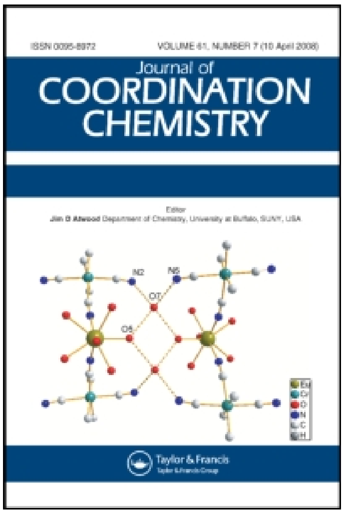

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Manganese(II) complexes with bis(3-halo-2-hydroxy- 5-methylacetophenone)ethylenediamine; structure, characterization and redox behavior

Aurel Pui[a]
[a] Faculty of Chemistry, “Al. I. Cuza” University, 700506-Iasi, Romania

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Manganese(II) complexes with bis(3-halo-2-hydroxy-5-methylacetophenone)ethylenediamine; structure, characterization and redox behavior

AUREL PUI*

Faculty of Chemistry, "Al. I. Cuza" University, Bvd. Carol I, No. 11,
700506 – Iasi, Romania

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A series of manganese(II) complexes containing tetradentate Schiff-base ligands have been synthesized. The Schiff-base ligands were obtained by condensation of salicylaldehyde, 2-OH acetophenone or 2-OH, 3-X, 5-methyl acetophenone with ethylenediamine (X = Cl, Br, I). The complexes have been characterized by elemental analysis, IR, UV-VIS, ESMS, EPR spectroscopy, cyclic voltammetry and thermal analysis. The cyclic voltammograms of the complexes exhibit quasi-reversible behavior. The electrochemical potentials are influenced by the methyl and halogen atoms grafted on the ligand molecules. An EPR spectrum for the polycrystalline sample shows one broad isotopic signal as compared with the six lines for frozen solution in DMF.

Keywords: Manganese(II) complexes; Schiff bases; Synthesis; Characterization; Cyclic voltammetry; EPR; Magnetic and thermal studies

1. Introduction

Transition metal cations such as Co(II), Cu(II), Mn(II), Mn(III), Cr(III), etc., form metallic complexes with quadridentate Schiff bases, which have been the subject of several investigations [1–5]. Complexes of transition metals with Salen derivatives have been used in solution as biomimetic catalysts for oxygen atom transfer, as catalysts for enantioselective epoxidation, as catalysts for organic redox reactions and as mediators for other oxidative processes [6–10]. Manganese complexes play an essential role in biological redox chemistry [11]. At present, manganese complexes with Schiff bases are involved in catalytic epoxidation of olefins and other substrates and for design of artificial metalloproteins [12, 13].

This article reports the synthesis and characterization of a series of coordination compounds of manganese(II) with Schiff bases. The redox potential of the Mn(II) complexes can be regulated by substituents grafted on the aromatic ring and in the azomethynic position. The properties of these complexes are compared with those of

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*Email: aurel@uaic.ro

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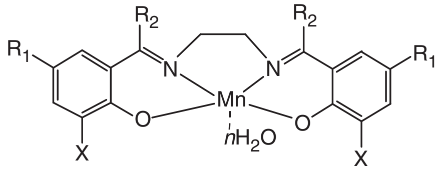

$n = 2$ for complexes **2** and **3**, and $n = 0$, for complexes **4**, **5** and **6**.

X	R_1	R_2	Name	Notation
H	H	H	Manganese(II) Salen	(**1**)
H	H	CH_3	Di-methyl Salen manganese(II)	(**2**)
H	CH_3	CH_3	Tetra-methyl Salen manganese(II)	(**3**)
Cl	CH_3	CH_3	Di-chloro tetra-methyl Salen manganese(II)	(**4**)
Br	CH_3	CH_3	Di-bromo tetra-methyl Salen manganese(II)	(**5**)
I	CH_3	CH_3	Di-iodo tetra-methyl Salen manganese(II)	(**6**)

Figure 1. General formula of the Mn(II) complexes.

the MnSalen (**1**) and Mn(dMeSalen) (**2**) complexes. The general formula of the Mn(II) complexes is presented in figure 1.

2. Experimental

2.1. *Materials and apparatus*

Solvents and starting materials were of analytical grade and used without further purification. Elemental analysis (C, H, and N) was performed by the Service of Microanalyses from Gif-sur-Yvette, France. ^{1}H-NMR spectra for ligands were recorded on a Brucker AM 250 or AC 250 spectrometers operating at 250 MHz. All spectra were obtained in $CDCl_3$ and chemical shifts calculated in ppm with respect to TMS ($\delta = 0$). UV–Vis spectra, in DMF solution ($c = 10^{-4}$ M), were taken on a DES device, operating with the SAFAS program. The FT IR spectra were obtained on a Bruker IFS 66 apparatus in KBr pellet.

Cyclic voltammetry experiments were performed on an Autlab apparatus. The recordings were made, at room temperature, in a 2 mM solution in DMF under argon atmosphere, using lithium perchlorate as supporting electrolyte. The following material was used for analysis: a vitreous carbon electrode ($A = 4.0\,\mathrm{mm}^2$), as working electrode; a saturated calomel electrode (SCE), as reference electrode and a platinum wire as auxiliary electrode.

ESMS spectra were recorded on an XCalibur device in $MeOH/CH_2Cl_2/H_2O$ solution at 3 kV.

The EPR spectra of the complexes have been recorded for the polycrystalline sample, in frozen DMF solution at 100 K on a Brucker Elexis apparatus. An EPR sample was prepared starting from 1.2 mg of complex dissolved in 2 mL of degassed DMF under argon. Approximately 0.3 mL of complex solution was then syringed into a quartz EPR tube sealed with a septum under argon. Then, the tube was placed in liquid nitrogen, for freezing, and then in an EPR device to be analyzed.

Magnetic susceptibility measurements were made on solid samples by a Quantum Desing model MPMS, SQUID. The measurements were calibrated using a recrystallized $HgCo(NCS)_4$ standard. The appropriate diamagnetic corrections were made.

Thermal analysis was carried out on a MOM Budapest device, within the temperature range 25–1000°C, at a heating rate of 10°C min^{-1}.

2.2. *Synthesis of the ligands*

The 2-hydroxy-3-chloro-5-methylacetophenone was obtained by Friedel-Crafts substitution of the corresponding 2-chloro-4 methylphenols with acetylchloride [14]. The 2-hydroxy-3-bromo-5-methylacetophenone was obtained by bromination of 2-hydroxy 5-methyl acetophenone with pyridiniumbromochromate (PBC) [15]. The 2-hydroxy-3-iodo-5-methylacetophenone was obtained by iodination of 2-hydroxy-5-methylacetophenone with I_2 in the presence of HgO [16]. The Schiff-base ligands were obtained by condensation of 2-hydroxy 3-halo-5-methylacetophenone with ethylenediamine in 2/1 molar ratio, in EtOH solution at 45°C and the mixture was stirred for 2 h [17]. After cooling to room temperature, the solid was filtered and successively washed with water, ethanol–water mixture and absolute ethanol. The ligands were analyzed by elemental analysis and ^{1}H NMR.

α,α'-Dimethyl Salen (dMeSalen), **2**, yellow (yield 91%). Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.82; H, 6.77; N, 9.41. ^{1}H NMR: 13.29 (s, 2H, OH), 7.54–7.24 (m, 4H, Har), 6.92–6.72 (m, 4H, Ar), 3.98 (s, 4H, CH_2), 2.84 (s, 6H, CH_3).

α,α',5,5′-Tetramethyl Salen (tMeSalen), **3**, yellow (yield 94%). Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.04; H, 7.46; N, 8.64. Found: C, 73.95; H, 7.52; N, 8.63. ^{1}H NMR: 12.98 (s, 2H, OH), 7.30–7.01 (m, 4H, Har), 6.84 (d, 2H, Ar), 3.96 (s, 4H, CH_2), 2.36 (s, 6H, CH_3), 2.28 (s, 6H, CH_3).

3,3′-Dichloro-α,α',5,5′-tetramethyl Salen (dCltMeSalen), **4**, yellow (yield 92%). Anal. Calcd for $C_{20}H_{22}Cl_2N_2O_2$: C, 61.08; H, 5.46; N, 7.12. Found: C, 60.94; H, 5.39; N, 7.08. ^{1}H NMR: 12.96 (s, 2H, OH), 7.25–7.20 (m, 4H, Ar), 4.00 (s, 4H, CH_2), 2.39 (s, 6H, CH_3), 2.26 (s, 6H, CH_3).

3,3′-Dibromo-α,α',5,5′ tetramethyl Salen (dBrtMeSalen), **5**, yellow (yield 88%). Anal. Calcd for $C_{20}H_{22}Br_2N_2O_2$: C, 49.82; H, 4.60; N, 5.81. Found: C, 49.78; H, 4.49; N, 5.78. ^{1}H NMR: 12.85 (s, 2H, OH), 7.44–7.23 (m, 4H, Ar), 4.00 (s, 4H, CH_2), 2.41 (s, 6H, CH_3), 2.27 (s, 6H, CH_3).

3,3′-Diiodo-α,α',5,5′-tetramethyl Salen (dItMeSalen), **6**, yellow (yield 83%). Anal. Calcd for $C_{20}H_{22}I_2N_2O_2$: C, 41.69; H, 3.85; N, 4.86. Found: C, 41.60; H, 3.78; N, 4.83. ^{1}H NMR: 12.99 (s, 2H, OH), 7.67–7.29 (m, 4H, Ar), 3.99 (s, 4H, CH_2), 2.39 (s, 6H, CH_3), 2.25 (s, 6H, CH_3).

2.3. *Synthesis of the complexes*

The manganese(II) complexes were synthesized by general methods [18]. To a stirred solution of 1 equivalent of ligand dissolved in 25 mL of ethanol at 40°C under argon was added 1 equivalent of $Mn(OAc)_2 \cdot 4H_2O$ dissolved in 5 mL water. The precipitate is deposited immediately. The mixture is further stirred at 40°C for 1 h. After cooling at room temperature, the solid is filtered under N_2 and washed with water, ethanol–water (1/1 vol) mixture and absolute ethanol. After drying *in vacuo*, the manganese complex is isolated and analyzed. The obtained yield and colors are: [Mn(dMeSalen)$(H_2O)_2$] (**2**), yellow solid, isolated (yield 65%), [Mn(tMeSalen)$(H_2O)_2$] (**3**) yellow solid, isolated

Table 1. Analytical, ESMS data and magnetic moments for the manganese(II) complexes.

Complexes	Formula	m/z	Anal.: Calcd (found) C (%)	H (%)	N (%)	μ_{eff} (BM)
2	$MnCi_8Hi_8N_2O_2 \cdot 2H_2O$	349.3	56.11 (55.95)	5.75 (5.67)	7.27 (7.23)	5.91
3	$MnC_{20}H_{22}N_2O_2 \cdot 2H_2O$	377.2	58.11 (58.02)	6.34 (6.25)	6.78 (6.73)	5.89
4	$MnC_{20}H_{20}Cl_2N_2O_2$	446.2	61.08 (59.92)	5.64 (5.57)	7.12 (7.09)	6.02
5	$MnC_{20}H_{20}Br_2N_2O_2$	535.0	44.89 (44.72)	3.77 (3.69)	5.23 (5.21)	6.01
6	$MnC_{20}H_{20}I_2N_2O_2$	629.4	38.18 (38.07)	3.20 (3.16)	4.45 (4.41)	5.98

(yield 72%), [Mn(dCltMeSalen)] (**4**), yellow solid, isolated (yield 68%); [Mn(dBrtMeSalen)] (**5**), yelow solid, isolated (yield 59%); [Mn(dItMeSalen)] (**6**), light brown solid, isolated (yield 53).

3. Results and discussions

3.1. *Synthesis and characterization*

The 2-hydroxy 3-halogeno 5-methyl acetophenones have been obtained by various methods of halogen introduction in the aromatic ring [14–16]. The Schiff base ligands (H_2L) have been prepared by condensation of the 2-HO, 3-X, 5-methyl-acetophenone derivative (where X is Cl, Br, I) with 1,2 ethylenediamine in 2 : 1 molar ratio [17]. The ligands were characterized after recrystallization from methanol by elemental analysis, ^{1}H NMR, IR and UV-VIS spectroscopy. They proved to be of high purity and the IR structure was in accord with that proposed for formation of the complexes presented in figure 1.

The manganese complexes were prepared by mixing equimolar solutions of $Mn(OAc)_2 \cdot 4H_2O$ in water with absolute alcoholic solution of the corresponding Schiff-base ligand [18]. The analytical data are shown in table 1.

The elemental analyses and the ESMS indicated formation of 1 : 1 molar ratio complexes. Complexes **1**, **2** and **3** contained two molecules of water. The other complexes **4**, **5**, and **6** had no coordinated water probably because of steric hindrance. ESMS spectra confirmed all these compositions. Figure 2 presents both obtained and simulated spectra for complex **5**.

Figure 2(a) shows formation of the 1/1 molar ratio complexes and their high purity by agreement with the simulated spectrum. The other peaks around the maxima were attributed to bromide isotopes. Similar results were obtained for the other complexes.

3.2. *Electronic spectra*

The electronic spectra of the free ligands in DMF show two strong absorption bands in the UV–Vis region (300–420 nm), which were attributed to the π–π* and n–π* transitions [19, 20]. The spectra of the Mn(II) complexes exhibited some modifications regarding the position and intensity of the characteristic bands for free ligands, as well as new weak, characteristic absorptions in the visible region. Sometimes, the

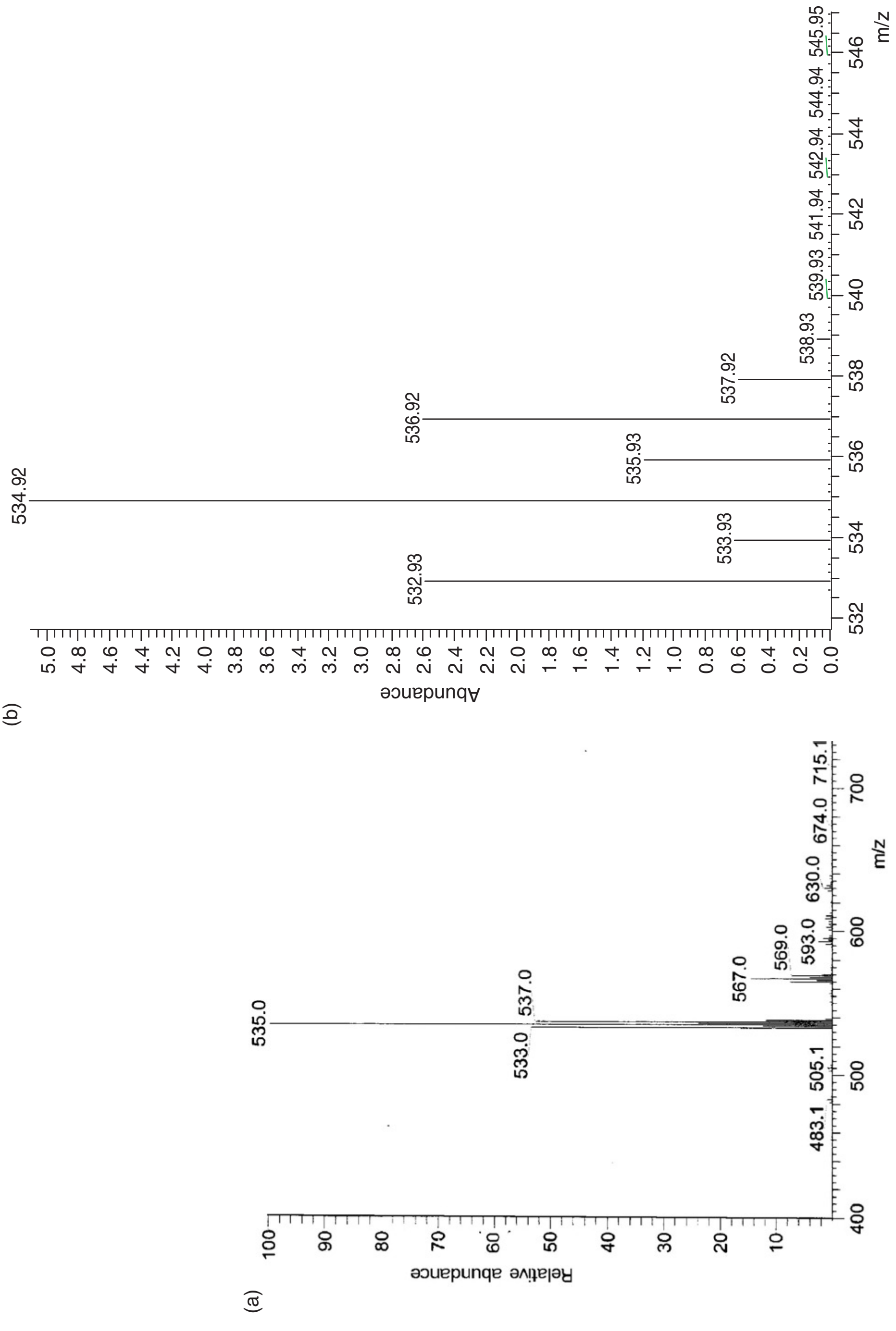

Figure 2. ESMS spectra for **5**: (a) obtained, (b) simulated.

Table 2. Electronic spectral data for the manganese(II) complexes in DMF.

Compounds	λ_1, nm (ε, $1\,mol^{-1}\,cm^{-1}$)	λ_2, nm (ε, $1\,mol^{-1}\,cm^{-1}$)	λ_3, nm (ε, $1\,mol^{-1}\,cm^{-1}$)	λ_4, nm (ε, $1\,mol^{-1}\,cm^{-1}$)
Mn(dMeSalen)	230 (3.00)	322 (3.23)	410 (3.27)	560 (2.51)
Mn(tMeSalen)	280 (3.25)	320 (3.32)	410 (3.24)	564 (2.33)
Mn(dCltMeSalen)	298 (3.29)	332 (3.19)	426 (3.28)	562 (2.53)
Mn(dBrtMeSalen)	276 (3.88)	324 (2.91)	444 (2.86)	570 (2.61)
Mn(dItMeSalen)	265 (4.17)	347 (3.96)	422 (3.08)	568 (2.47)

Table 3. Significant FT IR spectral bands (cm^{-1}) for the manganese complexes.

Compounds	ν_{H_2O}	$\nu_{C=N}$ Complexes	Free ligands	New bands ν_{M-N}	ν_{M-O}
Mn(Salen)	3450	1610	1603	523	465
Mn(dMeSalen)	3404	1609	1601	547	500
Mn(tMeSalen)	3432	1612	1605	518	433
Mn(dCltMeSalen)	–	1612	1604	541	530
Mn(dBrtMeSalen)	–	1614	1603	523	434
Mn(dItMeSalen)	–	1610	1601	516	429

weak d–d bands were not very well-defined and submerged in the tail of the charge transfer bands.

The UV–Vis bands for the Mn(II) complexes and their intensities are shown in table 2.

The manganese(II) complexes showed broad bands of low intensity in the UV–Vis range assigned to the spin-forbidden d–d transition or charge–transfer d–π* transitions [21].

The bands from 230–444 can be attributed to intraligand transitions, modified by complexation. Over the π–π* or n–π* transitions of the ligands, from 400–450, are superimposed d-d and d–π* transitions. The formation of the complexes were distinguished by the occurrence of new bands over 500 nm, attributed to the d–d or d–π* transitions for the divalent Mn(II) as well. In some cases the d–d transitions were not very well defined and observed as a shoulder.

3.3. *Infrared spectra*

The IR spectra of the ligands showed major bands around $1600\,cm^{-1}$ assigned to $\nu_{C=N}$, around 1560 and $1500\,cm^{-1}$, assigned to ring vibration, around $1280\,cm^{-1}$ assigned to OH phenolic deformation, around $1230\,cm^{-1}$, assigned to ν_{C-N} and around $1050\,cm^{-1}$ assigned to ν_{C-O} [21, 22]. In spectra of the complexes, the $\nu_{C=N}$ stretching mode is shifted to lower frequency with additional shifts in the bands corresponding to C–N and C–O compared with free ligands. Also, the characteristic ligand bands for the outside deformation the Ar–OH plane ($1280\,cm^{-1}$) were absent in the complexes, a consequence of the involvement of the oxygen anion into a σ-bond with the metallic center. Formation of the metal–oxygen σ-bond and metal-nitrogen π-bond cause new absorption bands in the 400–660 cm^{-1} region. The most important IR absorption frequencies of the manganese complexes and $\nu_{C=N}$ for the corresponding ligands are listed in table 3.

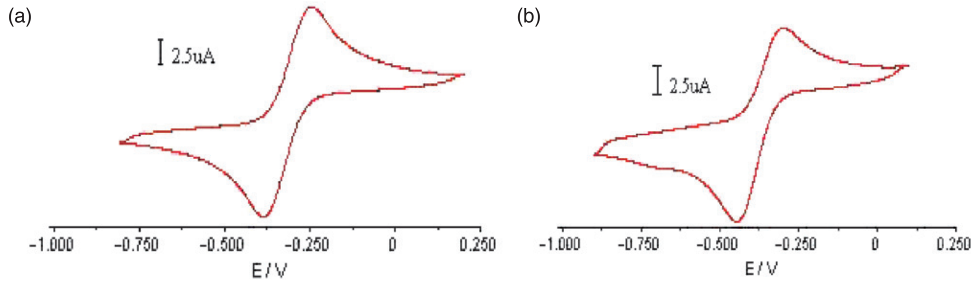

Figure 3. Cyclic voltammograms for complexes **1** (a), and **6** (b) $C_{MnL} = 2 \cdot 10^{-3}$ M, in DMF, scan rate = 0.1 V s^{-1}, *vs.* the saturated calomel electrode (SCE).

Table 4. Electrochemical data for the obtained complexes.

Compounds	E_{pa} (V)	E_{pc} (V)	ΔE (V)	$E_{1/2}$ (V)	$E'_{1/2}$ (V)
1	−0.243	−0.383	0.140	−0.313	0.153
2	−0.350	−0.496	0.145	−0.423	0.043
3	−0.388	−0.600	0.212	−0.494	−0.028
4	−0.311	−0.428	0.117	−0.370	0.096
5	−0.302	−0.442	0.140	−0.372	0.094
6	−0.300	−0.452	0.152	−0.376	0.096

$c = 2 \times 10^{-3}$ in DMF and 0.1 M $LiClO_4$; scan rate 100 mV s^{-1}; E_{pa} and E_{pc} are the anodic and cathodic peak potentials.

The IR spectra support formation of the complexes by coordination of manganese to the azomethinic nitrogen and to the phenolic oxygen [23].

According to the elemental analysis, UV–Vis and FT IR data we suggest that the complexes have the structure presented in figure 1.

3.4. *Electrochemistry*

Generally, redox potential is considered an important parameter in electron transfer processes and catalytic studies. Figure 3 shows the cyclic voltammograms, in DMF (*vs.* SCE), under argon, for **1** and **6**.

The values of the anodic and cathodic peaks (E_{pa}, E_{pc}), and of semiwaves ($E_{1/2}$), for the manganese complexes are listed in table 4.

The cyclic voltammetry showed a *quasi*-reversible behavior for all these complexes. For easy correlation of the obtained values with literature data, the $E_{1/2}$ value of the complexes are reported to ferrocenium couple (+0.466 V). The peaks (E_{pa} and E_{pc}) were assignable to $Mn(II) \rightleftharpoons Mn(III) + 1e^-$ (oxidation and reduction) processes [24]. The $E_{1/2}$ value for the Mn(III)/Mn(II) couple for **2** was found to be more negative than **1**, indicating that the presence of a methyl group in azomethynic position increases the electron density on the metallic ion, making it more oxidizable than **1**. The presence of a methyl group *para* to the oxygen leads to an increase of electronic density of the manganese, and the $E_{1/2}$ (also E_{pa} and E_{pc}) peaks become more negative.

The presence of electronegative substituents (Cl, Br, I) *ortho* to the oxygen, for complexes **4**, **5** and **6**, make oxidation of Mn(II) more difficult than **3**. The potentials of

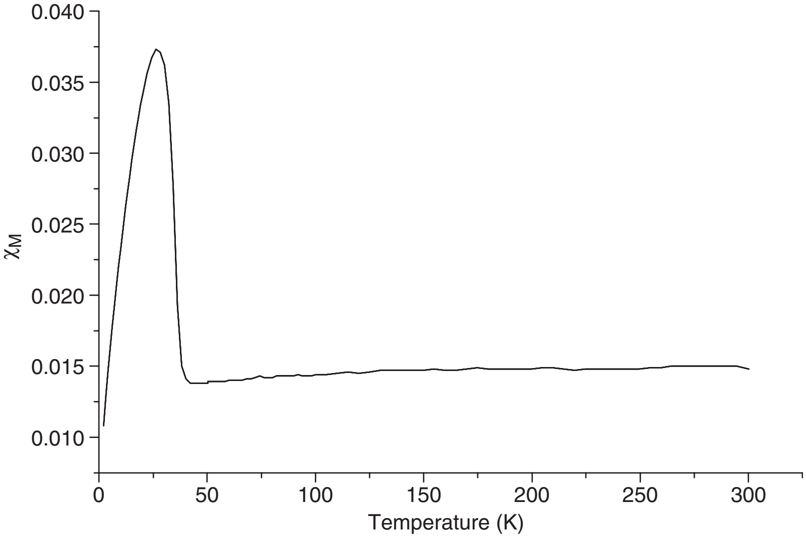

Figure 4. Magnetic susceptibility of **5** collected at 1000G plotted as χ_M *vs.* temperature (K).

4, **5**, and **6** were in agreement with the electronegative value (**4** > **5** > **6**) for the halogens. The effect of varying the substituents around the phenyl ring and in azomethynic position of the ligands leads to a window of 181 mV for this redox process. Thus, the redox behavior of Mn(II) complexes could be regulated by employing electron-withdrawing groups e.g. CH_3, Cl, Br, I, etc. on the aromatic ring or azomethynic position [25].

3.5. *Ground state electronic structure*

3.5.1. Magnetic measurement. The magnetic moment, μ_{eff} of these complexes was found to be in the range 5.71–6.10 μ_B (table 1), at 300 K. These values are in accord with the spin-only value of 5.92 μ_B as expected for an isolated $S = 1/2$ Mn(II) monomer. Variable-temperature magnetic susceptibility data (2–300 K) were collected for **5** in an applied magnetic field of 1000G (figure 4).

The susceptibility data turn over at 30 K, indicating the presence of an antiferromagnetic exchange interaction.

3.5.2. EPR studies. The EPR of the complexes were recorded for the polycrystalline sample as well as for DMF solution (figure 5). The EPR spectrum of the polycrystalline sample showed an isotopic signal centered approximately at the free electron g value (2.01). The EPR of the mononuclear complexes of manganese(II) should exhibit six hyperfine lines (^{55}Mn, number of lines $= 2I + 1$) [18]. The EPR spectrum of the frozen solution (in DMF) for **4** shows six lines (figure 4) arising due to hyperfine interaction between the unpaired electrons of the Mn(II) ions ($I = 5/2$). The broadening of the spectra in DMF solution was due to spin relaxation.

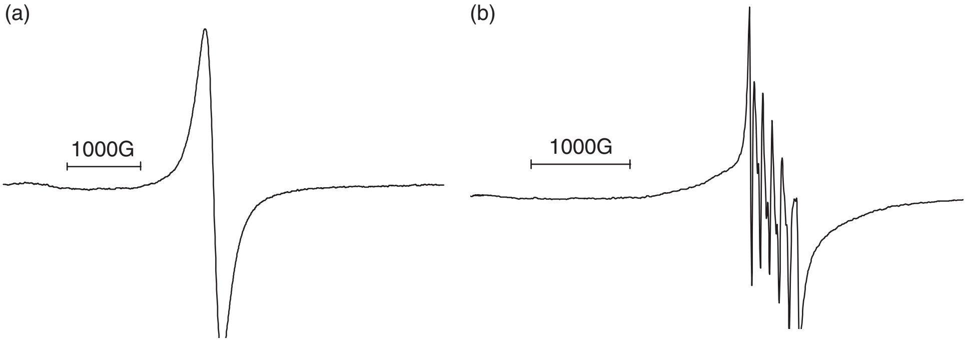

Figure 5. EPR spectra for **4**: polycrystalline (a) and DMF frozen solution (b), at 10 K.

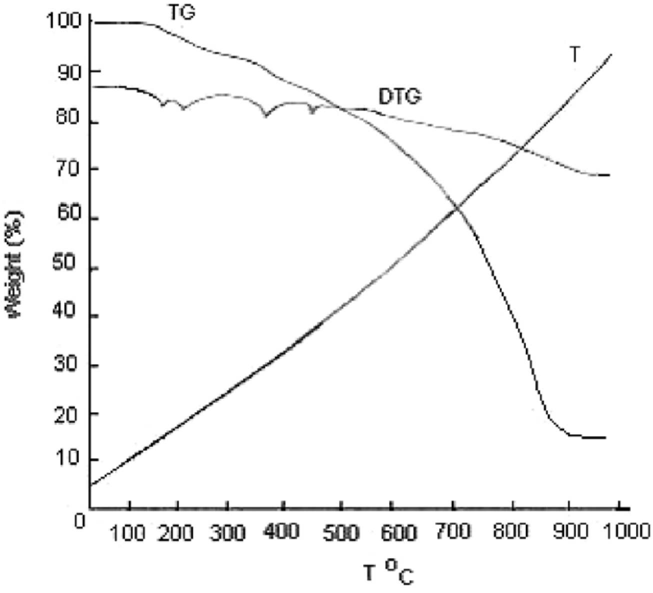

Figure 6. TG, DTG and *T* curves for **5**.

The characteristic values are $g = 2.009$, and $A = 96$, in agreement with the value for other Mn(II) complexes [21].

3.6. *Thermal analysis*

The TG and DTG studies were carried out in the range 25–1000°C representative TG and DTG were plotted for complex **5** in figure 6. Thermograms of all the complexes showed no weight loss up to 160°C, indicating the absence of free water in the complexes.

The first stage of decomposition (in two steps) occurring at 180–290°C with a loss of 11.2% is attributed to removal of the methyl (from the azomethynic and 5 position).

The second stage of decomposition at 290–360°C with a loss of 4.5% may be due to the loss of aliphatic diamine moiety. The next loss of mass corresponding to decomposition of the complexes started with a bromide. A metallic oxide Mn_3O_4 was formed as the final form (experimental: 14.18%, calculated: 14.26%) [26].

4. Conclusion

Mn(II) cations coordinate to tetradentate Schiff bases and form six-coordinate Mn(II) complexes with two water or solvent molecules in the axial positions. The UV–Vis and IR spectra show modification of the free ligand bands and the appearance of new bands, which are characteristic for the metal ion and for the metal–donor atoms bound by the ligands. The data from the cyclic voltammetry indicated a quasi-reversible behavior of the complexes. The ESMS and thermal analyses indicate the formation of the complexes **1**, **2**, and **3** with two coordination water molecules while complexes **4**, **5** and **6** are not coordinated with water, probably because of steric hindrance. The $E_{1/2}$ values are in concordance with the structure of the complexes. The EPR spectra and magnetic studies confirmed the manganese(II) electronic structure.

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