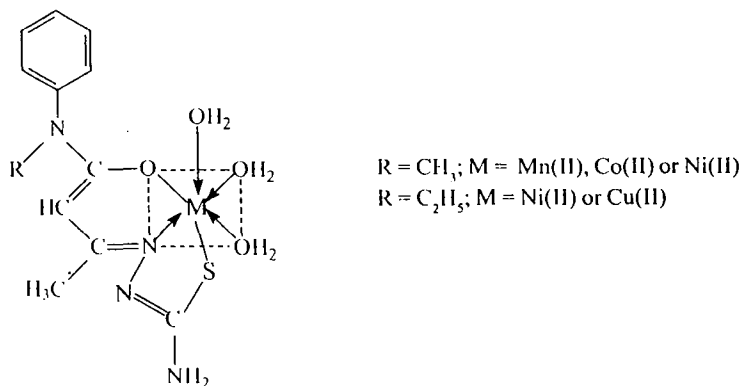


Fig. 2. Suggested Structures of the Complexes

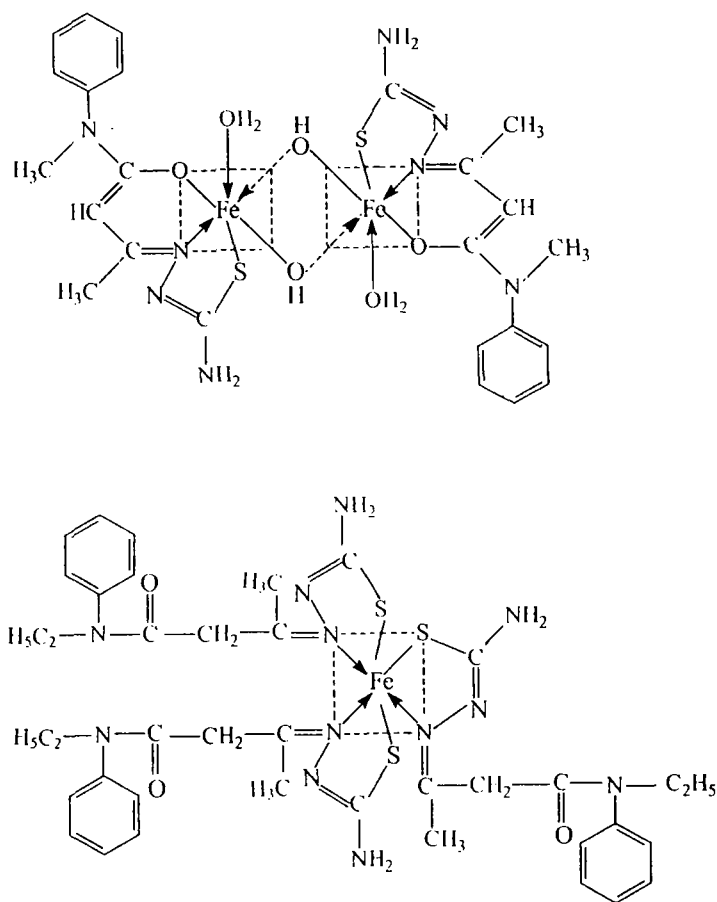


Fig. 3. Suggested Structures of the Fe(III) Complexes.

methyl derivative and 4:1 in the case of N-ethyl derivative) and refluxed for 2 h on a water bath. The resulting solution was evaporated to reduce the volume to 30 mL and stirred for 2 h. The pale yellow solid which formed was filtered off, washed several times with water and finally with methanol and dried in a desiccator over anhydrous calcium chloride. The products were recrystallized from methanol.

Preparation of the Complexes

A methanolic (20 mL) solution of the metal acetate (0.005 mol) was added slowly to a magnetically stirred hot ethanolic (25 mL) solution of the respective ligand (0.005 mol). Ferric chloride was used for the preparation of the Fe(III) complexes. The ligand to metal ratios of 1:3 and 1:2 provided better yields in the cases of the Fe(III) and Co(II) complexes of the N-ethyl derivative. The mixture was stirred for 2 h at room temperature. The solid complexes that separated out were filtered, washed thoroughly with water and finally with methanol. They were dried under reduced pressure over anhydrous calcium chloride.

Analytical Methods

The complexes were analysed for their metal content by standard methods¹². Carbon, hydrogen and nitrogen were determined by microanalysis using a Hitachi CHN-O rapid analyser. The sulfur and chlorine contents were determined gravimetrically as barium sulfate and silver chloride, respectively. The molar conductances of the complexes were determined using $\sim 10^{-3}$ M solutions in DMSO at $28 \pm 2^\circ$ C on a direct-reading Model 305 Systronic conductivity bridge and a dip type cell (cell constant = 1.083). The susceptibilities were determined at room temperature by the Gouy method using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as calibrant and diamagnetic corrections were made using Pascal constants¹³. The electronic spectra of the compounds were recorded on a UV-Vis-1601 Shimadzu spectrophotometer using the Nujol mull technique¹⁴. The IR spectra were recorded on a FTIR 8101 Shimadzu spectrophotometer in the range $4000\text{--}400\text{ cm}^{-1}$ by using KBr discs. The ^1H NMR spectra were recorded on a Varian 300 NMR spectrometer using CDCl_3 or DMSO-d_6 as solvents. Thin layer chromatographic analyses were carried out on silica gel plates using ethylacetate-acetone (1:1) solvent.

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