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Synthesis, characterization and structure assessment of mononuclear and binuclear lowspin manganese(II) complexes derived from oxaloyldihydrazones, 1,10-phenanthroline and 2,2'-bipyridine

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## Abstract

Low-spin manganese(II) complexes  $[Mn^{II}(H_2slox)(bipy)]$  (1),  $[Mn^{II}(H_2slox)(phen)]$  (2),  $[Mn^{II}(H_2slox)(phen)]$ .1.5.H<sub>2</sub>O (2a),  $[Mn^{II}(H_2nph)(bipy)]$ .H<sub>2</sub>O (3) and  $[Mn^{II}(H_2nph)(phen)]$ .H<sub>2</sub>O (4) were synthesized from oxaloyldihydrazones in methanolic-water medium. The stoichiometry of the complexes was established by analytical, molecular weight and thermoanalytical data. Based on the data obtained from molar conductance, UV-visible, Infrared spectral, magnetic moment and electron paramagnetic resonance spectroscopic studies, the structures of the complexes have been established. From molar conductance it is suggested that all the complexes are non-electrolyte in DMF medium. The complex (2a) is monomeric in nature whereas the complexes (1) to (4) are dimeric based on the molecular weight data. The effective magnetic moment of complexes (1) to (4) show metal-metal interaction while complex (2a) has no metal-metal interaction. The complexes (1) – (4) show two quasi-reversible metal centred electron transfer reaction involving  $Mn^{II}/Mn^{0}$  redox reactions in DMF medium.

#### Introduction

Manganese plays an important role in various biological redox processes, viz., in catalases [1] and in oxygen-evolving photosystem II (PS-II) [2, 3]. As a cofactor of proteins it is involved in processes including metabolism and wound healing. Manganese is the necessity of the body for the function of the mitochondria in the form of the antioxidant enzyme manganese superoxide dismutase (MnSOD). Superoxide and other reactive species, by products of cellular respiration that can cause oxidative damage when they are not adequately controlled by antioxidant systems such as MnSOD and its cycloplasmic counterpart CuZnSOD. This redox imbalance is implicated in a number of diseases including cancer and inflammatory, cardiovascular and neuro-degenerative diseases [4]. Mn ribonucleotide reductase shows the conversion of nucleotides to deoxynucleotides [5], and oxalate degradation by oxalate oxidase [6] and oxalate decarboxylase [7, 8]. Consequently, manganese complexes of polyfunctional molecules in different oxidation states have attracted attention of inorganic chemists [9-10] in recent years. Although high-spin manganese(II) and (III) complexes have been extensively studied, yet low-spin manganese(II) and (III) complexes are very few in number. Manganese(II) ion 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. Thus cyano- [11], phosphine [12], dithiolate ligand [13] and oxime ligands [14] and some hydrazone ligands [15] have been reported to give low-spin Mn(II) complexes.

Hydrazones are potential multinuclear molecules and are capable of giving monometallic [16], homo-bi, tri metallic [17], hetero- bi, tri metallic [18] and multimetallic complexes. These ligands exhibit keto-enol tautomerism in their metal complexes and can exist in staggered, syncis and anti-cis conformation in metal complexes. Because of their multidentate nature, they are able to provide metal complexes of different stereochemistries depending upon the preferred

orientation of metal valences in three-dimensional space. Further, the continuous search for new materials exhibiting higher performance than those used currently are necessity of time in order to meet the requirements of daily changing technology. In this regard, the design and synthesis of functional materials with interesting geometric configurations depends upon the choice of suitable ligands with fixed geometry and flexible coordination capacity. In this connection, it is imperative to mention that 1,10-phenanthroline ligand has a rigid framework as chelating donor ligand and exhibits excellent coordination ability with transition metals ions [19]. 2,2'-bipyridine is also a related ligand although it has flexible framework.

Oxaloyldihydrazones are capable of stabilizing metal ions in higher oxidation states [20, 21] and in combination with 1,10-phenanthroline and 2,2'-bipyridine ligands are capable of providing more amazing and interesting compounds because of significantly different nature of N and O donor sites. Thus, 1,10-phenanthroline nitrogen atoms are soft donor atoms and are capable of stabilizing lower oxidation states of transition metals but the hydrazone ligands possess relatively hard donor atoms and stabilize transition metal ions in their higher oxidation states. Hydrazones used in the present study have been derived from condensation of oxaloyldihydrazine and o-hydroxy aromatic aldehydes. They possess as many as eight oxygen and nitrogen atoms and offer several alternate modes of bonding.

Literature survey shows that the work on synthesis, characterization and structure of metal complexes of monohydrazide based ligands and their Schiff bases has been carried out in some detail [16, 22, 23], the corresponding work on their dihydrazone congeners is quite meager [17, 18, 24]. Moreover, the work on manganese complexes with dihydrazones in low-spin state is almost non-existent. Hence, in view of the multidentate nature of oxaloyldihydrazones and their possibility to offer several alternate modes of bonding in complexes, and almost non-existent

work on low-spin manganese complexes of dihydrazones, in the present paper are synthesized and characterized some low-spin manganese(II) complexes from oxaloyldihydrazones viz disalicyaldehyde oxaloyldihydrazone (H<sub>4</sub>slox) and bis(2-hydroxy-1-naphthaldehyde) oxaloyldihydrazone (H<sub>4</sub>nph) (Figure 1). The stoichiometry of the complexes has been established using elemental analyses molecular weight and thermoanalytical data. Based on the data obtained from molar conductance, magnetic moment, electronic, infrared spectroscopies and ESR studies, the structural assessment of the complexes has been carried out. Cyclic voltammetric studies has been employed to observe the electron transfer reactions in the complexes.

#### **Experimental Section**

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

#### **Physical measurements**

Manganese [25] was determined by standard literature procedure. Carbon, hydrogen and nitrogen analyses were carried out by Perkin-Elmer 2400 CHNS/O Analyser. Molecular weight of the complexes was determined in spectroscopic grade DMSO solution by the freezing point depression method. DMSO (dimethyl sulfoxide) was kept over 4 Å molecular sieves prior to use. The molar conductance was measured on a Direct Reading Conductivitymeter-303 with a dip type conductivity cell at room temperature at 10<sup>-3</sup> M dilution in DMF (N, N'-dimethylformamide) solution. The loss of weight of the complexes was determined by heating the compounds at 110 °C, 180 °C and 220 °C for 4 hours in open atmosphere in an electronic oven. The thermogravimetric analysis (TGA) were carried out on the Perkin-Elmer STA 6000 (Simultaneous Thermal Analyzer) model in a ceramic crucible under dynamic nitrogen

atmosphere. The DTA (Differential Thermal Analysis) standard used in the experiment is Pt 10 % Rh. Infrared spectra were measured on Perkin-Elmer, model 983 spectrophotometer in the range 4000 – 400/500 cm<sup>-1</sup> with samples investigated as KBr discs. Room temperature magnetic susceptibility measurements were made on Sherwood Magnetic Susceptibility Balance MSB-Auto. The susceptibility corrections were done by using Pascals Constant [26]. The electronic spectra of the complexes at 10<sup>-5</sup> M in DMF solution were measured from 200-1100 nm on a Perkin Elmer Lamda 25 UV/Vis Spectrophotometer at room temperature. 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 using TCNE (Tetracyanoethylene) (g = 2.0027) as an internal marker. 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 (3M 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.

# Molecular weight determination

Molecular weight of the complexes was determined using DMSO ( $K_f = 4.07$ ) [27] as a solvent, employing Beckman's freezing point depression instruments. It consisted of a Beckman thermometer and a stirrer with a non-conducting handle of wood which was fitted into a tube through a rubber stopper fixed at its upper end. This tube was supported through a rubber stopper in a bigger glass tube thoroughly purged with dry dinitrogen and functions as a dry nitrogen jacket which ensures slow and uniform cooling of the inner tube. The outer tube is immersed in a 1,2-dimethyl-3-nitrobenzene (F.P. 15 °C) freezing bath taken in a glass jar. The jar was covered with a plastic lid carrying three holes was covered with a jar. The inner tube is inserted through

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one hole, a large metal stirrer and an ordinary thermometer are inserted through second and third hole. The molecular weight apparatus was enclosed in a dry box that was constantly purged with dry nitrogen to minimize the error due to highly hygroscopic nature of DMSO. All of the samples were placed in an entry port and purged overnight with dry nitrogen before bringing them into the dry box.

Twenty grams DMSO was taken into the thoroughly cleaned and dried freezing point tube purged with dry nitrogen. About 0.6 g of the complex was accurately weighed and inserted into the DMSO solution. The tube was heated to dissolve the compound and then brought to room temperature. Finally, the upper surface of the liquid in the tube was purged with dry nitrogen and then adjusted into the outer tube. The freezing point temperatures of the solvent and the solutions were directly measured with this apparatus through a magnifying glass fitted into the dry box.

## Preparation of disalicyaldehydeoxaloyldihydrazone (H<sub>4</sub>slox)

The disalicyaldehydeoxaloyldihydrazone ( $H_4$ slox) was prepared according to the procedure described in the literature [20a].

#### Preparation of bis(2-hydroxy-1-napthhaladehyde)oxaloyldihydrazone (H<sub>4</sub>nph)

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

Bis(2-hydroxy-1-napthhaladehyde)oxaloyldihydrazone (H<sub>4</sub>nph) was prepared by condensing oxaloyldihydrazine (3 g, 25.42 mmol), in hot H<sub>2</sub>O (100 mL) with 2-hydroxy-1-naphthaladehyde (8.75 g, 50.84 mmol) in ethanol (20 mL) over hot plate at 70 °C with constant

stirring for 1 h. The yellow precipitate thus obtained was washed with hot H<sub>2</sub>O-ethanol and dried over anhydrous CaCl<sub>2</sub>.

#### **Preparation of [Mn(H<sub>2</sub>slox)(bipy)] (1)**

The complexes were prepared by two general procedures. Typical procedures are given below.

A solution of  $MnSO_4.H_2O$  (0.09 g, 0.5 mmol) in 20 mL water was added to a mixed suspension of  $H_4$ slox (0.16 g, 0.5 mmol) and 2,2'- bipyridine (0.23 g, 1.5 mmol) in 10 mL MeOH under stirring to get a homogeneous suspension. The reaction mixture was refluxed for 6 hours, a light yellow compound was obtained. The compound was filtered, washed with water-methanol, methanol and then with ether and dried over anhydrous CaCl<sub>2</sub>. (Yield: 82 %)

The other complexes were also prepared by following the above method in which in complex (2), instead of 2,2'-bipyridine, 1,10-phenanthroline (0.29 g, 1.5 mmol) was taken. In complex (3), a solution of MnSO<sub>4</sub>.H<sub>2</sub>O (0.09 g, 0.5 mmol) in 20 mL water was added to the mixed suspension of H<sub>4</sub>nph (0.21 g, 0.5 mmol) and 2,2'- bipyridine (0.23 g, 1.5 mmol) in 10 mL MeOH. Similarly, in complex (4), instead of 2,2'- bipyridine, 1,10-phenanthroline was taken. (Yield: 78 % (2), 70 % (3), 75 % (4))

In the second procedure, the MnSO<sub>4</sub>.H<sub>2</sub>O, H<sub>4</sub>L (H<sub>4</sub>slox and H<sub>4</sub>nph) and BB (BB = 2,2'bipyridine/1,10-phenanthroline) were taken in the molar ratio of 1:1:1 and isolated as above. (Yield: 76 % (2a))

#### **Results and discussion**

The complexes were prepared by two general methods. In the first method, the  $MnSO_4.H_2O: H_4slox/H_4nph$  and 2,2'-bipyridine/1,10-phenanthroline were taken in a 1:1:3 molar ratio in methanolic-water medium and refluxed for 6 hours. In the second method, the reactants

were refluxed for 6 hours keeping MnSO<sub>4</sub>.H<sub>2</sub>O, H<sub>4</sub>slox/H<sub>4</sub>nph and 2,2'-bipyridine/1,10phenanthroline at 1:1:1 molar ratio. Both the methods gave complexes having similar composition and properties except in case of the reaction mixture MnSO<sub>4</sub>.H<sub>2</sub>O, H<sub>4</sub>slox and 1,10phenanthroline in which case both the methods gave complexes having different properties from magnetic and EPR point of view. Thus, the reaction mixtures in 1:1:3 molar ratio gave low-spin complexes involving metal-metal interaction, that the reaction mixture in 1:1:1 molar ratio gave complex having normal magnetic moment in case of MnSO<sub>4</sub>.H<sub>2</sub>O, H<sub>4</sub>slox and 1,10phenanthroline reaction mixture and in other cases, the same complexes were obtained as in case of 1:1:3 molar ratio.

The complexes with their colour, decomposition point, elemental analyses, molecular weight, magnetic moment and molar conductance are given in Table 1 and 2. On the basis of elemental analyses, molecular weight and thermal analyses, the complexes have been found to have composition  $[Mn^{II}(H_2L)(BB)]$   $(H_4L = H_4slox, H_4nph; BB = 2,2'-bipyridine, 1,10-phenanthroline). The complexes are either light yellow or yellow in colour. The complexes were insoluble in common organic solvents but soluble in highly coordinating solvents viz., DMF and DMSO. In comparison with the elemental analyses (Table 1) for both the found and calculated percentages for different elements reveal that the compositions of the synthesized complexes coincide well with the proposed formulae i.e., 1:1:1 molar ratio for Mn:H<sub>4</sub>L:BB. The composition of the complexes has also been corroborated from thermoanalytical and molecular weight data. The complexes (1) and (2) show weight loss neither at 110 °C nor at 180 °C ruling out the possibility of presence of water or methanol molecules either in the lattice or coordination sphere. However, the complexes (2a), (3) and (4) show weight loss equal to 1.5, 1 and 1 water molecule, respectively at 110 °C. This reveals that these water molecules are present$ 

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in the lattice structure of complexes. But these complexes show no weight loss at 180 °C ruling out the presence of water or methanol molecules in their coordination sphere. All complexes show weight loss corresponding to one 2,2'-bipyridine/1,10-phenanthroline molecule when they are heated at 220 °C for 4 hours in an electronic oven. This indicated the presence of these secondary ligands in the first coordination sphere of the complexes.

We tried to crystallize the complexes under different experimental conditions using various solvents, and combination of solvent systems. Both saturated and dilute solutions of the complexes in various solvent systems such as DMF, DMSO, DMF-H<sub>2</sub>O, DMSO-CH<sub>3</sub>CN, DMF-CH<sub>3</sub>CN, DMSO-CH<sub>2</sub>Cl<sub>2</sub> and DMF-CH<sub>2</sub>Cl<sub>2</sub> each was kept for 1 and 2 months under observation at ambient temperature to grow crystals. Further, the solutions were gently evaporated in a hot air electronic oven at 40 °C, 50 °C and 60 °C to promote crystal growth. Effort was also done to grow crystals from the reaction mixture by layering a solution of the metal salts with a solution containing the ligand in methanol solutions. Again, the metal salt solutions mixed with the ligand solutions 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, MnSO<sub>4</sub>.H<sub>2</sub>O (0.5 mmol) and a mixture of H<sub>4</sub>slox (0.5 mmol) and 2,2'-bipyridine (1.5 mmol) were placed in the main arm of a branched tube (branch tube method). A mixture of CH<sub>3</sub>CN and DMSO (15 : 85 v/v, 15 mL) was carefully added to fill the arms, the tube was sealed and reagents containing arms immersed in an oil bath at 60 °C, while the other arm was kept at ambient temperature. The same procedure was also applied for crystallizing the complexes (2), (3) and (4) by taking MnSO<sub>4</sub>.H<sub>2</sub>O (0.5 mmol) and a mixture of H<sub>4</sub>slox/H<sub>4</sub>nph (0.5 mmol) and1,10-phenanthroline/2,2'-bipyridine (1.5 mmol). Similarly, complex (2a) was also tried to crystallized following the same procedure by taking MnSO<sub>4</sub>.H<sub>2</sub>O (0.5 mmol), a mixture of H<sub>4</sub>slox (0.5 mmol) and 1,10-phenanthroline (0.5

mmol). Unfortunately, in all our efforts, only amorphous compounds precipitated which prevented analysis of the complexes by X-ray crystallography.

#### Molar conductance

The molar conductivity (Table 2) of the complexes (1) – (4) falls in the region 0.9-1.7  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> at 10<sup>-3</sup> M dilution in DMF. This suggests that all the complexes are non-electrolyte in this medium.

#### **TGA studies**

In order to assess the thermal stabilities of the molecular framework of the complexes, thermogravimetric analytical study was carried out for all of them. The complexes (1) and (2) show one kind of thermal behavior while remaining complexes show different kind of thermal behavior. The TGA graph of complex  $[Mn^{II}(H_2 \text{slox})(\text{bipy})]$  (1) and  $[Mn^{II}(H_2 \text{nph})(\text{phen})].H_2O$  (4) has been given in (Figure S1 and S2). After losing surface water molecules, complexes (1) and (2) decompose in two temperatures ranges 314-360; 468-566 and 488-606 °C, respectively. The weight losses in the temperature range 314-360 °C are 79.26 % and 75.36 %, which corresponds to loss of one molecule of dihydrazone devoid of four oxygen atoms alongwith one molecule of 2,2'-bipyridine and 1,10-phenanthroline (theo: 81.01 % in complex (1) and 78.71 % in complex (2)), respectively. The residues obtained at 360 °C are 15.88 % and 20.29 % in complexes (1) and (2), respectively. The residue in complex (1) corresponds to the formation of  $MnO_2$  (theo: 15.71 %) but in case of complex (2), the residue (20.29 %) is higher than the theoretical weight of MnO<sub>2</sub> (theo: 15.56 %) although the IR spectra of the residues in the complexes match with one another. This suggests the presence of some impurity in the residue, most probably, carbonaceous impurity, in complex (2). After 360 °C, the residue shows slow weight loss upto 468 and 488 °C, losing weight of about 1.45 % and 1.07 %, respectively, at temperature interval

of 20 °C. The second moderate weight loss step is initiated at 468 and 488 °C which is completed at 566 and 607 °C temperatures at which the weight of residue vanishes in both complexes, respectively.

The complexes (3) and (4) decompose in three major steps as against the complexes (1) and (2) which decompose in two major steps. They lose about 3.00 % and 3.04 % of weight in the temperature ranges 80-130 and 80-150 °C, respectively. These weight losses correspond to loss of one water molecule (theo: 2.76 % in complex (1) and 2.66 % in complex (2)), present most probably, in the lattice structure. At temperatures 150 °C, the decomposition of complexes commences, first losing secondary ligands 2,2'-bipyridine and 1,10-phenanthroline molecules, followed by decomposition of primary dihydrazone ligand. Secondary ligands decompose in two minor steps in the temperature ranges 130-337 °C and 150-328 °C. The weight losses in these temperatures ranges are 24.62 % and 16.58 %, respectively. The weight loss of 24.62 % in complex (3) corresponds to loss of one 2,2'-bipyridine molecule (theo: 23.89 %) but that the weight loss of 16.58 % in complex (4) is much less than that of one molecule of 1,10phenanthroline (theo: 26.63 %). This suggests that the remaining portion of 1,10-phenanthroline molecule decomposes alongwith the primary dihydrazone ligand in the temperature range 328-387 °C. This is evident from the fact that the weight loss in the above temperature is 61.11% which is higher than that of the theoretical weight of dihydrazone ligand (theo: 57.90 %) devoid of two oxygen atoms by 3.21 %. The weight of the residues obtained at 386 °C is found to be 12.68 % and 19.27 %, respectively. The weight of the residue in the complex (3) suggests the formation of  $MnO_2$  (theo: 13.32 %). However, the weight of the residue in complex (4) is much higher than that of the theoretical weight of MnO<sub>2</sub> (theo: 12.85 %). This might be explained by the presence of carbonaceous impurities in the residue. The weight of the residue in complex (4)

corresponds to that of  $MnO_2$  at a temperature of 550 °C (12.13 %), but the residues show no stability at any stage beyond 386 °C until the weight vanishes at 654 °C and 702 °C, respectively.

The complex (2a) [Mn<sup>II</sup>(H<sub>2</sub>slox)(phen)].1.5H<sub>2</sub>O shows more or less similar decomposition behavior to complexes (3) and (4). The loss of weight observed in the temperature range 60 - 135 °C is 4.47 % which corresponds to loss of 1.5 water molecules (theo: 4.61 %) present in the lattice. Further, the weight loss observed in the temperature range 298 -366 °C is (exp: 30.13 %). This weight loss corresponds to loss of one 1,10-phenanthroline molecule (theo: 30.72 %). The loss of one 1,10-phenanthroline molecule at such a high temperature reveals its coordination to the metal centre. The coordinated ligand decomposes in two steps 366- 485 °C and 485- 643 °C. The total weight loss in this temperature range 36.62 % which is less than the theoretical weight of 49.82 % of H<sub>4</sub>slox devoid of two oxygen atoms. This indicates the remaining portion of ligand further decomposes along with generated manganese oxide until the heating process is stopped at 899 °C. However, even at this temperature, complex decomposition and weight loss process is not stopped. But the IR spectra of the residue at 899 °C matches with that of an authentic sample of MnO<sub>2</sub> which suggests formation of MnO<sub>2</sub> as the end product. The mass of end product is 9.90 % which is less than the theoretical value of mass of MnO<sub>2</sub> (theo: 14.84 %). This indicates that the newly formed MnO<sub>2</sub> vaporizes at higher temperature.

#### Molecular weight

The molecular weight of the complexes (Table 2) was determined in DMSO ( $K_f = 4.07$ ) [27] as a solvent, employing Beckmans' freezing point depression instruments. The experimentally determined value for the complex (2a) is (570 ± 27) which is very near to the

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theoretical molecular weight (559) for monomeric formulation of complex. This suggests that the complex (2a) is monomeric in nature. This was also corroborated by effective magnetic moment of the complex which rules out any metal-metal interaction in the structural unit of the complex.

On the other hand, the experimentally determined molecular weights for the complexes (1) to (4) are  $(1090\pm55)$ ,  $(1150\pm55)$ ,  $(1234\pm60)$  and  $(1370\pm55)$ , respectively. These molecular weights are close to the values for dimeric formulation for the complexes. This suggests that the complexes (1) to (4) are dimeric. This is also corroborated by lower magnetic moment of the complexes which displays metal-metal interaction in the structural unit of the complexes.

#### **Magnetic moment**

The effective magnetic moment values (Table 2) for the complex (2a) is 1.74 B.M at 298 K which is very close to the spin only value for one unpaired electron. This reveals that the complex has low-spin character at ambient temperature and idealized  $t_2^5$  (Mn<sup>II</sup>) configuration [28]. The  $\mu_{eff}$  value for the complex dismisses the possibility of orbital contribution to the magnetic moment and any metal-metal interaction in the structural unit of the complex.

In the remaining complexes, the  $\mu_{eff}$  value falls in the region 0.52 – 0.92 B.M. These values are less than the spin-only magnetic moment (1.73 B.M). This suggests that there is a considerable magnetic exchange interaction between the metal ions in the structural unit of the complexes.

The magnetic moment for the complexes (1) to (4) is considerably reduced as compared to that on the no-interaction basis. Such a decrease in  $\mu_{eff}$  value might occur either due to super exchange via overlap of the metal orbitals with the orbitals of the bridging oxygen atoms of phenolate/naphtholate oxygen atoms [29] or due to direct overlap of metal orbitals of one structural unit with the metal orbitals of other structural unit. An alternative route of metal-metal interaction is provided by bridging secondary ligands viz 1,10-phenanthroline or 2,2'-bipyridine groups. In this case the metal orbitals overlap with the orbitals of 1,10-phenanthroline or 2,2'-bipyridine and the magnetic interaction is communicated to another metal ion through electron cloud of pyridyl rings via nitrogen atoms. Such an electron exchange through bridging ligands has been proposed by McCleverty et al. [30] from their studies on molybdenum complexes derived from bridging ligands. Hence, in the present case, it is proposed that magnetic interaction from one manganese ion to second manganese ion in the structural unit of the complexes is communicated through the secondary bridging ligands 1,10-phenanthroline or 2,2'-bipyridine.

It is imperative to mention that we understand that the Mn(II) and Mn(III) ions form low spin complexes with strong field ligands like cyanide, phosphine and dithiolate [11-13] but cases are known where other nitrogen and oxygen donor ligands also form low-spin complexes and sufficient evidence is available for this contention [14, 15, 31]. Our ligand used in the present study also bears similarly with reported oxygen and nitrogen donor ligands like oximes giving low-spin and high-spin complexes. Further, it is our experience also in dihydrazone coordination chemistry that the formation of low-spin and high-spin complexes depends upon the nature of metal salts and ligand. Most probably, the use of the manganese(II) sulphate and the ligand in the present study makes suitable combination to give low-spin complexes under appropriate reaction conditions.

# Electron paramagnetic resonance spectroscopy

The EPR spectra of the complexes (1) and (2a) in powder form at RT and LNT have been shown in (Figure S3-S6). The EPR parameters for the complexes have been given in Table 3. The complexes show isotropic spectra in polycrystalline state at RT as well as LNT. The  $g_{av}$  value for all the complexes is ~2.025 at RT while at LNT, it falls in the region 2.020-2.025.

These values reveal that the complexes have almost similar stereochemistry at RT as well as LNT in polycrystalline state  $g_{av}$  value for complex (1) in polycrystalline state at LNT is 2.020 which is different from that at RT (2.025). This indicates that at LNT, the complex attains more symmetrical structure than that at RT. This may be due to compression of molecule at LNT. It is evident from the width of the spectra at RT and LNT, the complex (2a) shows different magnetic behaviour from the remaining complexes, while the width of the central peak decreases in complex (2a), in going from RT to LNT, that in the remaining complexes, the width increases. This fact may be understood in terms of the normal magnetic moment value for complex (2a) and anomalously low value of magnetic moment for the remaining complexes suggesting metalmetal interaction in the structural unit of complexes. The complexes show a single signal in the region ~2.025 G in polycrystalline phase. The appearance of single signal in the region ~2.025 G reveals that the complexes have a pure doublet ground state at RT as well as bot temperature.

The complex (2a) shows an isotropic spectrum with  $g_{av}$  value equal to 2.025 G at LNT in DMSO glass. This value is same as those in the polycrystalline phase at RT and LNT. This shows that this complex in DMSO glass has the same structure as that in the polycrystalline phase. The complexes (1), (2) and (4) show weak splitting in DMSO glass at LNT but a fully resolved spectrum is observed in case of complex (3). Further, in the complexes (3) and (4), the  $g_{av}$  values in DMSO are 2.020 and 2.010 which are different from the values at RT and LNT in polycrystalline state. This indicates that in these complexes some bonds are broken followed by formation of new bonds which leads to the formation of more symmetrical structure at LNT in DMSO glass while the complexes (1), (2) and (4) show weakly resolved rhombic spectrum. The g-values for three components are 2.171, 2.040 and 1.971, respectively, for the complex (3)

which further split due to hyperfine coupling to give complex spectral features characteristic of the low-spin state of manganese(II) complexes. On the other hand, only very broad room temperature spectra are observed over g = 2-5 in the high-spin manganese(II) complexes. Further, in the distorted metal environment, a very complex spectrum is obtained at low temperature (77 K) over a very wide range as a result of zero field splitting.

The complexes (1) and (4) show hyperfine splitting at LNT in DMSO glass with hyperfine coupling constant (<sup>55</sup>Mn, I = 5/2) falling in the range 85-92 G. The reported values for hyperfine coupling constant fall in the region 75-100 G, while most of the observed values fall generally in the region 90-100 G. In our case the experimentally observed A<sub>Mn</sub> value falls in the region 85-92 G, which lies on the border range of reported values. The border range values of the experimentally observed hyperfine coupling constant may be result of the moderately strong d $\pi$ -p $\pi$  metal-ligand interactions.

#### UV visible spectra

The electronic spectral bands for ligands and metal complexes have been listed in Table 4 along with their molar extinction coefficients. The electronic spectra of the complexes have been shown in (Figure S7-S9).

The H<sub>4</sub>slox ligand shows two bands at 304 and 341 nm which are assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions respectively, while the H<sub>4</sub>nph ligand shows three bands each appearing as a couplet in the spectrum giving rise to overall six bands. These bands appear at 318, 330; 375, 391; and 433, 486 nm, respectively. The bands at 318 and 330 may be assigned to  $\pi \rightarrow \pi^*$  transition, those at 375 and 391 nm to  $n \rightarrow \pi^*$  transition. The bands at 375 and 391 nm are characteristic of naphthaldimine fraction of ligand as has been observed in many

monohydrazones [17, 18]. The weak bands at 433 and 486 nm have their origin in some hidden intra-ligand transitions present on the ligand molecule.

The H<sub>4</sub>slox bands remain almost unshifted on complexation, while  $\pi \rightarrow \pi^*$  transition in H<sub>4</sub>nph is blue shifted by 4 nm. This shows bonding of dihydrazones to the metal centre. On the other hand, the  $n \rightarrow \pi^*$  transition in uncoordinated ligand H<sub>4</sub>nph at 375 and 391 nm merge into one another giving rise to again blue shift by 2 - 5 nm. The hidden bands at 433 and 486 nm in (H<sub>4</sub>nph) are shifted to longer wavelength 2 - 3 nm and 5 - 6 nm, respectively. This shows the effect of complexation on the ligands. In addition to the ligand bands, the complexes (1), (2), and show two new bands in the regions 405 - 418 and 473 - 681 nm with molar extinction coefficients in the region 150-1600 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>. Due to high molar extinction coefficients, the band in the region 405 - 418 nm is assigned to have charge-transfer character, most probably, from transfer of charge from occupied molecular orbital located on the phenolate ion to unoccupied molecular orbital located on metal centre. The complexes (3) and (4) show another new band at ~460 nm which again has very high molar extinction coefficient and hence, it is attributed to have its origin due to charge-transfer from naphthoxide ion to metal centre. However, this band may also contain contribution due to split components of  $({}^{2}A_{2g}, {}^{2}T_{1g} \rightarrow {}^{2}T_{2g})$ transition. Weak band in the region 473 - 613 nm appears in all complexes which is suggested to be due to another component of split transition  $({}^{2}A_{2g}, {}^{2}T_{1g} \rightarrow {}^{2}T_{2g})$  centred on the Mn(II) ion [32].

# IR spectra

The bands for v(OH+NH); vC=O and vC=N for H<sub>4</sub>slox and H<sub>4</sub>nph are observed at 3434, 3278, 3207, 3150; 1669; 1620, 1603 cm<sup>-1</sup> and 3622, 3492, 3161; 1682; 1621, 1595 cm<sup>-1</sup>, respectively. Both the ligand also show strong bands at 1536; 1276, 1262 cm<sup>-1</sup> (H<sub>4</sub>slox) and 1536

and 1284 cm<sup>-1</sup> (H<sub>4</sub>nph) which may be attributed to amide II + v(C-O)(phenolic/naphtholic) and  $\beta$ (C-O)(phenolic/naphthalolic), respectively.

The complexes (1) to (2a) show strong bands at 3443, 3278, 3207; 3435, 3240, 3208 and 3452, 3280, 3206, 3240; 1669; 1620, 1603; 1618, 1609 and 1619, 1603 cm<sup>-1</sup> due to v(OH+NH), vC=O and vC=N stretchings [16, 22, 23], respectively. These bands remain either unshifted or slightly shifted in their position and reveal that the ligand is bonded to the metal centre in keto form. The band at 1536 cm<sup>-1</sup> which is due to the amide II + v(C-O)(phenolic) band also remains unchanged in frequency in the complexes which suggests weak bonding between phenolate/ naphtholate oxygen atoms and metal centre [23a]. The  $\beta$ (C-O) band shifts to lower frequency by ~3-4 cm<sup>-1</sup> in position in both the complexes (1) to (2a) indicating weaker bonding between phenolate oxygen atoms and metal centre. Such a bonding pattern of hydrazones with metal ions has been reported by Manoharan et. al. [33] and established by IR and X-ray crystallography. The weak band in the region 557 - 576 cm<sup>-1</sup> is assigned to v(M-O)(phenolate) [33, 34].

The complexes (3) and (4) show similar spectral features (Table 5) to that of uncoordinated ligand suggesting coordination of dihydrazone to the metal centre in keto form [18]. The v(OH + NH) bands in the region 3034 - 3466 cm<sup>-1</sup> in both the complexes (3) and (4), remain unshifted or slightly shifted in their position. But we have refrained from drawing any conclusion regarding bonding of -OH and -NH groups to the metal centre. However, the strong vC=O band at 1682 cm<sup>-1</sup> in free ligand splits into two bands in both the complexes (3) and (4). One band is slightly shifted by 1 (complex 3) and 3 cm<sup>-1</sup> (complex 4) and appears at 1683, 1662 and 1685, 1663 cm<sup>-1</sup>, respectively, while the other band shifts to lower frequency by 21 (complex 3) and 22 cm<sup>-1</sup> (complex 4) and appears at 1662 and 1663 cm<sup>-1</sup>, respectively. However, on an average, still they fall (~1674 cm<sup>-1</sup>) in the region in which uncoordinated vC=O groups have

been reported to absorb. Hence, it is suggested that vC=O groups remain uncoordinated in the complexes. Sufficient evidence is available for this contention in literature on hydrazone complexes established by IR and X-ray crystal structure [17f]. The strong couplet at 1621 and 1594 cm<sup>-1</sup> (vC=N) shifts to higher frequency and appears at 1622 cm<sup>-1</sup> in the complexes (3) – (4). The shift of vC=N band to higher position by 1 cm<sup>-1</sup> shows that there is a flow of naphthly ring electron density to metal centre through azomethine nitrogen atoms which is consistent with the coordination of azomethine nitrogen atom to manganese metal centre [17]. Both the complexes show slightly shifted or unshifted bands at 1536 and 1284 cm<sup>-1</sup> due to amide II + v(C-O)(naphtholic) and  $\beta$ (C-O) vibrations when compared to the free ligand spectra. This is due to weak coordination of naphtholate oxygen atoms to the metal centre and non-coordination of >C=O group.

The complexes (1) and (3) show new medium intensity bands at 731, 654 cm<sup>-1</sup> and 744, 656 cm<sup>-1</sup>, respectively. These bands are attributed to out-of-plane motion of the hydrogen atoms as expected for two identical groups of four hydrogens each [35] and in plane ring deformation mode of 2,2'-bipyridine [36]. The complexes (2), (2a) and (4) show a medium to strong intensity bands at 828, 828 and 820 cm<sup>-1</sup>. This band may be assigned to the hydrogen atoms on the central ring. Further, these complexes show strong band at 756, 755 and 744 cm<sup>-1</sup> which are attributed to the out-of-plane motion of the hydrogen atoms on the heterocyclic rings of 1,10-phenanthroline.

# Cyclic voltammetry

The cyclic voltammograms for the complexes (1) to (3) have been shown in (Figure S10-S12). The cyclic voltammetric data for the complexes have been presented in Table 4.

All of the complexes display three reductive waves in the forward scan and three oxidative waves in the anodic scan except the complex (1) which shows four reductive waves in

the forward scan. Further, the complex (2) also shows only one oxidative wave at +0.65 V. All complexes invariably show two redox couples in the region ( $E_{1/2} = +0.33$  to +0.39 V;  $\Delta E$  (130-250 mV) and (E<sub>1/2</sub> = -0.81 to -1.00 V;  $\Delta E$  (140-350 mV), respectively. A comparison of the cyclic voltammograms of the complexes with those of the free dihydrazones reveals that there is no redox wave in the region +0.33 to +0.39 V in the free dihydrazone. Hence, first redox couple in the region +0.33 to +0.39 V may be attributed to arise due to metal centred redox reaction  $Mn^{II}/Mn^{I}$ . The  $\Delta E$  for this redox couple falls in the region 130-250 mV which reveals its quasireversible nature. When the position of the second redox couple in the region -0.81 to -1.00 V  $(E_{1/2})$  in the complexes is compared with the cyclic voltammograms of the free dihydrazones, it is found that it is very near to the reductive waves at -1.32 V and -0.98 V in H<sub>4</sub>slox and H<sub>4</sub>nph, respectively. Hence, it is suggested that the second redox couple has some contribution from both metal centred electron transfer reactions as well as ligand centred electron transfer reaction. This metal centred electron transfer reaction may be attributed to the electrode reaction Mn<sup>I</sup>/Mn<sup>0</sup>. Apart from these metal centred electron transfer reactions, the complexes show two irreversible reductive waves in the region -0.14 to -0.34 V and -1.54 to -1.64 and an oxidative wave in the region +0.72 to +1.57 V, respectively. In the free dihydrazone H<sub>4</sub>nph, there is a reductive wave at -0.34 V but there is no wave in this region in free ligand H<sub>4</sub>slox. Hence, the reductive wave in the region -0.14 to -0.34 V in the complexes is attributed to arise due to some ligand centred electron transfer reaction. As there is no reductive wave in this region in the free ligand H<sub>4</sub>slox, it seems that ligand gets excited on complexation to give electron transfer reaction. Similarly, the reductive wave in the region -0.81 to -1.00 V also arises due to activation of ligand on complexation as there is a reductive wave at this position in free dihydrazones. It is imperative to mention that these reductive waves do not have their counterparts in the anodic scan either in the

free ligand or in the complexes. This is consistent with the reductive product undergoing chemical reactions over the longer time scales. This suggests that the species corresponding to the wave is unstable in DMF and does not survive long in DMF solution either in free ligand or in metal complexes. Hence, the reductive wave in the region -0.81 to -1.00 V corresponds to generation of the ligand based phenoxyl radical [37-39]. Hence, this irreversible wave is also considered to arise from ligand centred electron transfer reaction. It is worth noting that with the highly negatively charged dihydrazone ligands bonded to the metal centre, it is expected to help make the reduction at the metal centre unfavorable, leading to quite negative  $E_{pc}$  values [40]. Apart from these waves, all complexes invariably show a new oxidative wave in the region +0.72 to +1.57 V, which, most probably, arises due to oxidation of >C=N group [41]. The difference between reductive and oxidative waves falls in the region 140-350 mV which is much more than one electron uncomplicated electron transfer reaction. This reveals that the metal centred electron transfer reaction is either quasi-reversible or irreversible. The large peak separation originates, most probably, from a slow heterogeneous one electron exchange rather than from intervening homogeneous reaction [42]. The metal centred electron transfer reaction may be written as

$$[H_2LMn^{II}(BB)].nH_2O \xrightarrow{+e} [H_2LMn^{I}(BB)]^{-}.nH_2O \xrightarrow{+e} [H_2LMn^{0}(BB)]^{2-}.nH_2O$$

On the other hand, the complex (2) shows only one redox couple ( $E_{pc} = +0.13$  V,  $E_{pa} = +0.65$  V,  $E_{1/2} = +0.39$  V,  $\Delta E = 520$  mV). This may be assigned to metal centred electron transfer reactions. The irreversible reductive waves at -0.38 and -1.15 V are attributed to ligand centred electron transfer reaction. The species produced corresponding to these reduction reactions are unstable and do not survive long in DMF solution and return to original species. The metal centred electron transfer reaction may be written as

$$[Mn^{II}(H_2 slox)(phen)] \xrightarrow{+e} [Mn^{I}(H_2 slox)(phen)]^{-e}$$

On the basis of various physico–chemical and spectroscopic studies the complexes have, tentatively, been proposed to have the following structures (Figure 2 and 3).

## Conclusion

In the present paper, we have synthesized some low-spin manganese(II) complexes from oxaloyldihydrazones derived from condensation of oxaloyldihydrazine with salicyaldehyde and 2-hydroxy-1-naphthaldehyde. The complexes have been characterized by various physicochemical techniques and their structures have been discussed in the light of spectroscopic techniques. In all complexes, the principal dihydrazone ligand is present in keto-form. The complex (2) is monomeric while the remaining complexes are dimeric. In complex (2), the principal dihydrazone ligand is present in anti-cis configuration and secondary ligand 1,10phenanthroline as a chelating bidentate ligand. In the remaining complexes the principal dihydrazone ligands are present in syn-cis configuration. The dihydrazone ligands and the secondary bidentate ligands are coordinated to the metal centre as a bridging bis(monobasic bidentate) and bidentate ligands, respectively. In all complexes, the manganese(II) centre is present in distorted octahedral geometry. The complex (2) has normal magnetic moment corresponding to low-spin Mn(II) complexes while remaining complexes have anomalously low value of magnetic moment exhibiting metal-metal interaction in their structural unit. All complexes show two metal centred electron transfer reactions, while one electrode reaction is purely metal centred, the second electrode reaction has contribution from ligand centred electron transfer reaction along with metal centred electron transfer reaction.

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S1.	Complex and colour	M.P/	Elemental Analysis: Found (calcd.) %			
No.		D.P	Mn	С	Н	Ν
		(°C)				
1	[Mn <sup>II</sup> (H <sub>2</sub> slox)(bipy)]	>300	10.58	57.95	3.78	15.29
	Light yellow		(10.26)	(58.33)	(3,76)	(15.70)
2	[Mn <sup>II</sup> (H <sub>2</sub> slox)(phen)]	>250	10.19	60.49	3.58	14.87
	Yellow		(9.82)	(60.11)	(3.60)	(15.02)
2a	$[Mn^{II}(H_2 slox)(phen)].1.5$	>280	8.97	56.99	3.96	14.75
	$H_2O$		(9.37)	(57.34)	(3.95)	(14.33)
	Light yellow					, Y
3	[Mn <sup>II</sup> (H <sub>2</sub> nph)(bipy)].H <sub>2</sub> O	>300	8.05	62.81	4.03	12.44
	Yellow		(8.40)	(62.49)	(4.01)	(12.86)
4	[Mn <sup>II</sup> (H <sub>2</sub> nph)(phen)].H <sub>2</sub> O	>300	8.45	64.18	3.85	12.04
	Yellow		(8.11)	(63.81)	(3.87)	(12.40)

**Table 1.** Complex, colour, decomposition point and elemental analysis for manganese(II) complexes

 derived from oxaloyldihydrazones

a, synthesized from reaction of MnSO<sub>4</sub>.H<sub>2</sub>O, H<sub>4</sub>slox and 1,10-phenanthroline in molar ratio 1:1:1.

**Table 2:** Molecular weight, magnetic moment and molar conductance for manganese(II) complexes derived from oxaloyldihydrazones

Sl.	Complex	Molecular	Magnetic	Molar
No.		weight	Moment	Conductance
		(Exp.)	μ <sub>eff</sub> (BM)	$\Omega^{-1}$ cm <sup>2</sup> mol <sup>-1</sup>
		{Calcd.}		
1	[Mn <sup>II</sup> (H <sub>2</sub> slox)(bipy)]	(1090±55)	0.92	0.9
		{535}		
2	[Mn <sup>II</sup> (H <sub>2</sub> slox)(phen)]	(1150±55)	0.78	1.2
		{559}		
2a	$[Mn^{II}(H_2 slox)(phen)].1.5H_2O$	(570±27)	1.74	1.3
		{586}		
3	[Mn <sup>II</sup> (H <sub>2</sub> nph)(bipy)].H <sub>2</sub> O	(1234±60)	0.52	1.7
		<i>{</i> 653 <i>}</i>		
4	[Mn <sup>II</sup> (H <sub>2</sub> nph)(phen)].H <sub>2</sub> O	(1370±55)	0.81	1.5
		{667}		

Table 3: EPR for manganese(II) complexes derived from oxaloyldihydrazones

Sl.	Compounds	Phase	Temperature	$g_{av}$	A <sub>mn</sub>	Width
No.			_		(G)	$(\Delta H)$
1	[Mn <sup>II</sup> (H <sub>2</sub> slox)(bipy)]	Solid	RT	2.025	-	100
			LNT	2.020	-	110
	Y	DMSO	RT	-	-	-
			LNT	2.025	88	-
2	[Mn <sup>II</sup> (H <sub>2</sub> slox)(phen)]	Solid	RT	2.025	-	105
			LNT	2.025	-	120
		DMSO	RT	-	-	-
			LNT	2.021	85	-
2a	$[Mn^{II}(H_2 slox)(phen)].1.5H_2O$	Solid	RT	2.025	-	90

			LNT	2.025	-	75
		DMSO	RT	-	-	-
			LNT	2.025	-	-
3	[Mn <sup>II</sup> (H <sub>2</sub> nph)(bipy)].H <sub>2</sub> O	Solid	RT	2.025	-	120
			LNT	2.025	-	130
		DMSO	RT	-		-
			LNT	2.020	86	-
4	[Mn <sup>II</sup> (H <sub>2</sub> nph)(phen)].H <sub>2</sub> O	Solid	RT	2.025	-	95
			LNT	2.025	-	110
		DMSO	RT	-	- /	-
			LNT	2.010	92	-

**Table 4:** Electronic spectral bands and electrochemical parameters for manganese(II) complexes derived from oxaloyldihydrazones

Complex and (complex number)	blex and (complex number) Electronic Electrochemical parameters				
	Spectral band	Scan rate 100 mV/s.			
	-				
	DMF	Reduction	Oxidation	E <sub>1/2</sub>	ΔE
	solution	$E_{pc}(V)$	$E_{pa}(V)$		(mV)
	$\lambda_{max}(\epsilon_{max})$		-		
	nm(dm <sup>3</sup> mol <sup>-</sup>				
	$^{1}$ cm <sup>-1</sup> )				
[Mn <sup>II</sup> (H <sub>2</sub> slox)(bipy)]	303 (23400),	-	+0.79	-	-
(1)	340 (26766),	+0.26	+0.51	+0.39	250
	418 (1600),	-0.34	-	-	-
	581 (700)	-1.00	-0.84	-0.92	160
		-1.54	-	-	-
[Mn <sup>II</sup> (H <sub>2</sub> slox)(phen)]	303 (17870)	+0.13	+0.65	+0.39	520
(2)	340 (21000)	-0.38	-	-	-
	412 (1520)	-1.15	-	-	-
	575 (110)				
$[Mn^{II}(H_2 slox)(phen)].1.5H_2O$	303 (21450),	-	+0.72	-	-
(2a)	340 (24300),	+0.24	+0.45	+0.35	210
	405 (1250),	-1.11	-0.88	-1.00	230
	473 (150)	-1.64	-		-
[Mn <sup>II</sup> (H <sub>2</sub> nph)(bipy)].H <sub>2</sub> O	314 (12700),	-	+1.57	-	-
(3)	326 (15400),	+0.31	+0.44	+0.38	130
	373 (15700),	-0.32	-	-	-
	435 (3900),	-0.98	-0.63	-0.81	350
	461 (3200),				
	489 (2700),				
Y	581 (300)				
$[Mn^{II}(H_2nph)(phen)].H_2O$	314 (21950),	-	+1.54	-	-
(4)	326 (26750),	+0.26	+0.40	+0.33	140
	370 (26850),	-0.14	-	-	-
	436 (3800),	-0.97	-0.83	-0.90	140
	460 (2550),				
	490 (2000),				

	613 (1200)				
Hislox	304 (13130)		+0.52	-0.95	370
114510X	341 (16990)	-1.32	10.52	0.75	-
H₄nph	318 (20275),	-	+0.09	-	-
-	330 (28625),	-0.34	-	-	-
	375 (36175),	-0.98	-	-	
	391 (29950),				
	433 (2175),				
	484 (300)				

**Table 5:** Significant IR spectral bands of oxaloyldihydrazones and their manganese(II) complexes

Complex and (complex	v(OH+NH	v(C=	v(C=N)	Amide	β(C-O)	v(M-O)	v (M-
number)	)	O)		II +	(phenoli	(phenola	N)
				v(C-O)	c/naphth	te/napht	
				(phenol	olic)	holate)	
				ic/naph			
				tholic)			
$[Mn^{II}(H_2 slox)(bipy)]$	3443(s)	1669	1620(s)	1536(s)	1273(w)	486 (w)	-
(1)	3278(s)	(s)	1603(s)		1262(s)		
	3207(s)			,			
$[Mn^{II}(H_2 slox)(phen)]$	3435(s,	1669	1618(s)	1536	1270(w)	530 (w)	655(s)
(2)	br)	(s)	1609(s)	(m)	1258(w)		
	3240(ssh)						
	3208(ssh)						
$[Mn^{II}(H_2 slox)(phen)].1.5$	3452(s)	1669	1619(s)	1536(s)	1273(w)	486 (w)	-
H <sub>2</sub> O	3280(s)	<b>(s)</b>	1603(s)		1262(s)		
(2a)	3206(s)						
		Y					
[Mn <sup>II</sup> (H <sub>2</sub> nph)(bipy)].H <sub>2</sub> O	3437(s)	1683	1622(s)	1535(s)	1284(s)	553 (w)	-
(3)	3245 (w)	(s)					
	3034(s)	1662					
	<u>&gt; `</u>	(s)					
[Mn <sup>II</sup> (H <sub>2</sub> nph)(phen)].H <sub>2</sub> O	3466(s)	1685	1622(s)	1535(s)	1283(m)	555 (m)	-
(4)	3341(s)	(s)					
	3254(s)	1663					
	3181(s)	(s)					
H <sub>4</sub> slox	3434(s)	1669	1620(s)	1536(s)	1276(m)	-	-
	3278(s)	(s)	1603(s)		1262(m)		
Y	3207(s)						
	3150(s)						
H <sub>4</sub> nph	3622(s)	1682	1621(s)	1536(s)	1284(s)	-	-
	3492(s)	(s)	1595(s)				
	3161(s)						



R = Dihydrazone ligand

R = H, disalicyaldehyde oxaloyldihydrazone (H<sub>4</sub>slox);

R = 5,6-benzo bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H<sub>4</sub>nph)



Figure 1. a) Structure of ligands (H<sub>4</sub>L); b) 1,10-phenanthroline(phen); c) 2,2'-bipyridine(bipy)



Figure 2. Tentatively proposed structure of complexes (1) to (4)



Figure 3. Tentatively proposed structure of complex (2a)

# Highlights

- Mononuclear and binuclear manganese(II) complexes from oxaloyldihydrazones have been synthesized in methanolic-water medium and characterized.
- > All manganese(II) complexes are low-spin.
- > All complexes are non-electrolyte in DMF medium.
- There is metal-metal interaction in complexes (1) to (4), but the complex (2a) show no metal-metal interaction.
- ➤ The complexes (1) to (4), show two quasi-reversible metal centred electron transfer reactions involving Mn<sup>II</sup>/Mn<sup>I</sup>/Mn<sup>0</sup> redox reactions in DMF medium.