## Journal of Molecular Structure 1151 (2018) 343-352



Contents lists available at ScienceDirect

# Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

# Low-spin manganese(II) and high-spin manganese(III) complexes derived from disalicylaldehyde oxaloyldihydrazone: Synthesis, spectral characterization and electrochemical studies





Ibanphylla Syiemlieh <sup>a</sup>, Arvind Kumar <sup>b</sup>, Sunshine D. Kurbah <sup>a</sup>, Arjune K. De <sup>c</sup>, Ram A. Lal <sup>a, \*</sup>

<sup>a</sup> Department of Chemistry, Centre for Advanced Studies, North-Eastern Hill University, Shillong, 793022, India

<sup>b</sup> Department of Chemistry, Faculty of Science and Technology, The University of Wes- Indies, St. Augustine, Trinidad and Tobago

<sup>c</sup> Department of Science and Humanities, Tripura Institute of Technology, Narsingarh, 799009, Tripura, India

## ARTICLE INFO

Article history: Received 9 May 2017 Received in revised form 16 September 2017 Accepted 18 September 2017 Available online 19 September 2017

Keywords: ESR Oxaloyldihydrazone Redox activity Low-spin manganese(II) High-spin manganese(III)

# ABSTRACT

Low-spin manganese(II) complexes [Mn<sup>II</sup>(H<sub>2</sub>slox)].H<sub>2</sub>O (1), [Mn<sup>II</sup>(H<sub>2</sub>slox)(SL)] (where SL (secondary ligand) = pyridine (py, 2), 2-picoline (2-pic, 3), 3-picoline (3-pic, 4), and 4-picoline (4-pic, 5) and highspin manganese(III) complex Na(H<sub>2</sub>O)<sub>4</sub>[Mn<sup>III</sup>(slox)(H<sub>2</sub>O)<sub>2</sub>].2.5H<sub>2</sub>O have been synthesized from disalicyaldehyde oxaloyldihydrazone in methanolic - water medium. The composition of complexes has been established by elemental analyses and thermoanalytical data. The structures of the complexes have been discussed on the basis of data obtained from molar conductance, UV visible, <sup>1</sup>H NMR, infrared spectra, magnetic moment and electron paramagnetic resonance spectroscopic studies. Conductivity measurements in DMF suggest that the complexes (1-5) are non-electrolyte while the complex (6) is 1:1 electrolyte. The electronic spectral studies and magnetic moment data suggest five - coordinate square pyramidal structure for the complexes (2–5) and square planar geometry for manganese(II) in complex (1). In complex (6), both sodium and manganese(III) have six coordinate octahedral geometry. IR spectral studies reveal that the dihydrazone coordinates to the manganese centre in keto form in complexes (1 -5) and in enol form in complex (6). In all complexes, the ligand is present in *anti*-cis configuration. Magnetic moment and EPR studies indicate manganese in +2 oxidation state in complexes (1-5), with low-spin square planar complex (1) and square pyramidal stereochemistries complexes (2-5) while in +3 oxidation state in high-spin distorted octahedral stereochemistry in complex (6). The complex (1) involves significant metal - metal interaction in the solid state. All of the complexes show only one metal centred electron transfer reaction in DMF solution in cyclic voltammetric studies. The complexes (1 -5) involve Mn<sup>II</sup> $\rightarrow$ Mn<sup>I</sup> redox reaction while the complex (6) involves Mn<sup>III</sup> $\rightarrow$ Mn<sup>II</sup> redox reaction, respectively.

© 2017 Elsevier B.V. All rights reserved.

# 1. Introduction

Manganese is an essential trace element occurring in the biological systems [1,2], and plays a significant role in electron and oxygen transfer processes in nature with iron and copper. Although manganese occurs in some of the enzymes as Mn(II), in other biological systems, it occurs in higher oxidation states, such as Mn(III) and Mn(IV) like oxygen evolving complex [3] and as Mn(III)

\* Corresponding author. E-mail address: ralal@rediffmail.com (R.A. Lal). in manganese superoxide dismutase. The divalent high-spin manganese complexes are quite common in the field of coordination chemistry. They do not have strong stereo - chemical preferences as it is controlled by the nature of the ligand and hence its complexes can exist in square planar, tetrahedral, trigonal bipyramidal, square pyramidal, octahedral and pentagonal bipyramidal stereochemistries etc. Although high-spin manganese(II) complexes have been extensively studied but low-spin manganese complexes are very few in number. Manganese(II), has very high spin-pairing energy amongst 3d metal ions. Hence, ligands with very strong ligand fields only can induce low-spin character on manganese ion. Cyano- [4,5], phosphine- [6], dithiochelate ligands [7], and oxime ligands [8]. Goswami and co-workers [9] and others [10,11] have recently reported low-spin manganese complexes. The manganese(II) complexes in low oxidation states are commonly 6 coordinate octahedral. Further, four coordinate Mn(II) or Mn(III) complexes in high-spin state are known to be present in distorted square planar or tetrahedral geometries but these geometries are uncommon for low-spin manganese(II) or manganese(III) complexes.

The hydrazones are multidentate molecules and find application in many fields such as pharmacology [12,13], analytical chemistry [14,15] and technology [16,17] etc. Such molecules are capable of exhibiting keto-enol tautomerism.

The polyfunctional dihydrazone used in the present study has been derived from condensation of oxaloyldihydrazine with salicyaldehyde. The two dihydrazone grouping are directly bonded to one another and hence give rise to better multidentate ligand than monohydrazones. It possesses as many as eight oxygen and nitrogen donor atoms offering several alternate modes of bonding and is capable of giving monometallic, homobimetallic, heterometallic, homomultimetallic and heteromultimetallic complexes.

It is evident from the literature survey that although work on metal complexes of monohydrazide based ligands and their Schiff bases has been carried out in some detail [18–20], those on metal complexes of dihydrazones are quite meagre [21–23]. Moreover, the work on manganese(II) and manganese(III) complexes with dihydrazones in low spin state is almost non-existent. Hence, in view of the polyfunctional nature of disalicyaldehyde oxaloyldi-hydrazone and its possibility to offer several alternate bonding mode in the complexes and meagre amount of work on the manganese(II) and manganese(III) complexes of dihydrazones, we have decided to explore the possibility of coordination of dihydrazone to manganese(II) under different experimental conditions and isolate the resulting complexes and characterize them in solid and solution state. The electron transfer reactions of the complexes have also been studied by cyclic voltammetry.

#### 2. Experimental section

All reagents and chemicals were E-Merck or equivalent grade, and all solvents were used as received.

### 2.1. Physical measurements

Manganese [24] was determined by standard literature procedure.

Carbon, hydrogen and nitrogen analyses were carried out on a Perkin-Elmer 2400 CHNS/O Analyzer. The molar conductance of the complexes at  $10^{-3}$  M dilution in DMF solution were measured on a Direct Reading Conductivitymeter-303 with a dip type conductivity cell at room temperature. The loss of weight of the complexes was determined by heating the compounds at 110 °C, 180 °C and 220 °C for 4 h in an electronic oven. The thermogravimetric analyses of the complexes were carried out on the perkin-Elmer STA 6000 (Simultaneous Thermal Analyzer) model in a ceramic crucible under dynamic nitrogen atmosphere. The heating rate of the complexes was maintained at 20 °C/min<sup>-1</sup>. The DTA standard used in the experiment is Pt 10% Rh. Infrared spectra in the range 4000–400/500 cm<sup>-1</sup> were measured on Perkin-Elmer, model 983 spectrophotometer with samples investigated as KBr discs. Room temperature magnetic susceptibility measurements were made on Sherwood Magnetic Susceptibility Balance MSB-Auto. The electronic spectra of the complexes at  $10^{-5}$  M in DMF solution were measured from 200 to 1100 nm on a Perkin Elmer Lamda 25 UV/Vis Spectrophotometer at room temperature. <sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance II-

400 MHz in DMSO-d<sub>6</sub>. Tetramethyl silane (TMS) was used as an internal standard. The ESR spectra of the complexes were recorded in powder form as well as in DMSO glass at room temperature and LNT at X-band frequency. The electron transfer properties of the complexes were studied by cyclic voltammetry using CH Instrument Electrochemical Analyzer under nitrogen atmosphere. The electrolytic cell comprises of 3 electrodes, the working electrode was Pt disk while the reference electrode and auxiliary electrode were Ag/AgCl (3 M KCl) separated from the sample solution by a salt bridge. 0.1 M Tetra-*n*-butyl ammonium perchlorate (TBAP) was used as the supporting electrolyte.

#### 2.2. Preparation of disalicyaldehyde oxaloyldihydrazone

Oxaloyldihydrazine was prepared by reacting diethyloxalate (20 mL) and hydrazine hydrate (13 mL) in 1:2 M ratios under stirring for 30 min. The product thus isolated was recrystallized from  $H_2O$ . (Yield: 95%)

Disalicylaldehyde oxaloyldihydrazone (H<sub>4</sub>slox) was prepared by condensing oxaloyldihydrazine (3 g, 25.42 mmol), in hot H<sub>2</sub>O (100 mL) with salicylaldehyde (6.20 mL) in ethanol (20 mL) over hot plate at 70 °C with constant stirring for 1 h. The light yellow precipitate thus obtained was washed with hot H<sub>2</sub>O-ethanol, ethanol and finally with ether and dried over anhydrous CaCl<sub>2</sub>. (Yield: 93%)

# 2.3. Synthesis of $[Mn(H_2 slox)].H_2O(1)$

 $MnSO_4 \cdot H_2O$  (1 g, 5.91 mmol) was dissolved in  $H_2O$  (60 mL). This solution was added to a solution of  $H_4slox$  (0.64 g, 1.963 mmol) in MeOH (20 mL) and it was stirred vigorously for  $\frac{1}{2}$  hour to get a homogenous suspension. The reaction mixture was then refluxed for 6 h and filtered. The residue was washed with  $H_2O$ -MeOH, MeOH and finally with ether and dried in an electronic oven. (Yield: 90%)

Synthesis of  $[Mn(H_2slox)(A)]$  [A = pyridine (2),  $\alpha$ -picoline (3),  $\beta$ -picoline (4),  $\gamma$ -picoline (5)]

The complexes (2–5) were also prepared by following essentially the above method in which either pyridine (2) or  $\alpha$ -picoline (3) or  $\beta$ -picoline (4) or  $\gamma$ -picoline (5) was added into the reaction mixture consisting of MnSO<sub>4</sub>·H<sub>2</sub>O and H<sub>4</sub>slox maintaining MnSO<sub>4</sub>·H<sub>2</sub>O:H<sub>4</sub>slox:A molar ratio at 1:1:4 and refluxed the reaction mixture for 6 h (complex 2) while stirring the reaction mixture at room temperature for 6 h (complex 3–5). (Yield: 80% (2), 75% (3), 82% (4), 80% (5))

# 2.4. Synthesis of $Na(H_2O)_4[Mn(slox)(H_2O)_2]$ .2.5H<sub>2</sub>O (6)

This complex was also prepared by following essentially the above method and adding  $Na_2CO_3$  to the reaction mixture obtained by mixing  $MnSO_4 \cdot H_2O$  and  $H_4$ slox maintaining  $MnSO_4 \cdot H_2O$ :H4slox:Na<sub>2</sub>CO<sub>3</sub> molar ratio at 1:1:3.(Yield: 68%)

## 3. Results and discussion

Synthesis of the complex (1) was achieved by reacting  $MnSO_4 \cdot H_2O$  with ligand (H<sub>4</sub>slox) in aqueous methanol medium under reflux (complex 1) for 6 h maintaining  $MnSO_4 \cdot H_2O$  and ligand molar ratio at either 3:1 or 2:1 or 1:1. On the other hand, the complex (2) was achieved by reacting  $MnSO_4 \cdot H_2O$ , H<sub>4</sub>slox and pyridine (complex 2) under reflux for 6 h maintaining  $MnSO_4 \cdot H_2O$ :H<sub>4</sub>slox:pyridine molar ratio at 1:1:4. But, the complexes [Mn(H<sub>2</sub>slox)( $\alpha$ -pic)<sub>2</sub>] (3), [Mn(H<sub>2</sub>slox)( $\beta$ -pic)] (4) and [Mn(H<sub>2</sub>slox)( $\gamma$ -pic)] (5) were obtained when the MnSO<sub>4</sub>·H<sub>2</sub>O, H<sub>4</sub>slox and secondary ligand (SL) ligand were stirred at room

temperature for 6 h maintaining MnSO<sub>4</sub>·H<sub>2</sub>O:H<sub>4</sub>slox:SL at 1:1:4 M ratio (SL =  $\alpha$ -picoline (3),  $\beta$ -picoline (4),  $\gamma$ -picoline (5)). The complex Na(H<sub>2</sub>O)<sub>4</sub>[Mn<sup>III</sup>(slox)(H<sub>2</sub>O)<sub>2</sub>].2.5H<sub>2</sub>O (6) was obtained when a mixture of MnSO<sub>4</sub>·H<sub>2</sub>O, H<sub>4</sub>slox and Na<sub>2</sub>CO<sub>3</sub> was refluxed for 6 h maintaining MnSO<sub>4</sub>·H<sub>2</sub>O:H<sub>4</sub>slox:Na<sub>2</sub>CO<sub>3</sub> in a 1:1:3 M ratio. It is imperative to mention that under the basic condition of Na<sub>2</sub>CO<sub>3</sub> the aerial oxidation of Mn(II) occurs to Mn(III) to give the complex Na(H<sub>2</sub>O)<sub>4</sub>[Mn<sup>III</sup>(slox)(H<sub>2</sub>O)<sub>2</sub>].2.5H<sub>2</sub>O.

The complexes with their colour, decomposition point, elemental analyses and magnetic moments and molar conductance are set out in Table 1.

On the basis of elemental analyses and thermoanalytical data, the compositions of the complexes have been established to be  $[Mn^{II}(H_2 slox)]$ ,  $H_2O(1)$ ,  $[Mn^{II}(H_2 slox)(A)]$   $[A = py(2), \alpha - pic(3), \beta - pic$ (4),  $\gamma$ -pic (5)] respectively. But, the composition of the complex (6) was found to be Na(H<sub>2</sub>O)<sub>4</sub>[Mn<sup>III</sup>(slox)(H<sub>2</sub>O)<sub>2</sub>].2.5H<sub>2</sub>O. All these complexes decompose above 300 °C without melting. This indicates that metal-ligand bonds have comparatively higher ionic character. The complex (1) showed weight loss corresponding to one water molecule at 110 °C suggesting its presence in the lattice structure of the complex while complexes (2-5) showed no weight loss at 110 °C ruling out the possibility of presence of water molecule in their lattice. Further, complexes (1-5) did not show any weight loss at 180 °C ruling out the possibility of coordination of water molecule to the metal centre. But the complexes (2) to (5) showed weight loss at 220 °C corresponding to one pyridine, 2picoline, 3-picoline and 4-picoline molecule, respectively. The expulsion of these donor molecules at such a high temperature indicates that they are coordinated to the metal centre. But the complex (6) showed weight loss corresponding to 2.5 water molecules at 110 °C while six water molecules at 180 °C. The loss of 2.5 water molecule at 110 °C indicate their presence in the lattice structure of the complex while six water molecule at 180 °C reflects their presence in the first coordination sphere at around metal centres.

An effort was taken up to crystallize the complexes in various solvent systems under different experimental conditions. Both saturated and dilute solutions of the complexes in various solvent systems were kept for 1 and 2 months under observation at ambient temperature to grow crystals. In order to promote crystal growth, the solutions were also gently evaporated at 40 °C, 50 °C and 60 °C in hot air electronic oven. An effort was too made to grow crystal from the reaction mixture when solution of the metal salts was layered with a solution containing the ligand in methanol. Again the metal salt solutions mixed with the ligand in solution in DMSO and DMF were also layered with diethyl ether and resulting solution in a small beaker was kept in a bigger beaker containing n-hexane. Further, the metal salt and ligand were placed in the main

arm of a branched tube (branched tube method). A mixture of acetonitrile and DMSO (15:85 v/v, 15 mL) was carefully added to fill the arms, the tube was sealed and the reagents containing arm immersed in an oil bath at 60 °C, while the other arm was kept at ambient temperature. Unfortunately, in all our efforts, only amorphous compounds precipitated which prevented analysis of the complexes by X-ray crystallography.

### 3.1. Molar conductance

The molar conductivity (Table 1) of the complexes (1-5) falls in the region 0.9–2.5  $\Omega^{-1}$ cm<sup>2</sup>mol<sup>-1</sup> at 10<sup>-3</sup> M dilution in DMF. This value suggested that the complexes are non-electrolyte in this medium [25]. On the other hand, the complex (6) showed molar conductance value equal to 75  $\Omega^{-1}$ cm<sup>2</sup>mol<sup>-1</sup> in DMF revealing that this complex is 1:1 electrolyte in this medium [25].

#### 3.2. Thermal studies

All of the complexes show loss of surface water molecules. After loss of surface water molecules, first significant loss of weight commences in complex (1) at 194 °C which is completed at 268 °C. The loss of weight corresponds to loss of one H<sub>2</sub>O molecule (exp: 4.5%, theo: 4.53%) in this temperature range (Fig. S1). The loss of one H<sub>2</sub>O molecule in such a high temperature range may indicate its presence either in the first coordination sphere around the metal centre or in the lattice in strongly hydrogen bonded form. When the vapours evolved in this high temperature range were passed through a trap containing anhydrous CuSO<sub>4</sub>, it turned out to be blue. The loss of water molecule in such a high temperature range in TGA studies may, most probably be due to hydrogen bond network that permeates the lattice [26]. The hydrogen bonding may be between the lattice - held water molecules and coordinated ligand to manganese(II) centre. When there is a loss of water molecule in such a high temperature range in TGA, caution must be exercised in the classification of water as a lattice held or coordinated on the basis of TGA alone, unless confirmed by X-ray crystallographic studies. However, on the basis of loss of mass at 130 °C, we assumed that one water molecule is present in the lattice of the complex by hydrogen bonding with the bonded dihydrazone ligand, but this still remains tentative unless confirmed by X-ray crystallography. The complex shows insignificant weight loss in the temperature range 268–305 °C. After 305 °C, significant and sharp weight loss occurs which continues upto 350 °C. The weight loss in this temperature range is equal to 71.73% which corresponds to loss of one ligand molecule devoid of 2 oxygen atoms, (theo: 72.54%) which combine with one atom of manganese to give MnO<sub>2</sub>. MnO<sub>2</sub> is obtained at 350 °C whose mass is 21.52% (theo: 21.91%). After this,

Table 1

Complex, colour, decomposition point and molar conductance for manganese(II) and (III) complexes derived from disalicyaldehyde oxaloyldihyd	razone (H <sub>4</sub> slox).
---	-------------------------------

Sl.	Complex and colour	M.P/D.P	Elemental Analysis Found (calcd.) %				Magnetic Moment	Molar Conductance	
No.		(°C)	Mn	С	Н	Ν	$-\mu_{eff}(BM)$	$\Omega^{-1}$ cm <sup>2</sup> mol <sup>-1</sup>	$\Omega^{-1}$ cm <sup>2</sup> mol <sup>-1</sup>
1	$[Mn(H_2 slox)] \cdot H_2 O$ Light yellow	<sup>&gt;</sup> 305	13.58 (13.83)	48.83 (48.38)	3.58 (3.55)	14.53 (14.10)	0.86	0.9	
2	[Mn(H <sub>2</sub> slox)(py)] Yellowish brown	<sup>&gt;</sup> 295	12.32 (11.99)	55.48 (55.03)	3.78 (3.74)	14.92 (15.28)	2.01	1.7	
3	$[Mn(H_2 slox)(\alpha-pic)]$ Yellowish brown	<sup>&gt;</sup> 298	11.37 (11.63)	56.41 (55.94)	4.08 (4.05)	14.12 (14.83)	2.09	2.2	
4	$[Mn(H_2 slox)(\beta-pic)]$ Yellowish brown	<sup>300</sup>	12.00 (11.63)	55.48 (55.94)	4.02 (4.05)	14.51 (14.83)	2.07	2.5	
5	$[Mn(H_2 slox)(\gamma-pic)]$ Yellowish brown	<sup>300</sup>	11.29 (11.63)	56.32 (55.94)	4.02 (4.05)	15.29 (14.83)	1.83	1.8	
6	Na(H <sub>2</sub> O) <sub>4</sub> ·[Mn(slox)(H <sub>2</sub> O) <sub>2</sub> ]·2.5H <sub>2</sub> O Dark brown	<sup>&gt;</sup> 300	10.37 (9.92)	) 35.21 (34.73)	4.96 (4.92)	10.03 (10.13)	4.95	75	

slow mass loss occurs along with the evaporation of the resulting product under reducing atmosphere of dinitrogen. At the temperature of about 800 °C, the mass vanishes. It is imperative to mention that the fact that the residue obtained is solely due to MnO<sub>2</sub> only, has been confirmed by recording its IR spectra (Fig. S2) which matches with that of the authentic sample. The decomposition behaviour of the remaining complexes seems to be almost same except the complex (6). After initial loss of surface solvent molecules, a significant weight loss step occurs in the temperature ranges 285-363 °C, 290-365 °C, 297-368 °C and 300-370 °C in the complexes (2) (Fig. S3), (3), (4)and (5), respectively. The weight losses in these temperature ranges are 70.25%, 77.25%, 77.61%, 71.64%, respectively, which correspond to the loss of ligand molecule devoid of four oxygen atoms (2), two oxygen atoms (3, 4) and four oxygen atoms (5), respectively together with loss of one molecule of pyridine or substituted pyridines (theo: 71.22% (2),  $\alpha$ picoline (theo: 78.57%),  $\beta$ -picoline (theo: 78.59%), and  $\gamma$ -picoline (theo: 72.04%) in each of the complexes, respectively [27]. The residual products so obtained have been cheracterized by IR spectroscopy. The IR spectra (Fig. S4) of the residues in complexes (2)-(5) match with an authentic sample of MnO<sub>2</sub> which confirms that the residual products in these complexes are MnO<sub>2</sub>. However, experimental weight losses in complexes (2) and (5) were found to be 23.68% and 23.13%, respectively, which was higher than that of MnO<sub>2</sub> (theo: 18.27% in complex (2) and theo: 17.76% in complex (5)). This indicated that in these complexes, the end products contain some carbonaceous material which gets oxidized at higher temperature only. But the formation of MnO<sub>2</sub> is not indicated at any stage distinctly as there is a continuous weight loss after 363 and 370 °C until the weight vanishes at 900 °C a temperature at which the heating process comes to stop. On the other hand, the end products obtained in complexes (3) and (4), corresponded to MnO<sub>2</sub> (exp: 18.25%, theo: 17.76%) for complex (3), and (exp: 17.37%, theo: 17.76%) for complex (4), respectively. After 365 and 368 °C, the oxides lose weight slowly and slowly until and unless at temperatures of ~900 °C, the weight vanishes completely. The complex  $Na(H_2O)_4[Mn^{III}(slox)(H_2O)_2]$ .2.5 $H_2O$  shows completely different decomposition behaviour as compared to the remaining manganese complexes (Fig. S3). The complex decomposes in three major steps in the temperature ranges 50–100 °C, 100–300 °C and 300 °C onwards, respectively. A mass loss of about 8.19% is observed in the temperature range 45–100 °C which corresponds to loss of 2.5H<sub>2</sub>O molecules (theo: 8.19%). The loss of these water molecules in this temperature range indicates their presence in the lattice structure of the complex. Another mass loss commences at 100 °C and continues upto 300 °C. The mass loss in this temperature range is equal to 19.12% suggesting loss of 6H<sub>2</sub>O molecules (theo: 19.50%). The loss of these six H<sub>2</sub>O molecules in the temperature range 100-300 °C reveals their presence in the first coordination sphere around the metal centre. After 300 °C, the decomposition of dihydrazone ligand starts which continues upto 900 °C. In the temperature range 300-900 °C, the mass loss is 45.85% which corresponds to loss of ligand molecule devoid of four oxygen atoms (46.75%). The residue obtained corresponds to NaMnO<sub>4</sub> (exp: 27.05%, theo: 25.63%) which has been confirmed by recording its IR spectrum which matches with that of an authentic sample of NaMnO<sub>4</sub> (Fig. S6). It is imperative to mention that complex (6) does not show its stability at any stage of it decomposition once the process has commenced.

#### 3.3. Magnetic moment

The complexes (1-5) have magnetic moment values (Table 1) in the range 0.86–2.09 B M at 298 K. This shows that the complexes have low spin character and idealized  $t_2^5$  (Mn<sup>II</sup>) configuration [28].

The low-spin d<sup>5</sup>system possesses one unpaired electron, hence should show magnetic moment values around 1.73  $\mu_B$ . However, due to orbital contribution, the magnetic moment increases [29], and has been reported to span the range 1.7–2.30  $\mu_B$  [28]. The experimentally observed values of the magnetic moment for the complexes (2–5) suggest that they are all low-spin at room temperature with orbital contribution to some extent.

On the other hand, the magnetic moment value of the complex (1) is 0.86  $\mu_B$ . This value is consistent with low-spin character of the complex. The magnetic moment value of the complex should be around the value for one unpaired electron, however, when orbital contribution is taken into consideration, the  $\mu_B$  value for complex (1) should fall around 2.18  $\mu_B$  [29]. This value suggests considerable magnetic exchange interaction within the structural unit of the complex. The magnetic moment of the complex (1) is considerably reduced as compared to that expected on the no interaction basis. Such a decrease in  $\mu_B$  value might occur either due to super exchange via overlap of the metal orbitals with the orbitals of the bridging oxygen atoms of phenolate group [29] or due to direct overlap of metal orbitals of one structural unit with the metal orbitals of other structural unit. The lower value of magnetic moment of complex (1) reveals a square planar environment in which metal has the ground term configuration  ${}^{4}A_{1g}(b_{2g}^{2}e_{g}^{2}a_{1g}^{1})$ .

Manganese(II) has the highest spin-pairing energy [30] among bivalent 3d metal ions and therefore only very strong-field ligands can induce low-spin character. Hence, low-spin manganese complexes are relatively uncommon [31]. A significant finding of our work shows that hydrazonato O, N coordination can be strong enough and effective in sustaining spin pairing.

The magnetic moment value for the complex (6) is 4.95  $\mu_B$ , which falls in the range expected for high-spin Mn(III) complexes with ground state configuration ( $f_{2g}^3 e_B^1 S = 2$ ). This value dismisses the possibility of any metal-metal interaction in the structural unit of the complex.

#### 3.4. UV visible spectra

The electronic spectral bands for dihydrazone and metal complexes have been listed in Table 2 along with their molar extinction coefficients.

The free dihydrazone ligand H<sub>4</sub>slox shows two absorption bands at 304 and 340 nm. The first band at 304 nm is attributed to  $\pi \rightarrow \pi^*$ transition while the band at 340 nm is attributed to  $n \rightarrow \pi^*$  transition. The band at 340 nm is characteristic of salicylalamine part of the ligand. This band has been reported in many monoacylhydrazones [18,19].

In addition to the ligand bands, the complexes possess an additional band in the region 405-430 nm. The molar extinction coefficient of this band lies in the region 1525-2500 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>. This band has much higher value of the molar extinction coefficients than the usual values for d-d transition bands. This band may be assigned to ligand-to-metal chargetransfer transition arising from transfer of charge, most probably, from phenolate oxygen atoms to Mn(II) centre. The d-d transitions in the Mn(II) complexes are both spin as well as laporte forbidden [30], and hence, they have very weak intensity. However, the band in the region 405-430 nm may have contribution from the dd transitions centred on the Mn(II) metal centre (Fig. S7). It is imperative to mention that the crystal field of any symmetry is unable to split the Mn(II)  $d^5$  high-spin configuration having a  ${}^{6}S$ ground term. Usually high-spin Mn(II) complexes show d-d transition rarely.

The complex (1) shows a broad spectrum in the region 385-420 nm with a shoulder at 410 nm. Its molar extinction coefficient is  $1797 \ \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  while the band at 400 nm is assigned



Electronic spectral bands and EPR data for manganese(II) and (III) complexes derived from disalicyaldehyde oxaloyldihydrazone (H<sub>4</sub>slox).

Sl. No.	Complex	Electronic spectral band	EPR parameters			
		DMF solution $\lambda_{max}(e_{max}) \text{ nm}(\text{dm}^3\text{mol}^{-1}\text{cm}^{-1})$	Temp.	Solid/Solution	g-Value	$A_{mn}(G)$
1	[Mn(H₂slox)]∙H₂O	306 (15725), 344 (19975), 410 (1797)	RT LNT RT LNT	Solid Solid DMSO DMSO	2.007 2.007 $g_{1/2} = 1.994$ $g_1 = 2.622$	  84 
2	[Mn(H <sub>2</sub> slox)(py)]	306 (18240), 344 (23920), 412 (1535)	RT LNT RT	Solid Solid DMSO	$g_{3/2} = 4.168$ 1.868 2.013 2.013 (2.007) 2.007	 78  
2	[Mp(]] slov(z pic)]	207 (20780)	LNT	DMSO	$g_1 = 2.121$ $g_2 = 2.058$ $g_3 = 2.004$ 2.007 1.007	_ _ 76
3	[wiii(H2SiOX)(a-pic)]	345 (28750), 418 (1525)	LNT RT LNT	Solid Solid DMSO DMSO	$1.997$ $1.997$ $g_{1/2} = 2.025$ $g_{3/2} = 4.198$ $g_1 = 2.120$ $g_2 = 2.041$	- - - -
4	[Mn(H <sub>2</sub> slox)(β-pic)]	306 (27060), 344 (34560), 405 (2100)	RT LNT RT LNT	Solid Solid DMSO DMSO	$g_2 = 2.041$ $g_3 = 1.919$ 1.994 $g_{1/2} = 2.025$ $g_{3/2} = 4.168$	 80   
5	[Mn(H-slox)(y-nic)]	306 (18900) 344 (23900) 412 (2500)	RT	Solid	$g_1 = 2.118$ $g_2 = 2.038$ $g_3 = 1.915$ 1.994 1.994	  80 
5		500 (10500), 544 (25500), 412 (2500)	LNT RT LNT	Solid DMSO DMSO	1.982 $g_{1/2} = 1.994$ $g_{3/2} = 4.221$ $g_1 = 2.132$ $g_2 = 2.041$ $g_3 = 1.918$	
6	Na(H <sub>2</sub> O) <sub>4</sub> ·[Mn(slox)(H <sub>2</sub> O) <sub>2</sub> ]·2.5H <sub>2</sub> O	306 (9450), 354 (8320), 370 (5820), 430 (4060), 470	RT LNT RT LNT	Solid Solid DMSO DMSO	2.007 2.006 2.006 feature less 2.006	84   
7	H <sub>4</sub> slox	304 (13130), 341 (16990)	-	_	_	_

to ligand-to-metal charge transfer transition, the shoulder at 410 nm is assigned to d-d transition from the partially spin-paired ground term.

 ${}^{4}A_{1g}(b_{2g}^{2}e_{g}^{1}a_{1g}^{1}) \rightarrow b_{2g}^{2}a_{1g}^{1}b_{1g}^{1}$ This reveals a square-planar environment for Mn (II) centre.

The high-spin Mn(III) complex (6) shows a broad band centred at 430 nm in addition to ligand band at 304 and 354 nm (Fig. S8). The band at 430 nm may be attributed to ligand to metal charge transfer transition because molar extinction coefficient of this band is 8060 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>. As this band is very broad in character, hence it is attributed to mask any weak band due to d-d transition centred on the Mn(III) metal. It is worth noting that the band in this region occurs in the range 405–412 nm in the complexes (2) to (5) while in the present complex occurs at 430 nm. This indicates the presence of extended conjugation in the ligand backbone in the complexed state resulted from enolization of the ligand. Because of the presence of the extended conjugation in the complex (6), the ligand band at 340 nm is also red shifted by 15 nm and appears at 354 nm characteristic of bonding of dihydrazone to the metal centre in the enol form.

Further, the complex (6) displays a broad absorption maxima with a shoulder at 470 nm in the UV visible region in the solid state (Fig. S9) as Nujol mulls and appears as a shoulder on the main peak at 430 nm which maximizes in the ultraviolet region. The peak at 470 nm seems to be a combination of metal-to-ligand charge-transfer and d-d transitions. As might be expected, the spectral feature of this complex is very similar to those reported in the literature [30]. It, therefore, seems plausible to propose that the low energy shoulder at 470 nm is d-d transition. In octahedral notation, this would correspond to  ${}^{5}E_{g} \rightarrow {}^{5}T_{2g}$  or its components in one or another lower symmetry group [30]. The appearance of only one shoulder in this region is, probably, due to greater absorption in the UV for the complex. The spectra possessed the same features as that in the solution state except that shoulder was more pronounced and shifted slightly to longer wavelength at 490 nm.

#### 3.5. Electron paramagnetic resonance spectroscopy

The X-band EPR spectra for the manganese(II) complexes have been recorded at RT and LNT in powder as well as in CH<sub>3</sub>CN - DMSO solution. The various EPR parameters for the complexes have been set out in Table 2. EPR spectra for some of the complexes have been given in (Figs. S10–12). The complexes (2) to (5) show isotropic spectrum in polycrystalline form at RT as well as at LNT. The  $g_{av}$  values for the complexes (2) to (5) fall in the regions 1.994–2.013 and 1.982–2.013 respectively at RT and LNT, in polycrystalline form. One remarkable aspect of ESR spectra is that  $g_{av}$  values for the complexes in the polycrystalline form at RT and LNT are almost same. This reveals that the complexes have almost similar stereo-chemistry at RT as well as LNT in polycrystalline state.

The manganese(II) complexes (2) to (5) show EPR signal in DMSO solution at RT, one signal is strong and appears at 1.994–2.025 while the other signal is weak and appears in the region 4.168-4.221. The signal in the region 4.168-4.221 disappears at LNT and only the signal in the region 1.868-2.007 remains persistently and becomes strong in intensity. The CH<sub>3</sub>CN-DMSO glass of the complexes at LNT gives a well resolved spectrum with six hyperfine lines [ $^{55}$ Mn, I = 5/2] with metal hyperfine coupling constant in the region 76-84 G. A value spans 75-100 G, the 90–100 G domain being more frequented [32]. Thus the hyperfine coupling constants for the present manganese(II) complexes fall in the lower limit of the reported ranges. The strong  $d\pi$ -p $\pi$  metalligand interactions might be responsible for these lower values of the experimentally observed hyperfine coupling constants. The hyperfine split signals in these complexes are more intense than those in the high-spin manganese(II) complexes, a feature characteristic of low-spin manganese (II) complexes.

The complexes (2) to (5) at room temperature exhibit an intense feature centred in the region 1.994–2.025 and a weak feature in the region 4.168–4.221 in CH<sub>3</sub>CN-DMSO glass. When the complex is cooled, the signal in the region 4.168–4.221 further weakens in intensity and finally vanishes at 77 K. The fact that the  $\Delta Ms = 2$  forbidden transition appears at RT indicates that the ground state at RT is not a pure doublet pair state. Instead, it is a mixture of doublet and quartet state [33]. As the low-field signal disappears, at low temperature, it suggests that the complex has a pure doublet ground state at low temperature. The weak signal in the region 4.168–4.221 in the complexes (2) to (5) may be related with a resonance with the excited manifold arising from the interaction between the quartet excited state of the complexes and doublet ground state of the other.

A poorly resolved rhombic spectrum is obtained in DMSO glass at 77 K for the complex (2) while fully resolved rhombic spectra in the complexes (3)–(5). The three g-components for the spectra of the complex further split due to hyperfine coupling to give complex spectral features characteristic of the low-spin state of manganese(II) complexes. In contrasts, the high-spin manganese(II) complexes show only very broad room temperature spectra spreading over g = 2-5 and very complex low temperature (77 K) spectra over a very wide range due to zero field splitting in the distorted metal environment.

The ESR features of the complex (6) are essentially different from those of the other complexes. This complex has similar asymmetrical isotropic spectra at RT and LNT in polycrystalline form as well as at LNT in DMSO glass. The average  $g_{av}$  value is 2.006. This shows that under these conditions, the complex has similar stereochemistry. On the other hand, the complex has a featureless spectrum at RT in DMSO solution. All the features of the EPR spectra reveal that the complex is a high spin Mn (III) complex.

# 3.6. <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectrum of free dihydrazone and Na  $[Mn(slox)(H_2O)_6]2 \cdot 5H_2O$  (6) were recorded in DMSO d<sub>6</sub> solution because of solubility regions.

<sup>1</sup>H NMR spectrum of ligand shows signals at δ 12.78, δ 11.09 and δ 8.89 ppm respectively. These signals are assigned to δ-OH, δ-NH, δ-CH=N- protons, respectively. A triplet in the region 6.50–8.00 ppm is attributed to phenyl protons. The appearance of

 $\delta$ -OH,  $\delta$ -NH and  $\delta$ -CH=N signals as singlet suggests that the free ligand exists in staggered configuration. The signals at  $\delta$  12.78 ppm and  $\delta$  11.09 ppm disappear on complexation. This reveals bonding of phenolate oxygen via deprotonation and carbonyl oxygen via enolization cum deprotonation to the metal centre. The most remarkable feature of <sup>1</sup>H NMR spectrum of complex is the appearance of two signals at  $\delta$  8.31 ppm and  $\delta$  9.10 ppm corresponding to  $\delta$ -CH=N protons as compared to a singlet at  $\delta$  8.89 ppm in free dihydrazone ligand. The azomethine proton signal shifts on an average to upfield by 0.19 ppm which indicates that the azomethine nitrogen atom is bonded to metal atom and that the phenyl ring electron density flows to Mn through azomethine nitrogen atom. The splitting of  $\delta$ -CH=N- proton signals suggests bonding of dihydrazone to the metal centre in anti-cis configuration as compared to that of dihydrazone which exist in staggered configuration in free state. The signal at  $\delta$  8.31 ppm is attributed to axial azomethine proton while the signal at  $\delta$  9.10 ppm to equatorial proton.

## 3.7. IR spectra

Some structurally significant IR bands for the free dihydrazone and the metal complexes have been set out in Table 3.

A peak to peak comparison of the IR spectra of the complexes with that of the free dihydrazone shows that the complexes (1)-(5)possess ligand in the keto form while the complex (6) contains ligand in the enol form. This is evident from the fact that the v(OH + NH) bands occurring in the region 3206-3435 cm<sup>-1</sup> in the ligand are either slightly changed in their position or remain almost upshifted [23]. Further, the carbonyl bands appearing at 1669 cm<sup>-1</sup>in the free dihydrazone also remains almost unshifted in position in complexes. This dismisses the possibility of coordination of NH and >C=O groups to the metal centre. However, their position does not rule out the possibility of involvement of NH and >C=O groups in the H-bonding in metal complexes asin free dihydrazone ligands. The bands at 1620 (s); 1603 (s); 1536 (s); and 1276 (m); 1262 (s) in free ligands attributed to  $\nu$ (C=N); Amide II +  $\nu$ (C–O)(phenolic) and  $\beta$ (C–O) (phenolic) also retain their position in the complexes. They are involved in hydrogen bonding as H > C = N - H - O. It appears that in these complexes the bonding of >C=N and phenolic O-O occur to the metal centre accompanied by breakdown of H - bond [21]. The strength of the bond H > C=  $N \rightarrow Mn - O -$  in complexes is almost same as that in the hydrogen bonding in uncoordinated free dihydrazone. On examining the spectra of the ligand and its complexes below 600 cm<sup>-1</sup>, a new weak band in the region 486-503  $\text{cm}^{-1}$  is assigned to  $\nu(\text{M-}$ O)(phenolate). The vC = O band in the complex (6) disappears on complexation reaveling the bonding of the ligand to the metal centre in enol form. This is also corroborated by the fact that the strong ligand at 1536 cm<sup>-1</sup> due to amide II +  $\nu$ (C–O)(phenolic) becomes stronger and broader in nature as compared to that in the free ligand. This indicates the origin of this band due to new -NCOgroup [34] produced as a result of enolization of ligand. Further, in the complex (6), an additional new weak band is observed at 462 cm<sup>-1</sup> in the low frequency region which shows bonding between enolate oxygen atoms and sodium metal centre [35]. It is imperative to mention that vC = N band appear as a doublet in all complexes which reveals the coordination of dihydrazone to the metal centre in anti-cis configuration.

## 3.8. Cyclic voltammetry

The redox properties of the complexes have been studied by cyclic voltammetry (CV) using a platinum working electrode in DMF under dinitrogen atmosphere with 0.1 M TBAP as a supporting

Table 3
Structurally significant IR spectral bands of disalicyaldehyde oxaloyldihydrazone ( $H_4$ slox) and it manganese(II) and (III) complexes.

Sl. No.	Complex	$\nu(OH + NH)$	ν(C==0)	ν(C==N)	Amide II +v(C–O) (phenolic)	$\beta$ (C–O) phenolic	ν(M-O)
1	[Mn(H₂slox)]·H₂O	3427(s) 3278(s) 3202(s)	1667(s)	1621(s) 1603(s)	1536 (s)	1275(s) 1262(s)	486 (w)
2	[Mn(H <sub>2</sub> slox)(py)]	3432(s) 3278(s) 3206(s)	1668(s)	1620 (ssh) 1600(s)	1535 (s)	1275(w) 1262(s)	485 (w)
3	[Mn(H <sub>2</sub> slox)(α-pic)]	3394(s) 3275(s) 3206(s)	1668 (s)	1620 (ssh) 1603 (s)	1536 (s)	1278 (w) 1265 (s)	502 (w)
4	$[Mn(H_2 slox)(\beta-pic)]$	3278(s) 3206(s)	1667(s)	1619(s) 1603(s)	1535 (s)	1275(w) 1262(s)	487 (w)
5	[Mn(H <sub>2</sub> slox)(γ-pic)]	3435(s) 3280(s) 3207(s)	1668(s)	1619(s) 1603(s)	1535 (s)	1275(w) 1262(s)	488 (w)
6	$Na(H_2O)_4 \cdot [Mn(slox)(H_2O)_2] \cdot 2.5H_2O$	3435(s)	_	1624(s) 1608(s)	1536 (s)	1278(s)	503 (w)
	H <sub>4</sub> slox	3434(s) 3278(s) 3207(s) 3150(s)	1669(s)	1620(s) 1603(s)	1536 (s)	1276(m) 1262(s)	_

Table 4

Electrochemical parameters for manganese(II) and (III) complexes derived from disalicyaldehyde oxaloyldihydrazone (H<sub>4</sub>slox) (Potential vs Ag/AgCl) at a scan rate of 100 mV/s

Sl. No.	Compound	Reduction E <sub>pc</sub> (V)	Oxidation E <sub>pa</sub> (V)	ΔΕ
1	$[Mn(H_2 slox)] \cdot H_2O$	_	+0.54	290
		-0.01	+0.28	-
		-0.85	_	400
		-1.40	-1.00	
2	$[Mn(H_2 slox)(py)]$	+0.26	+0.50	240
		-0.57	_	_
		-1.20	-1.00	200
3	$[Mn(H_2 slox)(\alpha - pic)]$	+0.10	+0.40	300
		-0.56	_	_
		-1.27	-1.21	60
4	$[Mn(H_2 slox)(\beta-pic)]$	+0.20	+0.69	410
		-0.42	_	_
		-1.06	-0.58	-
		_	-1.20	-
5	$[Mn(H_2 slox)(\gamma - pic)]$	_	+0.75	_
		-0.58	_	_
		-	+0.53	-
		-1.11	-0.90	210
6	$Na(H_2O)_4 \cdot [Mn(slox)(H_2O)_2] \cdot 2.5H_2O$	_	+0.68	_
		_	+0.33	_
		-0.13	+0.10	230
7	H <sub>4</sub> slox	_	+0.52	_
		-1.32	-0.95	370

electrolyte at several scan rates. The data have been presented in Table 4 at scan rate 100 mV/s.

The complexes (2) to (4) display three reductive waves in the regions (-0.10 V) to (+0.26 V), (-0.42 V) to (-0.57 V), (-1.06 V) to (-1.27 V) and two oxidative waves in the regions (+0.40 V) to (+0.69 V) and (-1.00 V) to (-1.21 V), respectively. Apart from these oxidative waves, the complex (4) shows another additional oxidative wave at -0.58 V. On the other hand, the complex (1) also shows three reductive waves at -0.01 V, -0.85 V and -1.40 V and also three oxidative waves at +0.54 V, +0.28 V and -1.00 V, respectively (Fig. S13). But only two reductive peaks at -0.50 V and -1.13 V are observed in the complex (5) while three oxidative peaks at +0.75 V, +0.53 V and -0.92 V, respectively (Fig. S14). It may be worthwhile to examine the redox potential of the free ligand viz. H<sub>4</sub>slox. It displays one reductive wave at -1.32 V and two oxidative waves at +0.52 V and -0.95 V, respectively. A comparison of the nature of the voltammograms of the complexes with that of the free dihydrazone confirms that the reductive wave in the region

(-1.06 V) to (-1.27 V) and oxidative wave in the region (-1.00) to (-1.20) appear very near to the reductive wave at -1.32 V and oxidative wave at -0.95 V in the free ligand, respectively. Hence, the reductive and oxidative waves in the regions (-1.06 V) to (-1.27 V) and (-1.00 V) to (-1.21 V), respectively, are very close to the reductive and oxidative waves at (-1.32 V) and (-0.95 V) in the uncoordinated ligand. Hence, these waves in the metal complexes arise due to consistently ligand centred electron transfer reactions. The complexes (2) to (5) consistently show an irreversible reductive wave in the region (-0.42 V) to (-0.58 V). This reductive wave does not have its counterpart in the anodic scan either in the free ligand or in the complexes. This is consistent with the reduction product undergoing chemical reactions over the longer time scales. This suggests that the species corresponding to this wave are unstable in DMF and do not survive long in the DMF solution either in the free ligand or in the metal complexes. Hence the reductive wave in the region (-0.42 V) to (-0.58 V) corresponds to generation of a ligand based phenoxyl radical [36]. Hence, this irreversible wave is also



Fig. 1. Tentatively proposed structure of complex [Mn(H<sub>2</sub>slox)].H<sub>2</sub>O (1).

considered to arise from ligand centred electron transfer reaction. This wave does not have its counterpart in the anodic scan either in the free ligand or in the complexes. It is imperative to mention that with the highly negatively charged dihydrazone ligand bonded to the metal centre, it is expected to help make the reduction of the metal centres unfavourable, leading to quite negative Epc values [37]. Apart from these waves, the complexes (2) to (4) invariably show a new reductive wave in the region (-0.10 V) to (+0.26 V) and the corresponding oxidative wave in the region (+0.40 V) to (+0.69 V). This wave is assigned to metal centred electron transfer reaction. It is worth noting that the uncoordinated ligand shows an oxidative wave at +0.52 V which is, most probably, due to oxidation of >C=N group [38]. This wave appears to be merged with the metal centred oxidative wave in the region +0.40 V to +0.69 V in the complexes. The difference between reductive and oxidative waves falls in the region 290-470 mV which is much more than one electron uncomplicated electron transfer reaction. This reveals that the metal centred electron transfer reaction is either quasireversible or irreversible. The large peak separation originates, most probably, from a slow heterogeneous one electron exchange rather than from intervening homogeneous reaction [39]. The electron transfer reaction may be represented as below

$$\begin{bmatrix} (H_2 slox) Mn^{II}(A) \end{bmatrix} \xrightarrow{+e} \begin{bmatrix} (H_2 slox) Mn^{I}(A) \end{bmatrix}^{-} \\ \xrightarrow{+e} \begin{bmatrix} (H_2 slox^{-}) Mn^{I}(A) \end{bmatrix}^{2-}$$

In the complex (1), the reductive waves at -0.85 V and -1.42 V along with it oxidative counterpart at -1.02 V may be attributed to ligand centred electron transfer reactions. Their origin may be explained in the same way as in the complexes (2) to (4). The reductive wave at -0.03 V and its oxidative counterpart at +0.31 V may be related to the electron transfer reaction centred on the metal centre. The  $\Delta$ E value for this redox couple is 340 mV which indicates its either quasi-reversible or irreversible nature. The oxidative wave at +0.54 V in the anodic scan does not have its



Fig. 2. Tentatively proposed structure of complex  $[Mn(H_2slox)(A)]$  (A = py (2), 2-pic (3), 3-pic (4), 4-pic (5)).

counterpart in the cathodic scan. It appears that the species produced corresponding to this wave is unstable and does not survive long in DMF and reverts back to original species. This wave may be attributed to generation of species corresponding to oxidation of  $^{2}C=N-$  group in the complex.

The complex  $[Mn(H_2slox)(\gamma-pic)]$  (5) shows only two reductive waves at -0.60 V and -1.13 V respectively. The reductive at -0.60 V does not have its oxidative counterpart in the reverse scan. This suggests that the species produced corresponding to this reductive wave are unstable and do not survive long in the DMF medium and revert to the original species. On the other hand, the reductive at -1.13 V has its oxidative counterpart at -0.91 V. The  $\Delta E$  value for this redox couple is 220 mV which reveals its quasi-reversible nature. The complex shows two more oxidative waves at +0.75 V and +0.53 V, respectively. The oxidative wave at +0.53 V is very near to the oxidative wave at +0.52 V in the ligand. Hence, this wave is assigned to the electron transfer reaction centred on the ligand. The only oxidative wave left is at +0.75 V which may be attributed to metal centred electron transfer reactions.

This complex (6) shows only one reductive wave at -0.31 V in the forward scan while three oxidative waves at +0.78 V, +0.34 V and +0.10 V in the reverse scan, respectively (Fig. S15). The reductive wave at -0.31 V corresponds to the oxidative wave at +0.10 V. The  $\Delta$ E value for this redox couple is 230 mV, which suggests its quasi-reversible nature. The other two oxidation waves at +0.78 V and +0.34 V do not have their counterparts in the forward scan (cathodic scan). Hence, these waves may be attributed to ligand centred electron transfer reactions. As these oxidative waves do not have their counterparts in the cathodic scan, the species produced corresponding to them do not survive long in the DMF solution and revert back to their original species.

On the basis of various physico – chemical and spectroscopic studies the complexes have, tentatively, been proposed to have the following structures (Figs. 1-3).



Fig. 3. Tentatively proposed structure of complex  $Na(H_2O)_4[Mn(slox)(H_2O)_2]$ .2.5 $H_2O$  (6).

## 4. Conclusion

Five new low-spin manganese(II) complexes and one high-spin manganese(III) complex have been prepared and reported in the present paper. In all complexes dihydrazone ligand is bonded to metal centre in anti-cis configuration. In the complexes (1)-(5) the ligand is present in the keto formwhile in complex (6) in enol form. The dihydrazone is bonded to metal centre as dibasic tetradentate ligand through phenolate oxygen and azomethine nitrogen atom in the complex (1)–(5) while as tetrabasic hexadentate ligand in enol form through phenolate oxygen atom and azomethine nitrogen atoms to one metal centre and enolate oxygen atoms to second metal atom. The Mn<sup>II</sup> in complex (1) is square planar while in complex(2) to(5) is five – coordinate square pyramidal. In complex (6), both the metal centres have distorted octahedral stereochemistry. The complex (1) involves metal-metal interaction while no such interaction is present in the remaining complexes. All of the complexes show only one metal centred electron transfer reaction in DMF solution in cyclic voltammetric studies. The tentative structures for the complexes have been proposed.

#### Acknowledgement

Authors are thankful to the Head, SAIF, IIT, Bombay, for recording EPR Spectra. Two of the authors I. Syiemlieh and S. D. Kurbah also would like to thank UGC, New Delhi for the award of NFHE Fellowship.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.molstruc.2017.09.052.

# References

 D.W. Foder, J. Hwang, J.E. Permar-Halun, in: A. Siegel, H. Siegel (Eds.), Metal lons in Biological Process, Marcel Dekker, Basel, Switzerland, 2000, pp. 527-557.

- [2] SJ. Smith, K.S. Hadler, G.R. Hanson, G. Schenk, N. Mitic, Binuclear Mn-Dependent enzymes, in: G.R. Hanson, LJ. Berliner (Eds.), Biological Magnetic Resonance: High Resolution EPR: Applications to Metalloenzymes and Metals in Medicine, vol. 29, Springer, NewYork, 2009.
- [3] V.J. Leveque, M.E. Stroupe, J.R. Lepock, D.E. Cabelli, J.A. Tainer, H.S. Nick, D.N. Silverman, Biochemistry 39 (2000) 7131.
- [4] N.G. Connelly, K.A. Hassard, B.J. Dunne, A.G. Orpen, S.J. Raven, G.A. Carriedo, V. Riera, J. Chem. Soc. Dalton Trans. 26 (1988) 1623.
- [5] P.T. Manoharan, H.B. Gray, Chem. Commun. (1965) 324.
- [6] S. Scheuermayer, F. Tuna, M. Bodensteiner, M. Scheer, R.A. Layfield, Chem. Commun. 48 (2012) 8087.
- [7] A. Jezierski, J. Mol. Struct. 115 (1984) 11.
- [8] (a) P. Basu, A. Chakravorty, Inorg. Chem. 31 (1992) 4980;
  (b) P. Basu, A. Chakravorty, J. Chem. Soc. Chem. Commun. 11 (1992) 809;
  (c) S. Ganguly, S. Karmakar, C.K. Pal, A. Chakraborty, Inorg. Chem. 38 (1999) 5984;

(d) S. Chattopadhyay, P. Basu, S. Pal, A. Chakravorty, J. Chem. Soc. Dalton Trans. 29 (1990) 3329.

- [9] A. Saha, P. Majumdar, S. Goswami, J. Chem. Soc. Dalton Trans. (2000) 1703.
- [10] (a) A.P. Forshaw, J.M. Smith, A. Ozarowski, J. Krzystek, D. Smirnov, S.A. Zvyagin, T.D. Harris, H.I. Karunadasa, J.M. Zadrozny, A. Schegg, K. Holldack, T.A. Jackson, A. Alamiri, D.M. Barnes, J. Telser, Inorg. Chem. 52 (2013) 144;
  - (b) E.A. Osorio, K. Moth-Poulsen, H.S.J. Zant, J. Paaske, P. Hedegard, K. Flensberg, J. Bendix, T. Bjornholm, Nano Lett. 10 (2010) 105;
     (c) F.A. Cotton, G. Wilkinson, P.L. Gaus, Basic Inorganic Chemistry, second ed.s., John Wiley and Sons, 1987;
  - (d) S. Amabilino, R.J. Deeth, Inorg. Chem. 55 (2016).
- [11] (a) D. Basumatry, R.A. Lal, A. Kumar, J. Mol. Struct. 1092 (2015) 122;
   (b) R.A. Lal, D. Basumatary, A.K. De, A. Kumar, Transit. Mater. Chem. 32 (2007) 481.
- [12] (a) B.D. Wang, Z.Y. Yang, P. Crewdson, D.Q. Wang, J. Inorg. Biochem. 101 (2007) 1492;
  (b) J. Patole, W. Sandbhor, S. Padhye, D.N. Deobagkar, C.E. Anson, A. Powell, Bioorg. Med. Lett. 13 (2003) 51;
  (c) C.D. Fan, H. Su, J. Zhao, B.X. Zhao, S.L. Zhang, J.Y. Miao, Eur. J. Med. Chem. 45 (2010) 1438;
  (d) S. Pasayat, S.P. Dash Saswati, P.K. Majhi, Y.P. Patil, M. Nethaji, H.R. Dash, S. Das, R. Dinda, Polyhedron 38 (2012) 198.
- [13] (a) S. Rollas, N. Gulerman, H. Erdeniz, II Farm. 57 (2002) 171;
   (b) J.V. Ragavendran, D. Sriram, S.K. Patel, I.V. Reddy, N. Bharathwajan, J. Stables, P. Yogeswari, Eur. J. Med. Chem. 42 (2007) 196.
- [14] (a) P. Liang, Y. Liu, L. Guo, J. Anal, At. Spectrom. 19 (2004) 1006;
   (b) Y.C. Sun, J.Y. Yang, S.R. Tzeng, Analyst 124 (1999) 421.
- [15] (a) D.B. Kiewicz, J. Siepak, Anal. Chim. Acta 353 (1997) 85;
- (b) R.J. Micic, R.M. Simonovic, B.B. Petkovic, Anal. Sci. 22 (2006) 793.
- [16] V. Getautis, J.V. Grazulevicius, M. Daskeviciene, T. Malinauskas, V. Gaidelis, V. Jankauskas, Z. Tokarski, J. Photochem. Photobiol. A Chem. 180 (2006) 23.
- [17] (a) A. Bieliauskas, V. Getautis, V. Martynaitis, V. Jankauskas, E. Kamarauskas, S. Krikstolaityte, A. Sackus, Synth. Met. 179 (2013) 27;
- (b) R. Lygaitis, V. Getautis, J.V. Grazulevicius, Chem. Soc. Rev. 37 (2008) 770. [18] R.L. Dutta, M.M. Hossain, J. Sci. Ind. Res. 44 (1985) 635.
- [19] (a) M.R. Bermejo, R. Pedrido, A.M.G. Noya, M.J. Romero, M. Vazquez, L. Sorace, New. J. Chem. 27 (2003) 1753;
- (b) S. Pal, S. Pal, J. Chem. Soc. Dalton Trans. (2002) 2102.
- [20] (a) G.A. Achazmi, A.A. Elmy, J. Coord. Chem. 62 (2009) 37;
   (b) R. Dinda, P. Sengupta, S. Ghosh, W.S. Sheldrick, Eur. J. Inorg. Chem. (2003) 363.
- [21] (a) S. Gupta, M.V. Kirillova, M. Fatima, C.G. da Silva, A.J.L. Pombiero, A.M. Kirillov, Inorg. Chem. 52 (2013) 8601;
  - (b) H.H. Monfared, R. Bikas, P.M. Anarjan, A.J. Blake, V. Lippolis, N.B. Arslan, C. Kazak, Polyhedron 69 (2014) 90;
  - (c) N.A. Lalami, H.H. Monfared, H. Noei, P. Mayer, Transit. Mater. Chem. 36 (2011) 669;

(d) S. Gopinathan, S.S. Tavale, V.G. Puranak, M.P. Degaonkar, Bull. Chem. Soc. Jpn. 41 (1994) 1797;

- (e) B. Ji, Q. Du, K. Ding, Y. Li, Z. Zhou, Polyhedron 15 (1996) 403;
- (f) A. Bonardi, S. Ianelli, C. Pelizzi, G. Pelizzi, C. Solinas, Inorg. Chim. Acta 232 (1995) 211;
- (g) R.A. Lal, S. Choudhury, A. Ahmed, R. Borthakur, M. Asthana, A. Kumar, Spectrochim. Acta A 75 (2010) 212;
- (h) R.A. Lal, M. Chakraborty, O.B. Chanu, S. Choudhury, R. Borthakur, S. Copperfield, A. Kumar, J. Coord. Chem. 63 (2010) 1239;
- (i) R. Borthakur, A. Kumar, R.A. Lal, Spectrochim. Acta A Mol. Biomol. Spectrosc. 149 (2015) 621;
- (j) R. Borthakur, U. Thapa, M. Asthana, S. Mitra, K. Ismail, R.A. Lal, J. Photochem. Photobiol. A Chem. 301 (2015) 6;
- (k) A. Ahmed, R.A. Lal, J. Mol. Struct. 1048 (2013) 321.
- [22] (a) H.H. Monfared, N.A. Lalami, A. Pazio, K. Wozniak, C. Janiak, Inorg. Chim. Acta 406 (2013) 241;
   (b) C. Das, P. Adak, S. Mondal, R. Sekiya, R. Kuroda, S.I. Gorelsky,
  - S.K. Chattopadhyay, Inorg. Chem. 53 (2014) 11426; (c) T. Sedaghat, M. Aminian, G. Bruno, H.A. Rudbari, J. Organomet. Chem. 737 (2013) 26;

(d) P. Paciorek, J. Szklarzewicz, A. Jasinska, B. Trzewik, W. Nitek, M. Hodorowicz, Polyhedron 87 (2015) 226;

(e) R.T. Sedaghat, L. Tahmadu, H. Motamashi, R.R. Martinez, D.M. Morales, J. Organomet. Chem. 737 (2013) 712;

(f) J.D. Ranford, J.J. Vital, Y.M. Wang, Inorg. Chem. 37 (1998) 1226; (g) L. Zhao, V. Niel, L.K. Thompson, Z. Xu, V.A. Milway, R.G. Harvey, D.O. Miller, C. Willson, M. Leech, J.A.K. Howard, S.L. Heath, J. Chem. Soc. Dalton Trans. (2004) 1446;

- (h) S. Roy, T.N. Mandal, A.K. Barik, S. Pal, R.J. Butcher, M.S. Fallah, J. Tercero,
- S.K. Kar, Dalton Trans. (2007) 1229: (i) H.H. Monfared, A. Farrokhi, S. Alavi, P. Maver, Trans. Mater. Chem. 38
- (2013) 267.
- [23] (a) X.M. Zhang, X.Z. You, Polyhedron 15 (1996) 1793;

(b) A. Bacchi, A. Bonardi, M. Carcelli, P. Mazza, P. Pelagatti, C. Pelizzi, G. Pelizzi, (b) A. Bacchi, A. Bollardi, W. Carcen, T. Mazza, T. Chago C. Solinas, F. Zani, J. Inorg. Biochem. 69 (1998) 101; (c) H. Yin, J. Cui, Y. Qiao, Polyhedron 27 (2008) 2157;

- (d) T. Sedaghat, Z. Shokohi-pour, J. Coord. Chem. 62 (2009) 3837; (e) T. Sedaghat, M. Naseh, H.R. Khavasi, H. Motamedi, Polyhedron 33 (2012)
- 435
- [24] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis Including Elementary Instrumentation Analysis, fifth ed.s., ELBS and Longman, London, 1989, p. 199, 367.
- [25] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
- [26] (a) A.C. Fabretti, C.G. Franchini, C.P. Preti, G. Tosi, Can. J. Chem. 19A (1980)

137:

- (b) J. Fujita, K. Nakamoto, M. Kobayashi, J. Am. Chem. Soc. 78 (1956) 3963.
- [27] A.V. Nikolaev, V.A. Logvinenko, L.I. Myachina, Thermal Analysis, vol. 2, Academic Press, New York, 1969.
- [28] B.N. Figgis, Trans. Faraday Soc. 57 (1961) 204.
- [29] U. Knof, T. Weyhermuller, T. Wolter, K. Wieghardt, J. Chem. Soc. Chem. Commun. (1993) 726.
- [30] A.B.P. Lever, Inorganic Electronic Spectrosocpy, second ed.s., Elsevier, New York, 1984, p. 75.
- S. Karmakar, S.B. Choudhury, A. Chakravorty, Inorg. Chem. 33 (1994) 6148.
  P. Basu, S. Pal, A. Chakravorty, Inorg. Chem. 27 (1988) 1848.
  E. Wasserman, L.C. Synder, W.A. Yager, J. Chem. Phys. 41 (1964) 1763.

- [34] M. Mashima, Bull. Chem. Soc. Jpn. 35 (1962) 423.
- [35] G.C. Percy, D.A. Thornton, J. Inorg. Nucl. Chem. 34 (1972) 3369.
- [36] (a) L. Benisvy, E. Bill, A.J. Blake, D. Collison, E.S. Davies, C.D. Garner, G. McArdle, E.J.L. McInnes, J. McMaster, S.H.K. Ross, C. Wilson, Dalton Trans. (2006) 258; (b) D. Parker, E.S. Davies, C. Wilson, J. McMaster, Inorg. Chim. Acta 360 (2007) 203.
- [37] S.A. Cameron, S. Brooker, Inorg. Chem. 50 (2011) 3697.
  [38] (a) H. Okawa, J. Nishio, M. Ohba, M. Todokoro, N. Matsumoto, M. Koikawa, S. Kida, D.E. Fenton, Inorg. Chem. 32 (1993) 2949;
  - (b) M. Koikawa, H. Okawa, J. Chem. Soc. Dalton Trans. (1988) 641.
- [39] C.N. Verani, E. Rentschler, T. Weyhermuller, E. Bill, P. Chaudhuri, J. Chem. Soc. Dalton Trans. (2000) 251.