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Synthesis and Characterization of Manganese(II), Nickel(II) and Copper(II) Complexes of 4-(Arylideneamino)-3-Mercapto-6-Methyl-1,2,4-Triazin-5(4H)-Ones

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SYNTHESIS AND CHARACTERIZATION OF MANGANESE(II), NICKEL(II) AND COPPER(II) COMPLEXES OF 4-(ARYLIDENEAMINO)-3-MERCAPTO-6-METHYL-1,2,4-TRIAZIN-5(4*H*)-ONES

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ABSTRACT

Manganese(II), nickel(II) and copper(II) complexes of 4-(2,6-dichlorobenzylideneamino)-3-mercapto-6-methyl-1,2,4-triazin-5(4*H*)-one (HL^1) and 4-(cinnamylideneamino)-3-mercapto-6-methyl-1,2,4-triazin-5(4*H*)-one (HL^2) have been synthesized and characterized. The IR spectra indicate that both HL^1 and HL^2 act as neutral or monobasic bidentate ligands, coordinating to metal ions *via* azomethine-N and either carbonyl-O or (thiolo or thiono)-S, depending on the metal ion. The magnetic and spectroscopic data suggest a distorted-octahedral geometry for the Ni(II) complexes, a square-planar geometry for $[L^1CuCl(H_2O)]$, a dimeric distorted octahedral geometry for both $[(L^2)_2Cu(H_2O)]_2$ and $[(HL)Mn(SO_4)(H_2O)_2]_2$. Such dimeric structures have been revealed by the subnormally low μ_{eff} values for the Mn(II) complexes, due to antiferromagnetic coupling between the two Mn(II) centers, and the diamagnetism of $[(L^2)_2Cu(H_2O)]_2$ is due to a quenching mechanism. ESR parameters support the structures of the Mn(II) and Cu(II) complexes and that the two azomethine nitrogens are coordinated to the Cu(II) ion in the $[(L^2)_2Cu(H_2O)]_2$ complex. DTA studies of the maganese(II) and copper(II) complexes are also reported.

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INTRODUCTION

1,2,4-Triazines possess a wide range of useful chemotherapeutic properties; they act as antiviral, antibacterial, antimalarial and antiinflammatory agents[1-4]. Their anticancer, antileukemia, antitumor and anti-HIV activities have been evaluated and found to be promising in some instances[5-8]. It is known that the existence of metal ions bonded to biologically active materials may enhance their activities. Chelating organic ligands containing the Schiff base linkage are also of biological importance; their metal complexes with an incomplete coordination spheres can serve as models for metalloenzymes that catalyse metabolic reactions of amino acids[9]. We report here the synthesis and characterization of manganese(II), nickel(II) and copper(II) complexes of two potentially biologically active mercapto-triazine Schiff base ligands, HL^1 and HL^2 (Fig. 1).

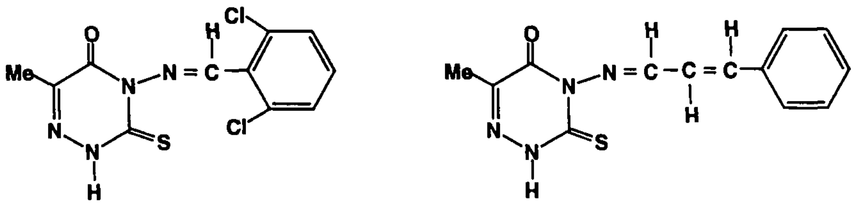
EXPERIMENTAL

Preparation of Ligands

The ligands HL^1 and HL^2 were prepared according to the following procedure. A mixture of 4-amino-3-mercapto-6-methyl-1,2,4-triazin-5(4*H*)-one (0.01 mol, 1.74 g) and the appropriate aldehyde {2,6-dichlorobenzaldehyde or cinnamylaldehyde} (0.01 mol, 1.75 or 1.32 g, respectively) was refluxed in MeOH (25 mL) for 1 h. The reaction mixture was cooled and the resulting precipitate was filtered, dried and recrystallized from MeOH to give pure HL^1 or HL^2 (2.69 or 2.17 g, respectively). HL^1 is a pale yellow solid and HL^2 crystallized as yellow lustrous sheets. The elemental analyses, yields and melting points of the free ligands HL^1 and HL^2 are presented in Table I. The ^1H and ^{13}C NMR spectral data of the ligands HL^1 and HL^2 in DMSO-d_6 are as follows:

4-(2,6-Dichlorobenzylideneamino)-3-mercapto-6-methyl-1,2,3-triazin-5(4*H*)-one (HL^1).
^1H NMR (DMSO-d_6), δ = 2.21 (s, 3H, CH_3), 7.56 - 7.60 (m, 3H, $H_{arom.}$), 8.90 (s, 1H, CH), 13.71 (s, 1H, SH). ^{13}C NMR (DMSO-d_6), δ = 16.59 (CH_3), 128.09, 129.56, 133.32, 134.91 ($C_{arom.}$), 147.37 (Me-$\underline{C}$=$N_{triazine}$), 149.44 (N=$\underline{C}$-SH), 169.44 ($\underline{C}$=N_{azine}), 170.43 ($\underline{C}$=O)

4-(Cinnamylideneamino)-3-mercapto-6-methyl-1,2,4-triazin-5(4*H*)-one (HL^2).
^1H NMR (DMSO-d_6), δ = 2.18 (s, 3H, CH_3), 6.99 (m, 1H, N=C-CH), 7.33 (d, J =9.2



HL^1 HL^2

Fig. 1. Structures of the Ligands

Hz,1H, HC=C-C=N), 7.40-7.77 (m, 4H, H_{arom}), 8.32 (d, 1H, *J* = 9.2 Hz, HC=N-C=C), 13.69 (s, 1H, SH). ^{13}C NMR (DMSO-d_6), δ = 16.86 (CH_3), 123.25 (HC-$\underline{C}$H=CH), 128.23, 129.05, 130.4, 134.81 (C_{arom}), 147.26 (Me-$\underline{C}$=$N_{triazine}$) 147.55 (=$\underline{C}$-Ph), 149.88 (N=$\underline{C}$-SH), 170.54 ($\underline{C}$=N_{azine}), 174.59 ($\underline{C}$=O).

Preparation of Complexes

The following general procedure was used. A hot EtOH solution (50 mL) of the ligand (0.001 mol, 0.315 g for HL^1 or 0.002 mol, 0.544 g for HL^2) and a hot H_2O-EtOH solution (1:1, 25 mL) of the divalent metal salts ($NiCl_2.6H_2O$, $MnSO_4.H_2O$ or $CuCl_2.2H_2O$) (0.001 mol; 0.238, 0.169 or 0.178 g, respectively) were mixed together and heated under reflux on a water bath for 3 h with occasional stirring. The reaction mixture was then concentrated by rotary evaporation under reduced pressure until the onset of preciptation of the products. The products were washed successively with H_2O, warm EtOH and Et_2O followed by drying in vacuo over P_4O_{10}.

Measurements

Infrared spectra were recorded as KBr discs on a Perkin Elmer 683 spectrophotometer in the 4000-200 cm^{-1} range. Electronic spectra were recorded as Nujol mulls on a Shimadzu 240 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained with a Brucker AC spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C measurements, using DMSO-d_6 as solvent with tetramethylsilane as a reference. Magnetic susceptibilities were measured by the Gouy method. Diamagnetic corrections were made using Pascal's constants. Electron spin resonance (ESR) spectra of

Table I. Colours, Melting Points, Yields, Elemental Analyses, Magnetic Moments and Conductivities of the Ligands and Their Complexes

Compound	Colour	M.p. °C	Yield (%)	Found (Calcd) %						μ_{eff} (B.M.) at 300 K	Λ_M[b]
				C	H	N	S	Cl	M		
HL^1 ($C_{11}H_8N_4OSCl_2$); 315[a]	pale-yellow	224	85	41.8 (41.9)	2.4 (2.5)	17.6 (17.8)	10.0 (10.2)	22.1 (22.4)			
$[L^1CuCl(H_2O)]$ ($CuC_{11}H_9N_4SO_2Cl_3$); 431.2	green	205	76	30.4 (30.6)	2.2 (2.1)	12.8 (13.0)	7.1 (7.4)	24.5 (24.7)	14.4 (14.7)	1.93	12
$[(HL^1)NiCl_2(H_2O)_2]$; ($Ni C_{11} H_{12}N_4SO_3Cl_4$); 480.7	brown	198	72	27.7 (27.5)	2.4 (2.5)	11.5 (11.65)	6.5 (6.65)	29.4 (29.5)	11.9 (12.2)	3.28	14
$[(HL^1)Mn(SO_4)(H_2O)_2]_2$ ($Mn_2C_{22}H_{24}N_8S_4O_{14}Cl_4$); 1004.4	orange	195	75	26.0 (26.3)	2.4 (2.4)	11.0 (11.15)	12.5 (12.75)	14.0 (14.1)	10.8 (11.0)	4.38	10
HL^2 ($C_{13}H_{12}N_4OS$); 272	yellow	195	80	57.1 (57.35)	4.3 (4.4)	20.4 (20.6)	11.7 (11.8)				
$[(L^2)_2Cu(H_2O)]_2$ ($Cu_2C_{52}H_{48}N_{16}S_4O_6$); 1248.4	brick-red	178	75	49.6 (50.0)	3.7 (3.8)	17.7 (18.0)	10.1 (10.3)		9.9 (10.2)	diamag.	10
$[(HL^2)_2NiCl_2]$ ($NiC_{26}H_{24}N_8S_2O_2Cl_2$); 674.2	brown	175	72	46.5 (46.3)	3.2 (3.6)	16.4 (16.6)	9.3 (9.5)	10.4 (10.5)	8.5 (8.7)	3.25	16
$[(HL^2)Mn(SO_4)(H_2O)_2]_2$ ($Mn_2C_{26}H_{32}N_8S_4O_{14}$); 918.7	yellow	183	78	33.6 (34.0)	3.3 (3.5)	12.0 (12.2)	11.7 (12.0)		11.8 (12.0)	4.53	12

[a] Formula weight; [b] Ω^{-1} cm^2 mol^{-1}

powdered samples were recorded on a Jeol JEX-FE 2XG spectrometer using 2,2'-diphenyl-1-picrylhydrazone (DPPH) as a standard (g = 2.0036). Differential thermal analyses (DTA) were performed in air using a DuPont 990 instrument from 27 to 550° C at a heating rate of 10° C min^{-1}. using Al_2O_3 as a reference. Microanalyses of C, H and N were obtained using a Perkin-Elmer 2400 CHN elemental analyzer. The chlorine and sulfur contents were determined gravimetrically. The complexes were analyzed for their metal content by EDTA titration[10]. Molar conductances in DMF were measured at room temperature on a Hanna 8733 conductivity meter.

RESULTS AND DISCUSSION

The ^{1}H and ^{13}C NMR assignments (Exptl part) confirm the preparation of the two mercapto-triazine Schiff base ligands HL^1 and HL^2. Both ligands exist in the thiol form in DMSO solution as revealed by the appearance of an ^{1}H NMR signal at 13.7 ppm due to the S-H proton and the absence of a ^{13}C NMR signal in the 180-196 ppm range for the C=S carbon[11] in their spectra. The two ligands are soluble in some solvents such as acetone, dioxane, dimethyl sulfoxide and in hot alcohol (ethanol or methanol).

The analytical data (Table I) indicate that the reactions of nickel(II) and copper(II) with HL^1 and HL^2 produce 1:1 and 1:2 (M:L) complexes, respectively, whereas the reactions of manganese(II) with both ligands yield only one type of complex of the stoichiometric formula $[(HL)Mn(SO_4)(H_2O)_2]_2$ (HL = HL^1 or HL^2). The complexes are insoluble in most common organic solvents but are soluble in DMSO, DMF and pyridine. The low molar conductances (10-16 Ω^{-1} cm^{-1} mol^{-1}) of 10^{-3} M solutions of the complexes in DMF indicate that they are non-electrolytes[12].

$$HL^1 + CuCl_2.2H_2O \xrightarrow{EtOH/H_2O,\ \Delta} [L^1CuCl(H_2O)]$$

$$2\ HL^2 + CuCl_2.2H_2O \xrightarrow{EtOH/H_2O,\ \Delta} \tfrac{1}{2}[(L^2)_2Cu(H_2O)]_2$$

$$HL^1 + NiCl_2.6H_2O \xrightarrow{EtOH/H_2O,\ \Delta} [(HL^1)NiCl_2(H_2O)_2]$$

$$2\ HL^2 + NiCl_2.6H_2O \xrightarrow{EtOH/H_2O,\ \Delta} [(HL^2)_2NiCl_2]$$

$$HL + MnSO_4.H_2O \xrightarrow{EtOH/H_2O,\ \Delta} \tfrac{1}{2}[(HL)Mn(SO_4)(H_2O)_2]_2$$

Infrared Spectra

The main IR spectral bands of the free ligands HL and their metal complexes along with their tentative assignments are given in Table II. The spectra of HL^1 and HL^2 display bands at 3149 and 3144 cm^{-1}, respectively, attributable to ν(N-H); strong bands at 1704 and 1695 cm^{-1}, respectively, assignable to ν(C=O); medium bands at 1603 and 1573 cm^{-1}, respectively, due to ν(C=N)(azine)[13]. The lower wave number of ν(C=N)(azine) of HL^2 as compared to that of HL^1 is due to the extended conjugation of C=N with C=C. The appearance of bands due to N-H along with bands at 1186 and 1172 cm^{-1} for HL^1 and HL^2, respectively, attributable to ν(C=S) without the appearance of bands in the 2500-2400 cm^{-1} region due to ν(S-H)[11,14,15], may be taken as evidence for the existence of the HL compounds in the thione form in the solid state. Both ligands contain a thioamide group (H-N-C=S) and should give rise four characteristic thioamide bands, namely I, II, III and IV in the regions 1500, 1300, 1000 and 800 cm^{-1}, respectively[15]. The thioamide bands I and IV are easily identified in all compounds. Therefore, the mode of bonding of sulfur as a ligand was decided on the basis of shifts on complexation of the thioamide bands I and IV, in addition to the shifts of the ν(C=S) and ν(N-H) bands. In the spectra of $[L^1CuCl(H_2O)]$ and $[(L^2)_2Cu(H_2O)]_2$, bands due to ν(C=O) remain nearly unchanged when compared to that of the free ligands HL, indicating that the carbonyl oxygen is not bonded to the copper(II) ion. Bonding of the azomethine nitrogen to copper(II) ion is suggested by the shifts to lower frequency by 15 and 25 cm^{-1} in the ν(C=N) of $[L^1CuCl(H_2O)]$ and $[(L^2)_2Cu(H_2O)]_2$, respectively, as compared to that of the free ligands HL. In the IR spectra of both copper(II) complexes, ν(C=S) bands of the ligands HL^1 and HL^2 at 1182 and 1172 cm^{-1}, respectively, disappeared. The thioamide band IV at 780 and 740 cm^{-1} in the spectra of HL^1 and HL^2, respectively, which has considerable ν(C=S) character[11,15,16], became weak in the IR spectra of the copper(II) complexes. The thioamide band I at 1508 and 1510 cm^{-1} in HL^1 and HL^2, respectively, having a contribution from ν(C-N) + δ(NH), became weak as a result of changing $S{=}\overset{H}{C}{-}N{-}H$ to $HS{-}\overset{H}{C}{=}N$ on complex formation. The bands at 3149 and 3144 cm^{-1} in HL^1 and HL^2, respectively, assigned to ν(N-H) disappeared. These observation indicate coordination

Table II. Important IR Spectral Bands (cm^{-1}) and Assignments

Compound	ν(OH)	ν(NH)	ν(C=O)	ν(C=N) azine	ν(C=S)	Thioamide bands		$\nu_3(SO_4)$	ν(M-O)	ν(M-S)	ν(M-N)
						I	IV				
HL^1	—	3149 s	1704 s	1603 s	1186 m	1508 s	780 s				
$[L^1CuCl(H_2O)]$	3226 b	—	1696 s	1589 s	—	1520 s	781 w		586 w	342 m	410 w
$[(HL^1)NiCl_2(H_2O)_2]$	3424 b	3150 s	1645 s	1580 m	1180 m	1510 s	777 s		583 w	—	416 w
$[(HL^1)Mn(SO_4)(H_2O)_2]_2$	3445 b	3148 s	1695 s	1580 m	1150 s	1512 s	788 w	1172 s 1067 m 1045 m	565 w	375 w	420 w
HL^2	—	3144 s	1695 s	1573 s	1172 s	1510 s	740 s				
$[(L^2)_2Cu(H_2O)]_2$	3246 b	—	1691 s	1541 m	—	1507 m	748 w		582 w	348 w	404 w
$[(HL^2)_2NiCl_2]$	—	3145 s	1692 s 1659 s	—	1168 m 1148 m	1510 s 1517 m	747 m 721 w		580 w	364 w	408 w
$[(HL^2)Mn(SO_4)(H_2O)_2]_2$	3427 b	3146 s	1695 s	1548 s	1145 m	1510 s	743 m	1172 m 1070 m 1050 m	564 w	370 w	421 w

s, strong; m, medium; w , weak; b, broad of the thiolate sulfur to copper(II) ion in both HL complexes. This conclusion is further substantiated by the appearance of new bands near 340 cm^{-1} in the spectra of both copper(II) complexes and assigned to ν(Cu-S)[17]. In case of [$L^1CuCl(H_2O)$], another new band appears at 303 cm^{-1} assigned to ν(Cu-Cl)[17]. The ν(Cu-Cl) band lies in the range for four-coordinate chloro copper(II) complexes and is rather characteristic for terminally bonded chloro ions[17].

The spectrum of [$(HL^1)NiCl_2(H_2O)_2$] showed no appreciable change in the position of ν(N-H) but shifts to lower frequency in the ν(C=O) and ν(C=N)(azine) bands indicate bonding of the azomethine ntrogen and carbonyl oxygen atoms to the nickel(II) ion. Coordination of the thione sulfur to nickel(II) is unlikely, since the C=S stretching mode, and the thioamide bands I and IV are almost unaffected in the spectrum of this complex. The IR spectrum of [$(HL^2)_2NiCl_2$] shows two different C=O bands at 1692 and 1659 cm^{-1}, characherstic of non-coordinating and coordinating C=O, respectively. Similarly, the spectrum also shows two different ν(C=S) bands at 1168 and 1148 cm^{-1}, two different bands for the thioamide I at 1510 and 1517 cm^{-1} and two bands for the thioamide IV at 777 and 721 cm^{-1}, assignable to non-coordinated and coordinated C=S thiono groups, respectively. No ν(C=N) band could be observed in the spectrum of this complex presumbly due to the trans configuration of the two coordinated azomethine groups around the nickel(II) ion which cooperatively cancel out any dipole moment change, thereby rendering each other IR inactive. No metal-chlorine band could also be observed in this complex perhaps due to the trans effect, but according to the elemental analyses and $AgNO_3$ test, the chloride ions are suggested to be coordinated to nickel(II) ion in this complex.

In the IR spectra of the manganese complexes [$(HL)Mn(SO_4)(H_2O)_2]_2$, appreciable shifts to lower frequency of the bands due to ν(C=N)(azine) and ν(C=S) (Table II) are observed, indicating the involvment of the azomethine nitrogen and thione sulfur in coordination to the manganese(II) ion. The bands observed near 1170, 1070 and 1040 cm^{-1} suggest the presence of a bidentate bridged sulfato groups in these two complexes[17,18].

The spectra of the hydrated complexes show broad bands centered in the 3470-3226 cm^{-1} range; bands in the 1570-1600 cm^{-1} range became broader than in the free HL and weak bands in the 850-900 cm^{-1} range are assigned to stretching, scissoring and twisting/rocking vibrational modes of coordinated H_2O molecules, respectively[17].

According to these IR data, the ligands HL act as neutral or monobasic bidentate ligands coordinated to the metal ions *via* the azomethine nitrogen and either the carbonyl oxygen or (thiolo or thiono) sulfur depending upon the metal ion[19,20].

Magnetic Studies

The room temperature magnetic moments of the HL metal complexes are given in Table I. The magnetic moment values for the nickel(II) and $[L^1CuCl(H_2O)]$ complexes are within the range of magnetically diluted nickel(II) and copper (II) complexes. The observed diamagnetism of the $[(L^2)_2Cu(H_2O)]$ complex may be due to the reduction of copper(II) to copper(I) by the ligand. This phenomenon has been reported for several copper(II) complexes with sulfur-containing ligands[21,22]. However, this possibility is ruled out based on the elemental analyses and electronic spectral data (to be discussed later) which support the existence of the copper(II) ion. Therefore, this complex represents one of the few copper(II) complexes in which the paramagnetism is almost quenched at room temperature[21-23]. This magnetic behaviour may be interpreted in terms of spin-spin interaction between the copper centers in the solid phase at room temperature. This interaction may take place either by the formation of σ or δ bond by overlapping of either two d orbitals or the extended molecular orbitals and one of the ligands donor orbitals. The low values of the room temperature magnetic moments of the manganese complexes of HL (4.30 and 4.53 B.M) compared to spin-only value (5.92 B.M.) may be due to atmospheric oxidation of Mn(II) to Mn(III) and/or the existence of some sort of molecuar association that would shorten the Mn-Mn distance *via* bridging ligands leading to antiferromagnetic coupling between Mn(II) ions[24-26] The oxidation phenomenon is ruled out on the basis of the elemental analyses data. The appearance of vibrational frequencies due to bidentate bridged sulfato groups suggests the association of Mn(II) ions *via* bridging sulfato anions, which is the factor responsible for lowering of μ_{eff} values at room temperature.

Electronic Spectra

The solid state electronic spectra for the free ligands HL and their metal complexes are listed in Table III. The spectra of the ligands HL^1 and HL^2 exhibit intense bands at

Table III. Solid State Electronic Spectral Bands (cm^{-1}) for HL and Their Metal Complexes

Compound	Intraligand and charge transfer bands	d→d bands
HL^1	36900; 32258; 27778	
$[L^1CuCl(H_2O)]$	37175; 30488; 23810	16103
$[(HL^1)NiCl_2(H_2O)_2]$	37106; 29674 ; 20800	16129
$[(HL^1)Mn(SO_4)(H_2O)_2]_2$	37173; 29412; 24390	
HL^2	35714; 31250; 27523	
$[(L^2)_2Cu(H_2O)]_2$	36336; 30227; 23810	18182
$[(HL^2)_2NiCl_2]$	36900; 30303; 25000	15775
$[(HL^2)Mn(SO_4)(H_2O)_2]_2$	36496; 29412; 26667	

35,900 and 35,700 cm^{-1}, respectively, due to π→π* transitions and bands in the 32,260-27,780 cm^{-1} region assignable to n→π* transitions. In all complexes, the π→π* transtion bands are replaced by a relatively broad band centered at ca. 37,000 cm^{-1}, that could be assigned to σ(N)→M(II) charge transfer transitions[27] overlapped with π→π* transitions. Bands due to n→π* transitions in the free ligands HL are merged into broad bands in the complexes centered at ca. 30,000 cm^{-1} that could be considered as composites of the remaining n→π* transition bands σ(S)→M(II) and other ligand to metal charge transfer transition bands[27]. The new bands (shoulders) that appeared in the 24,000-27,000 cm^{-1} region in the spectra of the complexes, are assigned to π(S)→M charge transfer transitions[27,28]. The spectra of the copper(II) complexes exhibit less intense bands at 16,100 and 18,200 cm^{-1} for $[L^1CuCl(H_2O)]$ and $[(L^2)_2Cu(H_2O)]_2$, respectively, assignable to d→d transitions. The band position of $[L^1CuCl(H_2O)]$ is in accord with square-planar copper(II) complexes[27,29]. Since this band is relatively broad and asymmetric, it could be considered as a composite of the three transitions $^2B_{1g}\rightarrow{}^2E_g, \rightarrow{}^2B_{2g}, \rightarrow{}^2A_{1g}$ assuming D_{4h} average microsymmetry for this complex. In case of the $[(L^2)_2Cu(H_2O)]_2$ complex, the band position is in accord with tetragonally-distorted octahedral copper(II) complexes[27] that belong to D_{4h} symmetry. According to this ligand field symmetry, the d→d band could be considered as a composite of $^2B_{1g} \rightarrow {}^2A_{1g}, \rightarrow {}^2E_g$ transitions. The third band that should be observed at ca. 14,000 cm^{-1} is absent in the spectrum of this complex perhaps due to its very low intensity and/or the distortion from the D_{4h} point group.

The electronic spectra of $[(HL^1)NiCL_2(H_2O)_2]$ and $[(HL^2)_2NiCL_2]$ gave bands at 16,120 and 15,380 cm^{-1}, respectively, due to d→d transitions. Such bands, in conjunction with magnetic moment values within the range 2.9-3.4 B.M. reported for free-spin hexa-coordinated nickel(II), for these complexes are consistent with tetragonally-distorted octahedral nickel(II) complexes. The bands are assigned as $^3B_{1g} \rightarrow {}^3A_{2g}^{a}$ transition $\{^3A_{2g}^{a}$ from $^3T_{1g}(F)\}$ in D_{4h} symmetry[30].

The $[(HL)Mn(SO_4)(H_2O)_2]_2$ complexes do not exhibit ligand field spectra in the visible region because of the very low intensities and spin-forbidden transitions of the high-spin d^5 configuration.

Electron Spin Resonance Spectra

The X-band ESR spectral data of powdered samples of the copper(II) and manganese(II) complexes at room temperature are listed in Table IV. The ESR spectrum of $[L^1CuCl(H_2O)]$ exhibits axial pattern with two g values, without hyperfine structure due to the enhanced spin-lattice relaxation of the organic ligand. The fact that $g_{||} > g_{\perp} > g_e$ for this complex, is consistent with the unpaired electron in the $d_{x2\text{-}y2}$ orbital. The G value, defined as $G = (g_{II} - 2)/(g_{\perp} - 2)$, is > 4 suggests that there is no exchange interaction between the copper(II) centers in the solid state. The g_{av} value is rather low, indicating considerable covalency, a consequence of a sulfur donor atom in the coordination sphere, and is consistent with values reported for square-planar copper(II) complexes with sulfur-nitrogen containing ligands[28]. The spectrum of the $[(L^2)_2Cu(H_2O)]_2$ complex shows a typical rhombic pattern with $g_3 > g_2 > g_1$ which is in accord with $d_{x^2-y^2}$ as the most probable ground state of copper(II) in a tetragonally-distorted octahedral ligand field. The low value of $g_{av} = 2.073$ is indicative of considerable covalent character, a consequence of sulfur donor atoms in the coordination sphere and suggests a geometry involving grossly misaligned tetragonal axes. The spectrum also displayed two pairs of ill-defined seven copper(II) hyperfine lines as a result of the zero field split transition in the 2,900-3,200 (G) region with an

Table IV. ESR Spectral Parameters[a] for Copper(II) and Manganese(II) Complexes

Compound	Parameters				
$[L^1CuCl(H_2O)]$	$g_{\parallel} = 2.207$	$g_{\perp} = 2.021$	$G = 9.857$		
$[(L^2)_2Cu(H_2O)]_2$	$g_3 = 2.137$	$g_2 = 2.061$	$g_1 = 1.996$	$g_{av} = 2.075$	$A_N = 15$ (G)
$[(HL^1)Mn(SO_4)(H_2O)_2]_2$	$g_{eff} = 1.911$				
$[(HL^2)Mn(SO_4)(H_2O)_2]_2$	$g_{eff} = 1.889$				

[a] in solid state at 300 K

average spacing of $A_{\parallel} = 40$ (G) and in the 3,600-3,800 (G) region with an average spacing of 35 (G). Such patterns are characteristic of a dinuclear copper(II) systems[31]. Such a dimeric structure is probable with non-sterically hindered coordinating ligands such as HL^2 due to the planarity afforded by the existence of a C=C group that enables the sulfur atom to reach two copper(II) centers simultaneously; it is, however, improbable with HL^1 due to the steric effect. The spectrum of $[(L^2)_2Cu(H_2O)]$ also showed superhyperfine splitting of five lines, consistent with the coordination of two equivalent nitrogens to copper(II). The A_N value is in agreement with the reported values for the coordination of azomehine-nitrogen to copper(II)[32].

The X-band ESR spectra for both $[(HL)Mn(SO_4)(H_2O)_2]_2$ complexes gave a single broad line at $g_{eff} = 1.900$ with absence of zero-field splitting. The broadness of these ESR absorptions is consistent with the presence of magnetically interacting manganese(II) ions in the solid state at room temperature[25]. Such dimeric structures probably contain octahedrally coordinated Mn(II) ions that are linked by sulfato bridges. This allows magnetic interaction between Mn(II) ions so that all the spectral lines are broadened to give one resultant line at $g_{eff} = 1.900$. The value of g_{eff} is, however, not very close to 2, as reported for Mn(II) dinuclear complexes[25], due to the enhanced covalency as a consequence of sulfur atoms in the coordination sphere.

Thermal Analysis

The DTA curves in Figures 2 and 3 of $[L^1CuCl(H_2O)]$, $[(L^2)Cu(H_2O)]_2$ and $[(HL)Mn(SO_4)(H_2O)_2]_2$ show three main peaks. The first endothermic peak occurs in

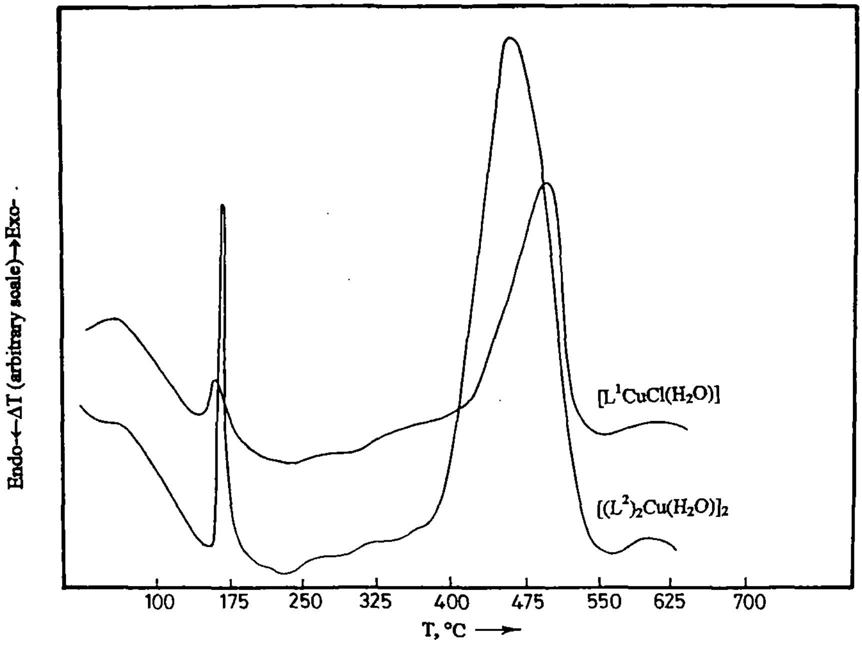


Figure 2. DTA Curves of Copper(II) Complexes

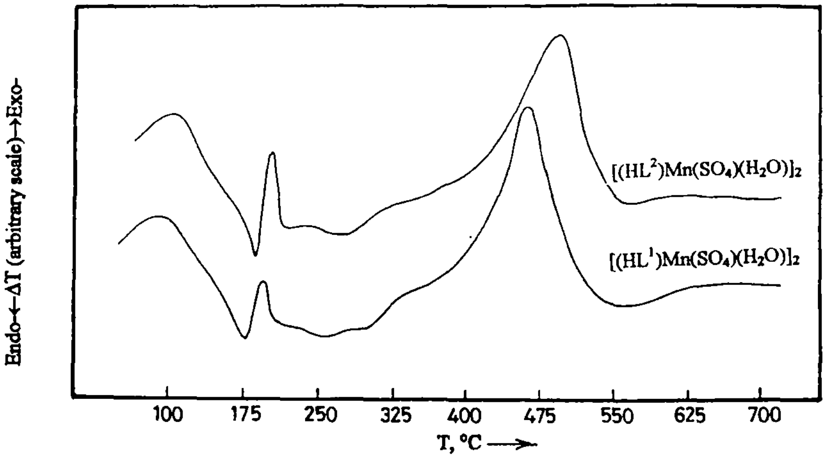
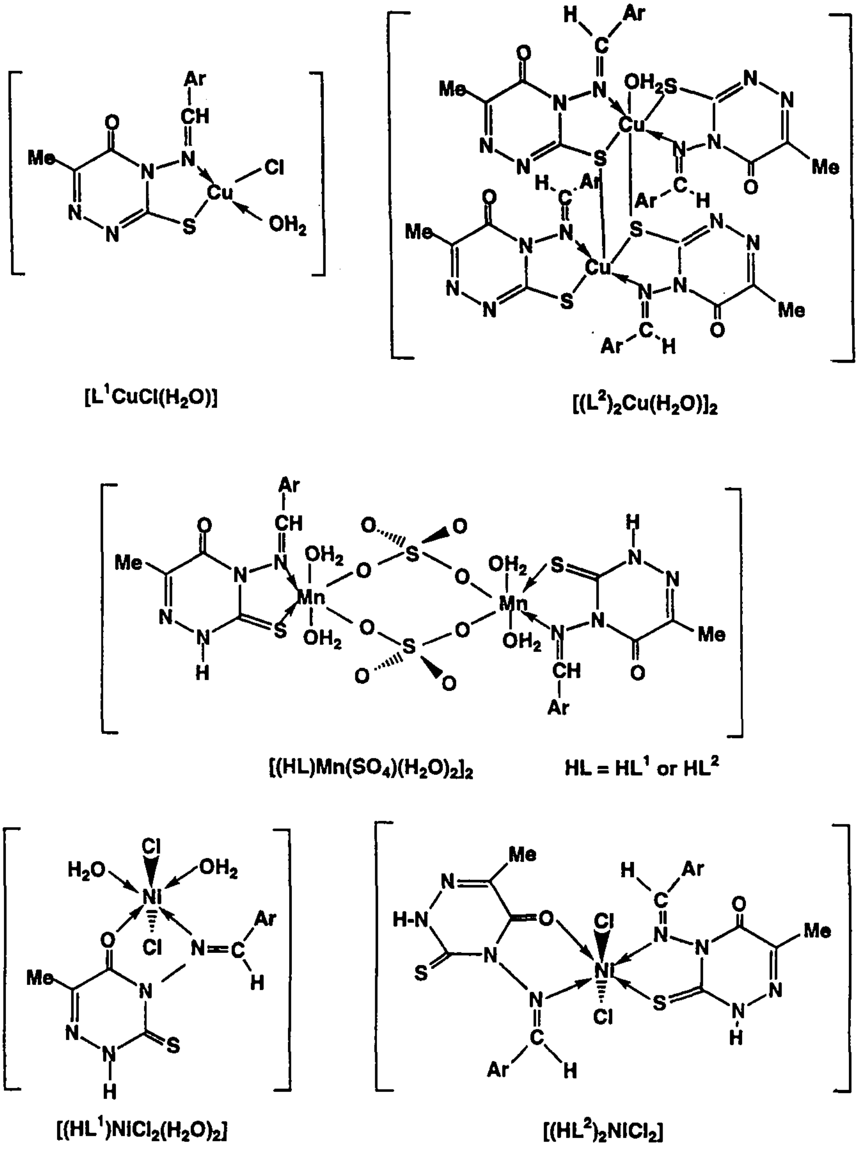


Figure 3. DTA Curves of Manganese(II) Complexes



$[L^1CuCl(H_2O)]$

$[(L^2)_2Cu(H_2O)]_2$

$[(HL)Mn(SO_4)(H_2O)_2]_2$ HL = HL^1 or HL^2

$[(HL^1)NiCl_2(H_2O)_2]$

$[(HL^2)_2NiCl_2]$

Ar = 2,6-$Cl_2C_6H_3$ (for HL^1 or L^1) and C_6H_5-CH=CH (for HL^2 or L^2).

Figure 4. Proposed Structures of the HL Complexes

the 148-183° C range corresponding to loss of coordinated water molecules[33]. The second sharp exothermic peak lies in the 161-200° C range and is assigned to phase transformation. Melting of the complexes takes place immediately after this step. It is notable that the melting of the complexes occurs at significantly lower temperatures than that of the corresponding free organic ligands. This could be attributed to the polarizing power exerted by metal ions leading to a decrease in the electron density on the active centers, weakening the intermolecular forces between the complex molecules in the lattice and/or due to the steric effect exerted by the bulky ligand groups. The third broad exothermic peak that appears in the 440-490° C range is assigned to the decomposition of the complex to metal oxide. It should be realized that, although the melting point of HL^1 (224° C) is higher than that of HL^2 (195°C), the temperature of the third stage decomposition for $[(HL^2)Mn(SO_4)(H_2O)_2]_2$ is higher than that of $[(HL^1)Mn(SO_4)(H_2O)_2]_2$. This could be due to the stability afforded by the sterically more suitable ligand HL^2 for chelation with metals ions.

Based on the elemental analysis, conductance, magnetic; and electronic, IR and ESR spectral studies, the proposed structures of the complexes are shown in Figure 4.

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