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Spectroscopic evaluation of manganese(II) complexes derived from semicarbazones and thiosemicarbazones

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Abstract

Manganese(II) complexes having the general composition $Mn(L)_2X_2$ [where L = isopropyl methyl ketone semicarbazone (LLA), isopropyl methyl ketone thiosemicarbazone (LLB), 4-aminoacetophenone semicarbazone (LLC) and 4-aminoacetophenone thiosemicarbazone (LLD) and $X = Cl^-$, $1/2SO_4^{2-}$] have been synthesized. All the complexes were characterized by elemental analyses, molar conductance, magnetic moment susceptibility, EI-mass, ^{1}H NMR, IR, EPR and electronic spectral studies. All the complexes show magnetic moments corresponding to five unpaired electrons. The possible geometries of the complexes were assigned on the basis of EPR, electronic and infrared spectral studies.

Keywords: Thiosemicarbazones; Semicarbazones; Spectroscopic; Manganese(II)

1. Introduction

Complexes of thiosemicarbazones with transition metal have received attention because of their biological activity including antitumer, antibacterial, fungicidal and anticarcinogenic properties [1–6].

Manganese and its compounds are widely used in analytical chemistry, metallurgical processes and paint and pigments industry. The complexes of manganese(II) play an excellent role in catalytic property [7–10]. Manganese metal has a well-established importance in the field of biology and medicine. A lot of articles are available on the physiology and biochemistry of manganese [11]. Ruminants manganese is present in the serum of blood as manganese(III) β-globulin and in erythrocytes as manganese porphyrin ring.

The current paper is focused on the spectral characterization of the newly synthesized ligands LLA, LLB, LLC and LLD (Fig. 1) and their complexes with manganese(II).

2. Physical measurements

The C, H and N were analyzed on a Carlo-Erba 1106 elemental analyzer; the nitrogen contents of the complexes were determined using Kjeldahl's method. Molar conductance was measured on an ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using $CuSO_4 \cdot 5H_2O$ as a callibrant. Electron impact mass spectra were recorded on JEOL, JMS, DX-303 mass spectrometer. ^{1}H NMR spectra were recorded on Hitachi FT-NMR, model R-600 spectrometer using $CDCl_3$ as solvent. Chemical shifts are given in ppm relative to tetramethylsilane. IR spectra (KBr) were recorded on a FTIR Spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer. EPR spectra of the complexes were recorded as polycrystalline sample and in the DMSO solution, at room temperature on E_4-EPR spectrometer using the DPPH as the g-marker.

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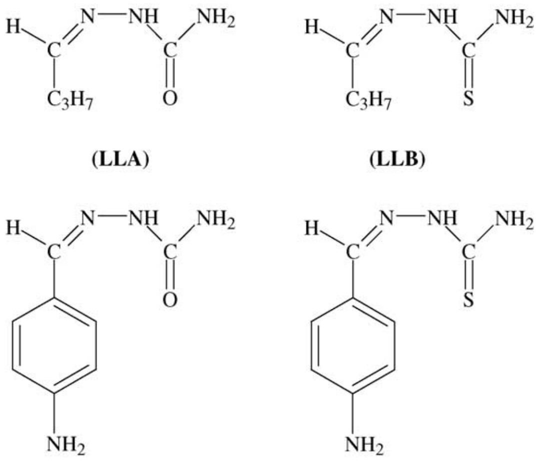


Fig. 1. Structure of the ligands.

3. Results and discussion

The molar conductance for these complexes has been determined in dimethylformamide (DMF). The results were in agreement for the nonelectrolytic nature for all the chloride complexes and 1:1 electrolyte for sulphate complexes [12] (Table 2). On the basis of the above data, the $[Mn(L)_2Cl_2]$ formula may be suggested for the chloro complexes, and $[Mn(L)]SO_4$ for sulphate complexes Table 1 [where L = LLA, LLB, LLC and LLD].

3.1. Infra red spectra of the ligands

Infrared spectra of the ligands show bands in the region ∼1628 and 1575 cm^{-1} which may be assigned to the symmetric or asymmetric [ν(C=N)] vibrations. A strong band in the region ∼770–782 cm^{-1} in thiosemicarbazones and ∼1692–1709 cm^{-1} in semicarbazones is due to the [ν(C=S)] and [ν(C=O)] groups, respectively. On complex formation, the position of these bands is shifted toward lower frequency as compared the metal free ligand, this indicates that the coordination takes place through the nitrogen, oxygen, and sulfur atoms of (C=N), (C=O) and (C=S) groups [13], respectively. Thus, it has been concluded that the semicarbazones and thiosemicarbazones act as bidentate chelating agent [7].

3.2. ^{1}H NMR spectra of the ligands

^{1}H NMR spectra of the ligands in DMSO show the signals [14] as follows (chemical shift in ppm):

3.2.1. Ligand (LLA)

δ 1.82 ppm (t) (3H, H_3C–C–), δ 8.58 ppm (s) (1H, HN–CO), δ 3.45 ppm (d) (2H, H_2N–CO), δ 1.18 (t), δ 2.48 (sextet), δ 4.41 ppm (d) (C_3H_7–C).

Table 1
Physical and elemental analysis data of the complexes

Complex	MW found (calculated)	Colour	M.p.[a] (°C)	Yield (%)	Elemental analysis data found (calculated, %)			
					Mn	C	H	N
(LLA) $C_6H_{13}N_3O$	144 (143)	Off white	229	68	–	50.32 (50.35)	9.21 (9.09)	29.22 (29.37)
(LLB) $C_6H_{13}N_3S$	161 (159)	Dirty white	220	78	–	45.17 (45.28)	8.03 (8.18)	26.57 (26.41)
(LLC) $C_9H_{12}N_4O$	192 (192)	Cream	204	70	–	56.38 (56.25)	6.36 (6.25)	29.03 (29.17)
(LLD) $C_9H_{12}N_4S$	209 (208)	Off white	210	73	–	52.01 (51.92)	5.92 (5.77)	26.83 (26.92)
$[Mn(LLA)_2Cl_2]$ $MnC_{12}H_{26}N_6O_2Cl_2$	(412)	Light brown	271	69	13.28 (13.35)	35.07 (34.95)	6.22 (6.31)	20.30 (20.39)
$[Mn(LLA)_2]SO_4$ $MnC_{12}H_{26}N_6O_6S$	(437)	Brown	260	66	12.50 (12.59)	32.88 (32.95)	6.03 (5.95)	19.13 (19.22)
$[Mn(LLB)_2Cl_2]$ $MnC_{12}H_{26}N_6S_2Cl_2$	(444)	Pale brown	291	72	12.54 (12.39)	32.58 (32.43)	5.81 (5.86)	18.99 (18.92)
$[Mn(LLB)_2]SO_4$ $MnC_{12}H_{26}N_6O_4S_3$	(469)	Brown	285	71	11.61 (11.73)	30.83 (30.70)	5.40 (5.54)	18.00 (17.91)
$[Mn(LLC)_2Cl_2]$ $MnC_{18}H_{24}N_8O_2Cl_2$	(510)	Brown	266	70	10.93 (10.78)	42.43 (42.35)	4.62 (4.71)	22.05 (21.96)
$[Mn(LLC)_2]SO_4$ $MnC_{18}H_{24}N_8O_6S$	(535)	Rust brown	253	63	10.41 (10.28)	40.29 (40.37)	4.40 (4.49)	21.02 (20.93)
$[Mn(LLD)_2Cl_2]$ $MnC_{18}H_{24}N_8S_2Cl_2$	(542)	Dull brown	260	65	10.06 (10.15)	39.97 (39.85)	4.37 (4.43)	20.74 (20.66)
$[Mn(LLD)_2]SO_4$ $MnC_{18}H_{24}N_8O_4S_3$	(566)	Brown	259	69	9.81 (9.72)	38.05 (38.16)	4.16 (4.24)	19.70 (19.79)

[a] Decomposition temperature.

Table 2
Molar conductance, magnetic moment and electronic spectral data

Complex	Molar conductance[a] (Ω^{-1} cm^2 mol^{-1})	[a]$\mu_{eff.}$ (B.M.)	λ_{max} (cm^{-1})	ε (L $mole^{-1}$ cm^{-1})
$[Mn(LLA)_2Cl_2]$	07	5.89	17890, 21846, 28872, 35936	34, 39, 68, 125
$[Mn(LLA)_2]SO_4$	114	5.96	22692, 27920, 36900	36, 63, 139
$[Mn(LLB)_2Cl_2]$	06	5.90	17750, 22354, 29108, 36293	34, 40, 69, 122
$[Mn(LLB)_2]SO_4$	118	5.99	21981, 28076, 36992	34, 66, 140
$[Mn(LLC)_2Cl_2]$	07	5.93	18258, 21982, 29320, 36182	35, 40, 71, 126
$[Mn(LLC)_2]SO_4$	105	5.98	23108, 27851, 36805	36, 65, 139
$[Mn(LLD)_2Cl_2]$	11	5.92	17912, 22416, 28766, 36377	34, 39, 69, 123
$[Mn(LLD)_2]SO_4$	119	5.97	22464, 27948, 37364	35, 65, 141

[a] Error limit, ±3%.

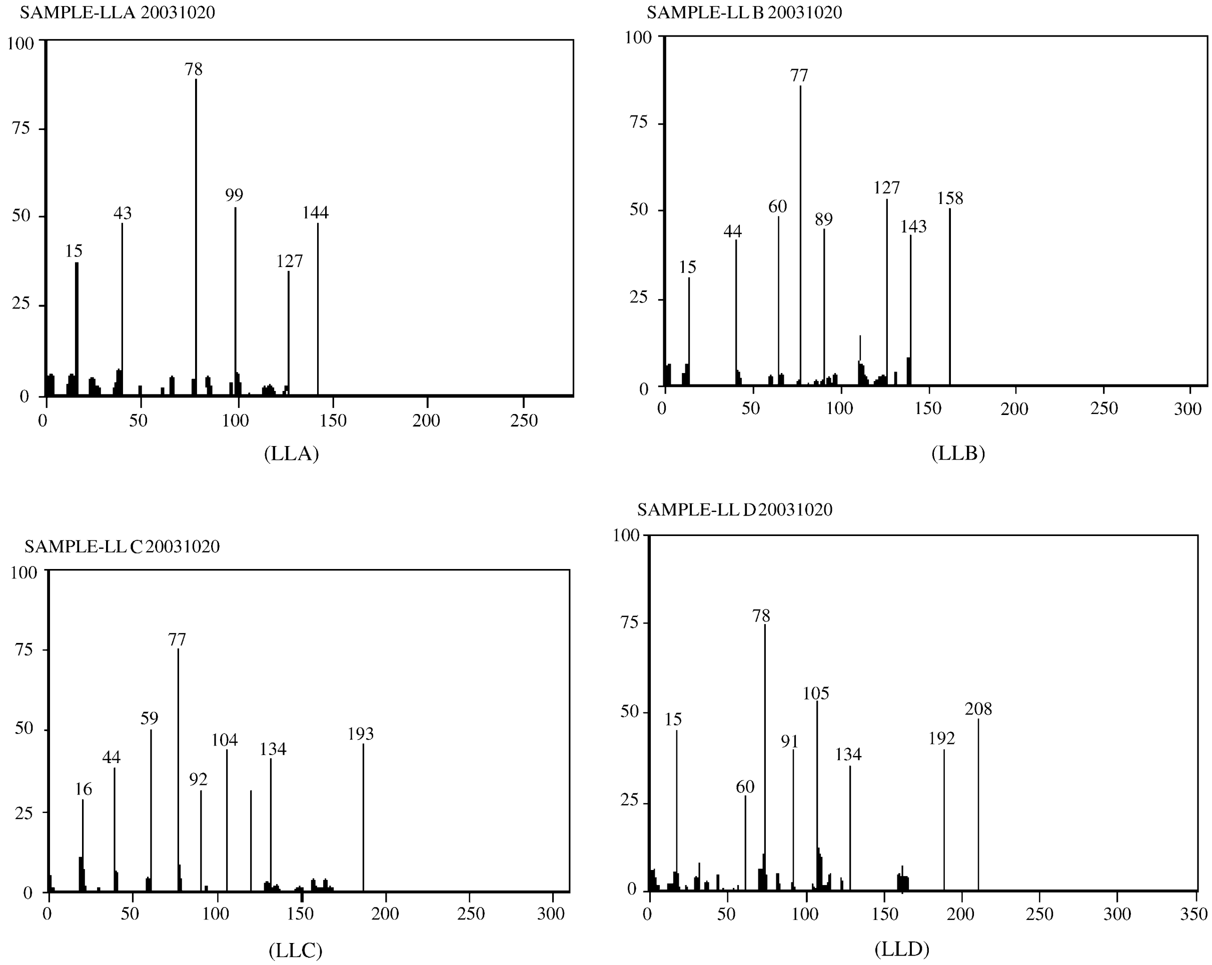


Fig. 2. Electron impact mass spectra of the ligands.

3.2.2. Ligand (LLB)

δ 1.84 ppm (t) (3H, H_3C–C–), δ 8.65 ppm (s) (1H, HN–CS), δ 3.59 ppm (d) (2H, H_2N–CS), δ 1.15 (t), δ 2.50 (sextet), δ 4.44 ppm (d) (C_3H_7–C).

3.2.3. Ligand (LLC)

δ 1.80 ppm (t) (3H, H_3C–C–), δ 8.57 ppm (s) (1H, HN–CO), δ 3.45 ppm (d) (2H, H_2N–CO), δ 7.11 ppm (m) (4H, –Ph–), δ 3.80 ppm (d) (2H, –Ph–NH_2).

3.2.4. Ligand (LLD)

δ 1.78 ppm (t) (3H, H_3C–C–), δ 8.63 ppm (s) (1H, HN–CS), δ 3.55 ppm (d) (2H, H_2N–CS), δ 7.10 ppm (m) (4H, –Ph–), δ 3.86 ppm (d) (2H, –Ph–NH_2).

3.3. Electron impact mass spectra of the ligands

EI mass spectra of the ligands (Fig. 2) confirm the proposed formula [15] by showing the following peaks.

3.3.1. Ligand (LLA)

Appearance of final peak at 144 amu ($C_6H_{13}N_3O$ calculated atomic mass 143 amu) and other peaks at 15, 43, 78, 99 and 127 amu may be due to different fragments. The intensity of these peaks gives an idea of the stability of these fragments.

3.3.2. Ligand (LLB)

Under the EI mass spectral study, it gives a final peak at 158 amu confirms the proposed formula ($C_6H_{13}N_3S$ calculated atomic mass, 159 amu) and other peaks at 15, 44, 60, 77, 89, 127 and 143 amu may be attributed to different fragments.

3.3.3. Ligand (LLC)

The presence of EI mass spectral peak at 193 amu confirms the proposed formula ($C_9H_{12}N_4O$ calculated atomic mass, 192 amu). A set of peaks observed in the range 16, 44, 59, 77, 92, 104, 119 and 134 amu are assigned to various fragments.

3.3.4. Ligand (LLD)

Presence of a peak at 208 amu support to the proposed formula ($C_9H_{12}N_4S$ calculated atomic mass 208 amu). The peaks due to the various fragments appears at 15, 60, 78, 92, 105, 134, 192 and 208 amu.

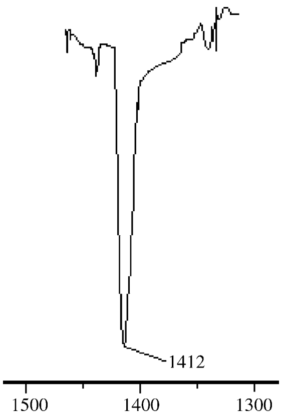


Fig. 3. IR spectral band of uncoordinated sulphate group in [Mn(LLB)$_2$]SO$_4$.

3.4. Chloride complexes [Mn(L)$_2$Cl$_2$]

Magnetic moment of the Mn(II) chloride complexes recorded at room temperature lies in the range 5.89–5.93 B.M. corresponding to high spin configuration corresponding to five unpaired electrons [16].

In the high spin octahedrally coordinated Mn(II) complexes, the lowest configuration $(t_{2g})^3(e_g)^2$ gives rise to the ground state $^6A_{1g}$. Since this is the only sextet level present, all the absorption bands must, therefore, be spin forbidden transitions. As a consequence of the sharpness of the bands, it is possible to obtain very accurate measurements of electronic transition energies with d^5 complexes. Such spectra, therefore, provide a very adequate test for the spectroscopic theory. The electronic spectra of the complexes (Table 2) show four weak intensity bands in the range 17 750–18 258 (ε = 34–35 L mole^{-1} cm^{-1}), 21 826–22 416 (ε = 39–40 L mole^{-1} cm^{-1}), 28 766–29 320 (ε = 68–71 L mole^{-1} cm^{-1}) and 35 936–36 377 cm^{-1} (ε = 122–126 L mole^{-1} cm^{-1}). These bands may be assigned to: $^6A_{1g} \rightarrow {}^4T_{1g}$ (^{4}G), $^6A_{1g} \rightarrow {}^4E_g$, $^4A_{1g}$ (^{4}G) (10B + 5C), $^6A_{1g} \rightarrow {}^4E_g$ (^{4}D) (17B + 5C) and $^6A_{1g} \rightarrow {}^4T_{1g}$ (^{4}P) (7B + 7C), respectively [17,18].

3.5. Sulphate complexes [Mn(L)$_2$]SO$_4$

Room temperature magnetic moment of the Mn(II) sulphate complexes lie in the range 5.96–5.99 B.M., these values are in tune with a high spin configuration.

The infrared spectra of the sulphate complexes (Fig. 3) show IR bands in the region of ~1408–1426(s) and ~615–622 cm^{-1} characteristic for the uncoordinated sulphate group [19].

The molar conductance measurements of the sulphate complexes recorded at room temperature in DMF solution were in the tune of 1:1 electrolyte [12]. The electronic spectra of the complexes (Fig. 4) recorded at room temperature in DMF solution show three bands in the range 21 981–23 108 (ε = 34–36 L mole^{-1} cm^{-1}), 27 851–28 076 (ε = 63–66 L mole^{-1} cm^{-1}) and 36 805–37 364 cm^{-1} (ε = 139–141 L mole^{-1} cm^{-1}), which may be assigned to the transitions: $^6A_{1g} \rightarrow {}^4T_{2g}$ (^{4}G), $^6A_{1g} \rightarrow {}^4T_{2g}$ (^{4}D), $^6A_{1g} \rightarrow {}^4A_{2g}$ (^{4}F), respectively [20]. These bands are characteristic for four coordinate tetrahedral Mn(II) complexes (Fig. 5).

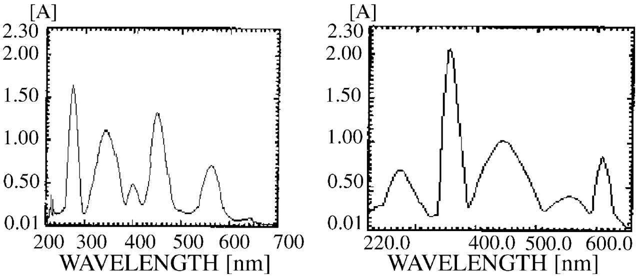


Fig. 4. Electronic spectra of the complexes.

An EPR spectra is readily detected even for large zero-field splitting, because d^5 is an odd electron system whose ground state is a Kramer's doublet and whose degeneracy is only completely removed by a magnetic field. The broad signal in the polycrystalline EPR spectra of Mn(II) complexes is attributed to forbidden transitions, where $M = \pm 1$ (M = electron spin quantum number). The broadening of spectra is due to immobilization of Mn(II) ion in the ligand results because the rotational motion of Mn(II) is highly restricted. Another origin of line broadening is due to spin relaxation, which is temperature dependent. All the Mn(II) complexes, under study, shows isotropic EPR spectra (Fig. 6), when recorded as polycrystalline sample. In DMF solution, Mn(II) complexes give EPR spectra containing the six lines, arising due to the hyperfine interaction between the unpaired electron with the ^{55}Mn nuclear (1 = 5/2). The nuclear magnetic quantum number M_1, corresponding to these lines are −5/2, −3/2, −1/2, +1/2, +3/2 and +5/2 from low to the high field. The g-tensor values have been calculated by the Kneubuhl method and the results are shown in Table 3.

The parameters B and C were calculated from the second and third transitions because these transitions are free from the crystal field splitting and depend on B and C parameters [16]. The values of Dq were obtained with the help of curve, transition energies versus Dq, as given by the Orgel [21] using

Table 3
EPR spectral data of the complexes

Complex	Temperature	g_{iso}	A_0
[Mn(LLA)$_2$Cl$_2$]	R.T.	1.9656	109.5760
[Mn(LLA)$_2$]SO$_4$	R.T.	1.9992	102.5000
[Mn(LLB)$_2$Cl$_2$]	R.T.	1.9986	121.6667
[Mn(LLB)$_2$]SO$_4$	R.T.	2.0014	119.6667
[Mn(LLC)$_2$Cl$_2$]	R.T.	2.0739	112.1678
[Mn(LLC)$_2$]SO$_4$	R.T.	2.0080	105.0000
[Mn(LLD)$_2$Cl$_2$]	R.T.	2.0152	105.9832
[Mn(LLD)$_2$]SO$_4$	R.T.	1.9998	106.4854

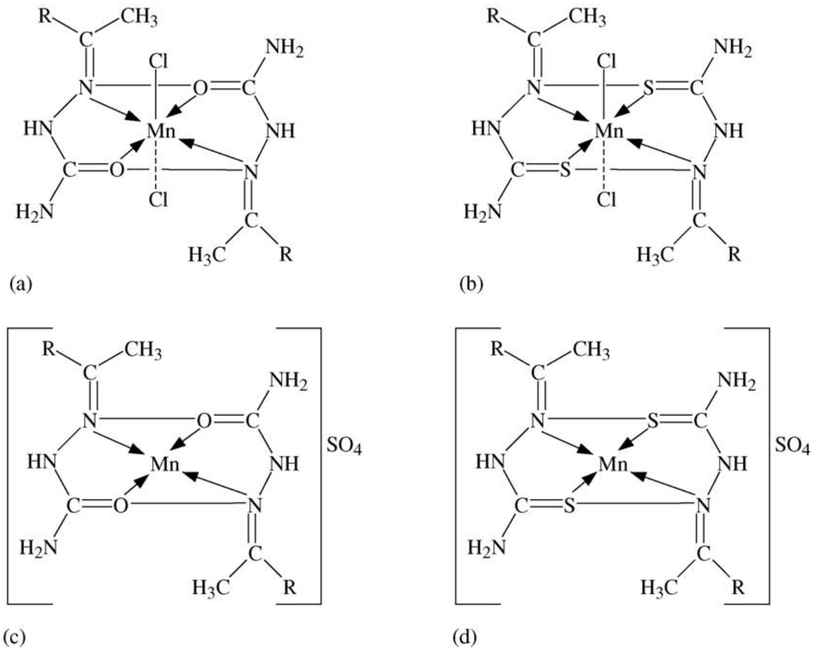


Fig. 5.

the energy due to the transition $^6A_{1g} \rightarrow {}^4T_{1g}$ (^4G). Parameters B and C are linear combinations of certain coulombs and exchange integral and are generally treated empirical parameters obtained from the spectra of the free ions. Slater Condon-shortly repulsion parameters F_2 and F_4 are related to Racah parameters B and C as: $B = F_2–5F_4$ and $C = 35F_4$, The electron–electron repulsion in the complexes is more than in the free ion, resulting in an increased distance between electrons, and thus, affects the size of the orbital. On increasing delocalization, the value of β decreases up to less than one in the complexes. The value of β can be calculated from the Nephelauxetic parameter for the ligand (h_x) and the Nephelauxetic parameter for the metal ion (km) as $(1-\beta) = h_x X$ km. The value of the parameter h_x for Mn(II) complexes have been calculated by using the co-valency contribution of Mn(II), while for the calculation of β, we used the numerical value of B for Mn(II) free ion which is 786 cm^{-1}. The observed values for parameter β and h_x suggest that the complexes, reported here, have appreciable ionic character [22,23]. The calculated values of the ligand field parameters are given in Table 4.

4. Experimental

All the chemicals used were of AnalaR grade, and procured from Sigma Aldrich and Fluka. Metal salts were purchased from E. Merck and were used as received.

4.1. Preparation of ligands

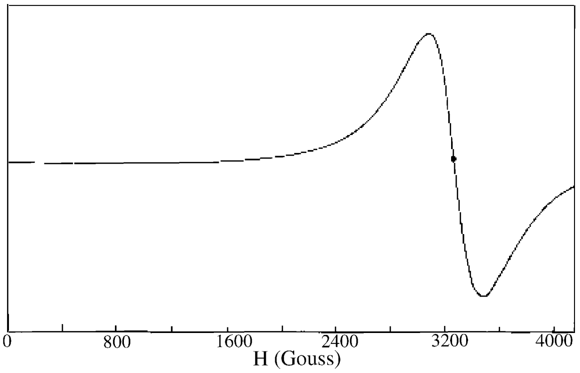
All the ligands were prepared by the methods reported earlier [24] by coupling of semicarbazide hydrochloride and thiosemicarbazide, respectively, with corresponding ketones.

4.2. Preparation of complexes

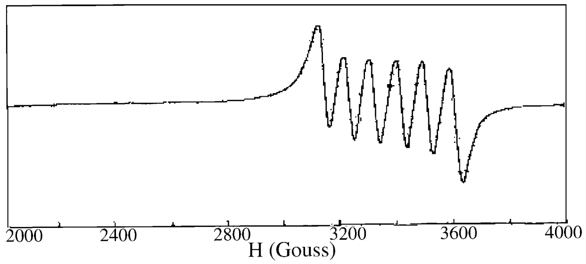
A general method has been adopted for the synthesis of the Mn(II) complexes. A hot (∼45 °C) aqueous ethanolic solution (20 mL, 1:1 v/v) of the hydrated metal salts (0.05 mole) and a hot ethanolic solution (20 mL) of the respective ligand (0.1 mole) were mixed with constant stirring. The mixture was refluxed for about 5 h at a temperature of ∼75 °C. On cooling the contents to a temperature of ∼5 °C, the com-

Table 4
Ligand field parameters of the complexes

Complex	Dq (cm^{-1})	B (cm^{-1})	β	C (cm^{-1})	F_4	F_2	ν_2/ν_1	h_x
$[Mn(LLA)_2Cl_2]$	1789	1003.71	0.64	2361.78	67.48	1341.11	1.22	5.14
$[Mn(LLA)_2]SO_4$	2269	1282.86	0.82	3018.28	86.24	1714.06	1.23	2.57
$[Mn(LLB)_2Cl_2]$	1775	964.86	0.61	2541.08	72.60	1327.86	1.26	5.57
$[Mn(LLB)_2]SO_4$	2198	1273.71	0.81	3067.78	87.65	1711.96	1.28	2.71
$[Mn(LLC)_2Cl_2]$	1826	1048.29	0.67	2299.82	65.71	1376.84	1.20	4.71
$[Mn(LLC)_2]SO_4$	2311	1279.14	0.81	3011.92	86.05	1709.39	1.21	2.71
$[Mn(LLD)_2Cl_2]$	1791	907.14	0.58	2668.92	76.26	1288.44	1.25	6.00
$[Mn(LLD)_2]SO_4$	2246	1345.14	0.86	2899.32	82.84	1759.34	1.24	2.00



(a) [Mn(LLA)$_2$Cl$_2$] as polycrstalline sample



(b) [Mn(LLA)$_2$Cl$_2$] in DMF solution

Fig. 6. Suggested structures of the complexes: chloro complexes of (a) semicarbazone and (b) thiosemicarbazone; sulphato complexes of (c) semicarbazone and (d) thiosemicarbazone.

plexes were separated out. They were filtered, washed with 50% ethanol and dried over P$_4$O$_{10}$ under vacuum. The complexes were recrystallized.

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