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Synthesis, and characterization of low- and high-spin manganese(II) complexes of polyfunctional adipoyldihydrazone: Effect of coordination of N-donor ligands on stereo-redox chemistry

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HIGHLIGHTS

- Low and high spin manganese(II) complexes have been synthesized from bis(2-hydroxy-1naphthaldehyde)adipoyldihydrazone.
- Manganese(II) center has low-spin and high spin configuration in the complexes.
- Manganese(II) center in complex (1) has square planar geometry while octahedral geometry in the remaining complexes.
- Ligand is present in keto form in all complexes.
- Complexes show redox chemistry.

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GRAPHICAL ABSTRACT

Reactions and structures of the Mn(II) complexes.

ABSTRACT

Manganese(II) complexes $[Mn^{II}(npahH_2)]$ (1), $[Mn^{II}(npahH_2)(A)_2]$ and $[Mn^{II}(npahH_2)(NN)]$ (where A = pyridine, (2); 2-picoline, (3); 3-picoline, (4); 4-picoline, (5) and NN = 2,2' bipyridine, (6); 1,10-phenanthroline, (7)) have been synthesized from bis(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone (npahH₄) in methanol. The composition of metal complexes has been established by elemental analyses. Complexes (1) and (3) have been characterized by mass spectral data also. Structural assessments of the complexes have been based on data obtained from molar conductance, magnetic moment, electronic, electron paramagnetic resonance and infrared spectral studies. Conductivity measurements in DMSO suggest that they are non-electrolyte. Electronic spectral studies suggest a six-coordinate octahedral geometry around the manganese center in complexes (2) to (7) and square-planar geometry in complex (1). IR spectral studies reveal that the dihydrazone coordinates to the metal in keto form with an anti-cis configuration. Magnetic moment, and EPR studies suggest manganese in +2 oxidation state in all complexes with high-spin distorted octahedral stereochemistry in complexes (2-7) while low-spin square-planar stereochemistry is involved with significant metal-metal interactions in the solid state in complex (1). Cyclic voltammetric studies reveal that the metal center cycles among the $Mn^{II} \rightarrow Mn^{I} \rightarrow Mn^{0}$ in complexes (2) to (7) and among $Mn^{II} \rightarrow Mn^{I}$ oxidation states in complex (1).

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Introduction

Studies have shown the ability of hydrazone based complexes of manganese as potential biomimics for manganese enzymes [1,3,4]. The present work constitutes the exploration of the coordination chemistry of manganese with ligand bis(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone (npahH₄). The ligand is rich and versatile, but has not yet been fully explored with transition metals. Our earlier work [2] with this ligand and manganese in alkaline condition reported Mn(IV) complexes in octahedral geometry.

The ligand derived from condensation of adipoyldihydrazide with 2-hydroxy-1-naphthaldehyde contains four methylene functions flanked by keto groups in addition to other functional groups like amide, azomethine and naphthol functions, each in duplicate. It offers a chemically flexible ligand framework because of free rotation of the two hydrazone groupings about C--C single bond and has a potential to offer any set of donor atoms depending upon the preferred stereochemical disposition of the metal valences and nature of the bonds formed in the coordination process. It is known that the metal complex stability increases with the topological complexity of the ligand recognized in the chelate effect, the macrocyclic effect, and the cryptate effect. Now, we want to retain the features of this tetraligand npahH₄ and explore the level of stability when a second monodentate or bidentate ligand coordinates to the metal center and compare the changes achieved in the topologically constrained environment of the metal complex. N-donor ligands being particularly active as functional biomimics for manganese enzymes [3,4], pyridine and its methyl derivatives were preferably selected as secondary ligands. Reports show that there are few known manganese complexes with pyridine bases and around twenty-five structures of Mn(II) complexes with 1,10-phenanthroline and its derivatives [5] are reported till date. In this article, we provide examples of these situations.

The divalent high-spin manganese complexes are common and they do not have strong stereo-chemical preferences and can exist both in tetrahedral and octahedral coordination environment depending on the structural demand of the coordinated ligand. But very few low-spin complexes of divalent manganese are currently known. Because of its higher spin-pairing energy amongst bivalent 3d ions, the ligands with very strong ligand fields only can induce low-spin character on manganese ion. Low-spin Mn(II) complexes have been known with cyano ligands [6,17], phosphine ligands [7], oxime ligands [8,19], and dithiochelate ligands [9]. Recently, a few low-spin manganese(II) complexes have been reported by various groups [10], and also by us in our earlier reported work with ligand bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone [11]. The lower oxidation state species of manganese(II) are commonly 6-coordinate. Coordination number four with a distorted square-planar or tetrahedral geometry is known for the high-spin Mn(II) [12,13] but uncommon for low-spin manganese(II). We report herein, a lowspin Mn(II) complex with square-planar geometry and provide examples of high-spin Mn(II) complexes with octahedral geometry.

In view of the meagre amount of work on manganese complexes of this dihydrazone, the monometallic complexes of manganese(II) have been synthesized and characterized. The composition of isolated metal complexes has been judged mainly from the elemental analysis, thermoanalytical data and mass spectral data. The structures of Mn(II) complexes have been discussed in the light of molar conductance, magnetic moment, electronic, infrared spectroscopic and EPR studies. The EPR spectroscopy and magnetic susceptibility studies have been used as a probe to study the molecular distortions caused by pyridine (py, **2**) and its derivatives, 2-picoline (2-pic, **3**); 3-picoline (3-pic, **4**); 4-picoline, (4-pic, **5**); 2,2'-bipyridine, (bpy, **6**); 1,10-phenanthroline, (phen, **7**) on the dihydrazone coordinated metal complex (**1**). The electron transfer reactions of the complexes have been studied with the help of cyclic voltammetry.

Experimental section

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

Physical measurements

Determination of manganese was done following the standard procedure [14]. C, H and N were determined microanalytically. The molar conductivity of the complexes at 10^{-3} M in DMSO solution were measured on a Systronics Direct Reading Conductivity meter-303 with a dip-type conductivity cell at room temperature. Room temperature magnetic susceptibility measurements were carried out on a Sherwood Scientific Magnetic Susceptibility Balance. Experimental magnetic susceptibility values have been corrected for diamagnetism by the procedures given by Figgis and Lewis [15]. Infrared (IR) spectra were recorded on a Bomen DA-8FT-IR spectrophotometer from 450 to 4000 cm^{-1} in KBr disks. Electronic spectra of the complexes at 10^{-2} M in DMSO solution were recorded from 200 to 1000 nm in DMSO on a Perkin-Elmer Lambda 25 UV-Vis spectrophotometer. EPR spectra of powdered samples as well as in solution were recorded at X-band frequency on a Varian E-112 E-line century series ESR spectrometer using TCNQ (g = 2.0027) as an internal field marker. FAB mass spectra of the complexes were recorded on a JEOLSX102/DA-6000 mass spectrometer/data systems using Argon/Xenon (6 kV, 10 mA) as FAB gas. Nitrobenzyl alcohol was used as the matrix. Cyclic voltammetric measurements were carried out using CH Instruments Electrochemical Analyzer under nitrogen atmosphere. The electrolytic cell comprises of 3-electrodes. The working electrode was a glassy-carbon disk from BAS and the reference electrode was an aqueous SCE separated from the sample solution by a salt bridge.

Preparation of bis(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone

Adipoyldihydrazide was prepared by reacting diethyl adipate (1.00 g) with hydrazine hydrate (0.55 g) in 1:2 molar ratio in 20 mL ethanol under reflux for 30 mins. The product was recrystallized from dilute ethanol.

Bis(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone (npahH₄) was then prepared by reacting a solution of adipoyldihydrazide (1.00 g) in 20 mL of ethanol with 2-hydroxy-1-naphthaldehyde (2.18 g) in 1:2 molar ratio in ethanol over a hot plate at 50 °C with constant gentle stirring. The yellow precipitate obtained on cooling the solution was thoroughly washed with ethanol and air dried (yield of 61.53%; m.p. > 300 °C).

Synthesis of $[Mn^{II}(npahH_2)]$ (1)

 $Mn(OAc)_2 \cdot 4H_2O$ (1.00 g) in methanol (20 mL) was added to a solution of bis(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone (1.97 g) in 20 mL methanol accompanied by stirring at 60 °C for 10 mins. The homogenous suspension was stirred vigorously for another half an hour, a yellow-brownish compound was obtained. The compound was filtered, washed with hot methanol and air dried (yield: 76%).

Synthesis of $[Mn^{II}(npahH_2)(A)_2]$ and $[Mn^{II}(npahH_2)(NN)]$ (where A = pyridine (py, 2); 2-picoline (2-pic, 3); 3-picoline (3-pic, 4) and 4-picoline (4-pic, 5) and NN = 2,2' bipyridine (bpy, 6) and 1,10-phenanthroline (phen, 7))

These complexes were also prepared by following essentially the above method and adding pyridine bases to the reaction mixture obtained by mixing $Mn(OAc)_2 \cdot H_2O$ and $npahH_4$ maintaining $Mn(OAc)_2 \cdot 4H_2O:npahH_4:pyridine molar ratio at 1:1:10 in case of$ pyridine bases and 1:1:2 in case of 2,2'-bipyridine and 1,10phenanthroline (yield: 60% (2), (3); 57% (4), (5); 51% (6) and (7)).

Results and discussion

The complexes with their color, decomposition point, analytical and magnetic moment data are set out in Table 1. Based on the analytical data, these complexes are suggested to have the compositions $[Mn^{II}(npahH_2)]$, $[Mn^{II}(npahH_2)(A)_2]$ and $[Mn^{II}(npahH_2)(NN)]$ (where A = py, (2); 2-pic, (3); 3-pic, (4); 4-pic, (5); NN = bpy, (6); phen, (7). The complexes are air-stable and insoluble in water and common organic solvents such as ethanol and acetone, but they dissolve freely in coordinating solvents like DMSO and DMF.

An effort was undertaken to crystallize the complexes in various solvent systems under different experimental conditions to establish their molecularity and structure by X-ray crystallography. Unfortunately, in all our efforts, only amorphous compounds precipitated preventing analysis by X-ray crystallography.

Molar conductance

The molar conductance values for the complexes are given in Table 1. The values lie in the range $1.5-3.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in DMSO that indicate their non-electrolytic nature in this solvent [16].

Thermal studies

All these complexes decompose above 300 °C without melting, indicating that the metal-ligand bonds have higher ionic character. The complexes do not show weight loss either at 110 °C or at 180 °C ruling out the possibility of the presence of water molecules either in the lattice structure or in the first coordination sphere around metal ion. Complexes (2)–(5) show weight loss at 220 °C corresponding to two pyridine/2-picoline/3-picoline/4-picoline molecules, while the complexes (6) and (7) show weight loss

corresponding to one bipyridine and one 1,10-phenanthroline molecule, respectively. The expulsion of these donor molecules at such a high temperature indicates that they are coordinated to the metal center.

Mass spectra

The FAB mass spectra of complexes (1) and (3) show a signal at m/z value 536 that results from the formation of $[Mn(npahH_2)]^+$ species. The species $[Mn(npahH_2)]^+$ in complex (1) results from the breakdown of the polymeric structure while in complex (3) this result from the loss of two 2-picoline molecules. Both the complexes show a peak at m/z value 483 that arise from the protonated ligand $[npahH_5]^+$ which results from the loss of a manganese atom in complex (1) and two 2-picoline molecules and one manganese atom in complex (3). Further, the complex (3) shows two prominent peaks at m/z value 678 which is attributed to $[Mn(npahH_2-C_3H_6)(2-picH^+)_2]$. The existence of these species in the mass spectra of these complexes indicates their monomeric nature.

Magnetic moment

The μ_B values of the complexes are presented in Table 1. The μ_B value of 1.12 B.M. for complex (1) suggests that it is a low-spin complex. Very few low-spin complexes of di- and tri-valent manganese are currently known [6–11,17–19]. Although the complex (1) should show μ_B value corresponding to one unpaired electron, considering orbital contribution, the μ_B value exhibited by the complex (1) should fall around ca. 2.18 B.M. [17]. Such a lowering in μ_B value indicates spin-spin coupling in the solid state between unpaired electrons belonging to different Mn(II) centers in the structural unit of the complex [24]. A decrease in the magnetic moment value of the complex (1) can occur due to direct overlap of metal orbitals of one structural unit with metal orbitals of other structural unit. Alternatively, the decrease in the μ_B value of this complex can occur due to superexchange via overlap of the metal orbitals with the orbitals of the bridging oxygen atoms of naphtholate group [19,25]. The μ_B value noted for the complex (1) is also suggestive of the fact that the complex is in a square-planar environment with the ground term ${}^{4}A_{1g}$ ($b_{2g}^{2} e_{g}^{2} a_{1g}^{1}$).

The μ_B values for complexes (**2**) to (**7**) in the range 5.83–5.96 B.M., fall within the range reported for Mn(II) complexes in the high-spin state ($t_{2g}^3eg^2$, S = 5/2). This rule out the possibility of

Table 1

Color, decomposition point, analytical, magnetic moment and molar conductance data for manganese(II) complexes of bis(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone (npahH₄).

Sl. no.	Complex	Color	D.P. (°C)	Analysis:found (Calcd)%			μ_{B} (B.M.)	Molar conductance Λm	
				Mn	С	Н	Ν		$(ohm^{-1} cm^2 mol^{-1})$
1.	[Mn ^{II} (npahH ₂)]	Yellowish-brown	>300	10.05 (10.28)	62.31 (62.80)	4.52 (4.49)	10.32 (10.47)	1.12	1.5
2.	[Mn ^{II} (npahH ₂)(py) ₂]	Yellowish-brown	>300	8.15 (7.94)	66.22 (65.80)	5.00 (4.91)	12.34 (12.12)	5.91	3.2
3.	[Mn ^{II} (npahH ₂)(2-pic) ₂]	Yellowish-brown	>300	7.50 (7.63)	66.23 (66.57)	5.32 (5.27)	11.91 (11.65)	5.83	2.8
4.	[Mn ^{II} (npahH ₂)(3-pic) ₂]	Yellowish-brown	>300	7.50 (7.63)	66.81 (66.57)	5.24 (5.27)	11.41 (11.65)	5.89	3.7
5.	[Mn ^{II} (npahH ₂)(4-pic) ₂]	Yellowish-brown	>300	7.42 (7.63)	66.80 (66.57)	5.31 (5.27)	11.32 (11.65)	5.96	2.6
6.	[Mn ^{II} (npahH ₂)(bpy)]	Yellowish-brown	>300	7.82 (7.96)	66.35 (65.99)	4.51 (4.63)	11.98 (12.16)	5.87	3.3
7.	[Mn ^{II} (npahH ₂)(phen)]	Yellowish-brown	>300	7.82 (7.69)	66.65 (67.13)	4.51 (4.48)	12.10 (11.75)	5.95	2.5

any spin-spin coupling in the solid state between unpaired electrons belonging to different Mn(II) centeres in the structural unit of the complexes [23].

Electronic spectra

The electronic spectral bands for dihydrazone and the metal complexes along with their molar extinction coefficient values are shown in Table 2.

The free ligand npahH₄ shows three bands at 290 (2041), 313 (2300) and 363 (1852) nm. The band at 290 nm is assigned to intraligand π - π * transitions while the bands in the region 313–363 nm are assigned to n- π * transitions. The bands in the region 313–363 nm are characteristic of the napthaldimine part of ligand as has been reported in several monoacyl hydrazones [11,20,21]. The last two bands in npahH₄ are split into two components, each in the complexes. The splitting of the ligand bands suggests that the two hydrazone fractions are not in the same plane. This, alternatively, suggests that the free dihydrazone exist with an anti-cis configuration as concluded from IR spectroscopic studies.

The spectra of complexes possess one additional band in the region 450–600 nm due to d–d transition. These appear to have contributions from ligand band at 363 nm which is, most probably, red shifted in complexes and as well as from charge transfer bands arising due to charge transfer from naphtholate oxygen atoms to metal center [11,21]. The d–d transitions in the Mn(II) complexes are very weak because they are both spin as well as laporte forbidden [22]. The spectrum of complex (1) displays a broad shoulder like absorption near 600 nm which may be assigned to a d–d transition from the partially spin-paired ground term

$${}^{4}A_{1g}(b_{2g}^{2}e_{g}^{1}a_{1g}^{1}) \text{ to the } b_{1g}^{1}(d_{xy}) \text{ orbital i.e. } (b_{2g}^{2}e_{g}^{1}a_{1g}^{1}) \longrightarrow (b_{2g}^{2}e_{g}^{1}a_{1g}^{1}b_{1g}^{1})$$

This may be consistent with a square-planar environment for Mn(II) complex.

For Mn(II) d⁵ high-spin configuration with a ⁶S ground term, crystal field of any symmetry cannot split it. Usually high-spin Mn(II) complexes rarely show d–d transitions. However, the complexes show low intensity peaks around 455–483 nm corresponding to ${}^{6}A_{1g}(F) - {}^{4}T_{2g}(G)$ transitions, as has been reported for Mn(II) octahedral complexes [11,21,24].

EPR spectra

The EPR magnetic parameters for the complexes are set out in Table 2. The EPR spectrum of the complex (1) in the crystalline powder form shows an isotropic signal with g = 2.019. The width of the signal at g = 2.019 is about 330 G which indicates spin exchange [10,24] between manganese(II) centers in the solid state which is consistent with a very low μ_B value of the complex. Although the essential features of the EPR spectrum of the complex in solution remain the same as in the polycrystalline state, yet the width of the signal in the g = 2.019 region is dramatically increased to about 500 G. This rules out the possibility of the presence of any exchange interaction in DMSO solution. This may be due to the breaking of polymeric structure resulted from coordination of highly donor solvent DMSO molecules to the metal center.

The ' A_{Mn} ' value of 100 G for complex (1) lies in the range reported for the low-spin manganese Mn(II) complexes without metal-metal interaction, the ranges 75–100 G, the 90–100 G domain being more frequented [11,20] by the low-spin manganese(II) complexes. The central resonance in this complex shows splitting into five components with average nitrogen superhyperfine splitting constant A_N equal to 12 G that indicate coordination of two nitrogen atoms to the manganese center [21].

The EPR spectra of the complexes (2) to (7) in the solid state are essentially similar to one another at LNT and show an isotropic signal with g-value in the region 2.019–2.038. This shows that these complexes have similar octahedral stereochemistry. No other signal is observed in the 8000 G span as would have been expected for non-cubic Mn(II) complexes with an appreciable zero-field splitting. On the other hand, in DMSO solution at RT, six hyperfine lines are obtained with ⁵⁵Mn hyperfine splitting constant falling in the range 94–104 G. This ⁵⁵Mn hyperfine splitting constant is characteristic of Mn(II) complexes rather than for Mn(IV) complexes.

Infrared spectra

Some structurally significant IR bands for free dihydrazone and complexes are given in Table 3. The IR spectral bands for the dihydrazone show a strong band at 1666 cm⁻¹ which are assigned to vC=O band. These bands on an average shift to lower frequency

Table 2

Important electronic spectral bands and EPR data for manganese(II) complexes of bis(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone.

Ligand/complex	λ_{max} (nm) (ε_{max} dm ³ mol ⁻¹ cm ⁻¹) for conc. 10 ⁻² M soln			oln	Temp.	Solid/soln	g-Value	$A_{Mn}(G)$
npahH ₄	290(2041)	313(2300)	363(1852)					
$[Mn^{ll}(npahH_2)]$ (1)	257(5735)	315(2890)	364(2460)	600(790)	LNT LNT	SOLID DMSO	2.019 2.007	_ 100
[Mn ^{II} (npahH ₂)(py) ₂] (2)	355 (6160)	483(4860)			LNT LNT RT	SOLID DMSO DMSO	2.019 2.036 2.226	- 100 96
[Mn ^{II} (npahH ₂)(2-pic) ₂] (3)	256 (8340)	316(4362)	365(3705)	448(2475)	LNT LNT RT	SOLID DMSO DMSO	2.038 2.019 1.944	- 94 94
[Mn ^{II} (npahH ₂)(3-pic) ₂] (4)	256(8340)	316(4362)	364(3753)	450(394)	LNT LNT RT	SOLID DMSO DMSO	2.038 2.019 1.804	- 94 94
[Mn ^{II} (npahH ₂)(4-pic) ₂] (5)	263(8270)	317(4194)	363(3532)	450(198)	LNT LNT RT	SOLID DMSO DMSO	2.032 2.006 1.840	- 94 94
[Mn ^{II} (npahH ₂)(bpy)] (6)	260(5760)	320(4570)	364(8080)	455(706)	LNT LNT RT	SOLID DMSO DMSO	2.036 1.994 1.838	- - 98
[Mn ^{II} (npahH ₂)(phen)] (7)	315(7637)	363(7320)	450(160)		LNT LNT RT	SOLID DMSO DMSO	2.032 2.010 1.890	- - 100

LNT: Liquid nitrogen temperature; and RT: Room temperature.

Table 3

Structurally significant Infrared spectral bands of bis(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone (npahH₄) and its monometallic manganese(II) complexes.

Sl. no.	Ligand/complex	ν(OH) + ν(NH)	v(C=0)	v(C=N)	Amide(II) + $v(CO)$ (naphtholic)	β(C—O) (naphtholic)	v(N—N)	v(M—O) naphtholic	v(M—N) py/bpy/phen vibration in plane
	npahH ₄	3300-3600(sbr) 3469(sbr) 3224(s) 3051(sbr)	1666(s)	1630(s) 1593(s)	1530(w)	1281(m)	1030(w)	_	_
1.	[Mn ^{II} (npahH ₂)]	3440(mbr) 3187(m) 3042(m)	1656(s)	1621(s) 1596(s)	1552(s)	1283(m)	1080(w)	600(wbr)	-
2.	[Mn ^{II} (npahH ₂)(py) ₂]	3430(sbr) 3180(mbr) 3000(m)	1650(s)	1615(s) 1600(s)	1540(s)	1310(w)	1080(w)	600(wbr)	690(m)
3.	[Mn ^{II} (npahH ₂)(2-pic) ₂]	3398(wbr) 3200(wbr) 3000(w)	1640(sbr)	1620(vs) 1600(vs)	1539(s)	1280(w)	1080(w)	600(wbr)	657(m)
4.	[Mn ^{II} (npahH ₂)(3-pic) ₂]	3402(wbr) 3170(w) 3000(w)	1664(s)	1620(vs) 1600(vs)	1539(s)	1301(w)	1070(w)	600(wbr)	680(wbr)
5.	[Mn ^{II} (npahH ₂)(4-pic) ₂]	3427 (sbr) 3170(mbr) 3038(m)	1664(mbr)	1620(vs) 1600(vs)	1539(vs)	1301(w)	1093(w)	600(wbr)	649(w)
6.	[Mn ^{II} (npahH ₂)(bpy)]	3425(mbr) 3186(w) 3047(w)	1654(s)	1620(s) 1599(s)	1540(m)	1300(w)	1095(w)	600(wbr)	660(wbr)
7.	[Mn ^{II} (npahH ₂)(phen)]	3410(mbr) 3332(w) 3304(w) 3186(m) 3043(m)	1654(m)	1622(s) 1598(m)	1538(m)	1283(m)	1084(w)	-	660(wbr)

Table 4

The electrochemical parameters for the dihydrazone and its monometallic manganese(II) complexes (Pot. vs SCE) at scan rates, 5 and 100 mV/s.

Ligand/complex	Epa (V)	Epc (V)	$E_{1/2}(V)$	$\Delta E (mV)$	Epa (V)	Epc (V)	$E_{1/2}$ (V)	$\Delta E (mV)$
	(Scan rate = 5 mV/s)			(Scan rate = 100 mV/s)				
npahH ₄	-				0.00 +0.35	-0.15 -	+0.075	150
[Mn ^{II} (npahH ₂)] (1)	-				+0.28	+0.18 (M _A)	+0.23	100
[Mn ^{II} (npahH ₂)(py) ₂] (2)	+0.27	+0.16 (M _A)	+0.215	110	0.27 (broad) +0.06			
	+0.18	$-0.07~(M_B)$	+0.125	250				
[MnII(npahH2)(3-pic)2] (4)	-				+0.29 -0.30	$-0.01 (M_A) \\ -0.55 (M_B)$	+0.15 -0.425	300 250
$Mn^{II}(npahH_2)(4-pic)_2](5)$	+0.25 (broad)	+0.20(broad)			+0.40 0.00	+0.10 (M _A) -0.26 (M _B)	+0.25 -0.13	300 260
[Mn ^{II} (npahH ₂)(bpy)] (6)	+0.27 +0.16	+0.02 (M _A) -0.07 (M _B)	0.135 0.115	250 230	+0.35 (broad)	+0.13 (broad)		
[Mn ^{II} (npahH ₂)(phen)] (7)	+0.30 -0.30	0.00 (M _A) -0.40 (M _B)	+0.15 -0.35	300 100	+0.38 (broad)	0.00 (broad)		

Manganese centered redox couple:

 $M_A: Mn(II) + e \rightleftharpoons Mn(I).$

 $M_B: Mn(I) + e \rightleftharpoons Mn(0).$

by 2–26 cm⁻¹ and appear in the region 1640–1664 cm⁻¹. Such a lower shift rule out the possibility of coordination of >C=O groups to the metal center, but is involved in strong intramolecular Hbonding with the secondary NH group in the complexes. This is also corroborated from the observation that the band in the region 500–400 cm⁻¹ which could be assigned to vM–O(carbonyl) is absent ruling out the possibility of coordination of carbonyl oxygen atom to the metal center either as such or enol form. This suggests that the dihydrazone is coordinated to the metal centre in keto form. The bands observed at 1630 and 1573 cm⁻¹ in free dihydrazone is assignable to vC=N bands. These bands appear as couplet in the complexes as well, with an average shift to lower frequency by 2–15 cm⁻¹ indicating coordination of >C=N group to the metal centre. This arises due to coordination of both the azomethine nitrogen atoms and naphtholate oxygen atoms of the same dihydrazone molecule to the same metal centre. This introduces steric crowding in the molecule. As a result one dihydrazone arm remains in the equatorial plane while the other hydrazone arm

Table 5

Stereochemistry and redox activity of manganese(II) complexes.

Complex	Spin & stereochemistry	Manganese centered redox activity (Scan rate)				
		100 mV/s	5 mV/s			
[Mn ^{II} (npahH ₂)] (1)	Low spin & square-planar	$Mn^{II} \stackrel{e_{-}}{\rightleftharpoons} Mn^{I}$	-			
[Mn ^{II} (npahH ₂)(py) ₂] (2)	High-spin & octahedral	-	$Mn^{II} \stackrel{e_{-}}{\leftrightarrow} Mn^{I} \stackrel{e_{-}}{\leftrightarrow} Mn^{0}$			
[Mn ^{II} (npahH ₂)(3-pic) ₂] (4)	High-spin & octahedral	$Mn^{II} \stackrel{e_{-}}{\leftrightarrow} Mn^{I} \stackrel{e_{-}}{\leftrightarrow} Mn^{0}$	-			
[Mn ^{II} (npahH ₂)(4-pic) ₂] (5)	High-spin & Octahedral	$Mn^{II} \stackrel{e_{-}}{\leftrightarrow} Mn^{I} \stackrel{e_{-}}{\leftrightarrow} Mn^{0}$	-			
[Mn ^{II} (npahH ₂)(bpy)] (6)	High-spin & octahedral	_	$Mn^{II} \stackrel{e_{-}}{\rightleftharpoons} Mn^{I} \stackrel{e_{-}}{\rightleftharpoons} Mn^{0}$			
[Mn ^{II} (npahH ₂)(phen)] (7)	High-spin & octahedral	-	$Mn^{II} \stackrel{e_{-}}{\rightleftharpoons} Mn^{I} \stackrel{e_{-}}{\rightleftharpoons} Mn^{0}$			



bpy, (6) and phen, (7)]

Fig. 1. Reactions and structures of the Mn(II) complexes.

attains an axial position. In this configuration, axial azomethine protons absorb at lower frequency as compared to equatorial azomethine protons which absorb at higher frequency in the IR spectra. A band at 1281 cm⁻¹ is assignable to β (C–O)(naphtholic) in the free dihydrazone. This shifts to higher frequency of 2–13 cm⁻¹ in the complexes and is associated with involvement of the naphtholic C–O group in coordination. Another weak broad band appear in at 600 cm⁻¹ is assigned to vM–O(naphtholate) that indicates π -electron density flows of aromatic ring to the metal center through the naphtholate oxygen atom. Pyridine bases absorb at around ~604 cm⁻¹ due to in-plane ring deformation mode. In the complexes (**2**) to (**7**), a new medium to weak band is observed in the region 649–690 cm⁻¹. This is attributed to arise due to in-plane ring deformation mode of pyridine bases indicating their coordination to the metal centre.

Cyclic voltammetry

The cyclic voltammograms of 2 mmol solutions of the ligand and complexes (1), (2) and (4) to (7) in DMSO under nitrogen with 0.1 M TBAP as a supporting electrolyte were run at several scan rates. The data have been set out in Tables 4 and 5 at scan rates of 5 and 100 mV/s.

The free ligand exhibits one quasi-reversible redox couple at +0.075 V ($E_{1/2}$) (ΔE = 150 mV) and an additional oxidative wave at +0.35 V against SCE. The oxidative and reductive waves in the complexes are well-separated from those associated with free dihydrazone. Hence, these waves are attributed to metal-centered electron-transfer reactions. Complex (1) show one metal centered quasireversible redox couple at +0.23 V attributed to Mn^{II}/Mn^I couple and the redox reaction of this couple is given as

$$[Mn^{II}(npahH_2)] + e \rightleftharpoons [Mn^{I}(npahH_2)]^{-1}$$

The complexes (2), (4) to (7) show two quasireversible redox couples. As an electron transfer kinetics and coupled chemical reactions depend upon the scan rate of the experiment, these waves are well resolved at a scan rate of 5 mV/s for complexes (2), (6) and (7) but are observed at higher scan rates for complexes (1), (3) and (5). The redox processes corresponding to first and second redox waves for complexes (2), (4) and (5) are assigned as:

$$[Mn^{II}(npahH_2)(A)_2] + e \xleftarrow{} [Mn^{I}(npahH_2)(A)_2]^{-1}(I)$$

$$\begin{split} & \left[Mn^{I}(npahH_{2})(A)_{2} \right]^{-1} + e \overleftarrow{\longrightarrow} \left[Mn^{0}(npahH_{2})(A)_{2} \right]^{-2}(II) \\ & (A = py, \, \textbf{(2)}; \ 3\text{-pic}, \ \textbf{(4)}; \ 4\text{-pic}, \ \textbf{(5)}) \end{split}$$

The metal-centered redox processes involved for complexes (6) and (7) are as follows:

$$\begin{split} & [Mn^{II}(npahH_2)(NN)] + e & \longleftrightarrow [Mn^{I}(npahH_2)(NN)]^{-1}(I) \\ & [Mn^{I}(npahH_2)(NN)]^{-1} + e & \longleftrightarrow [Mn^{0}(npahH_2)(NN)]^{-2}(II) \\ & (NN = bpy, (\mathbf{6}); \ phen, (\mathbf{7})) \end{split}$$

Examination of Table 4 shows that there is almost a regular trend observed in manganese-centered reduction potentials. Pyridine and its derivatives play important role in shifting the redox potential values that decreases in going from complex (1) without pyridine base to complex (2) with pyridine and complex (4) with 3-picoline to complex (5) with 4-picoline. This is attributed to enhanced removal of electron density towards the metal in going from complexes (1) to (5) due to basicity increase in the order pyridine < 3-picoline < 4-picoline. The inductive effects of methyl groups at different positions on pyridine are not equal. The inductive effect is higher on the complex (5) with methyl

substitution on pyridine at the para position. The oxidation potential of +0.40 V in complex (**5**) suggest the ease in removal of electron from this 4-methylpyridine substituent. Similarly, a negative shift in reduction potentials observed in going from complex (**1**) to complexes (**6**) and (**7**) with 2,2'-bipyridine and 1,10-phenanthroline ligand is attributed to increases in the flow of electron density towards the metal. The inclusion of the bidentate groups, 2,2'-bipyridine and 1,10-phenanthroline in complexes (**6**) and (**7**) respectively, resulted in enhanced basicity due to inductive and resonance effects on coordination to the manganese centre. The reduction electrochemistry of complexes (**2**) to (**7**) are enhanced by incorporation of pyridine and its substituent bases. The reduced manganese center exhibits stable two-electron chemical reversibility and may further be improvised by substitution with different functional groups.

Conclusions

This article reports the synthesis, characterization of Mn(II) complexes of ligand bis(2-hydroxy-1-naphthaldehyde) adipoyldihydrazone and the effect on their stereochemistry and redox activity upon coordination of various mono and bidentate nitrogen donor ligands. The dihvdrazone coordinates to Mn(II) through azomethine nitrogens and naphtholate oxygens with manganese occupying the NNOO coordination chamber. The dihydrazone donors are arranged around manganese in the equatorial plane while the axial positions are occupied by pyridine/2-picoline/3-picoline/4-picoline in complexes (2) to (5). In complexes (6) and (7), the nitrogens from azomethine of dihydrazone and bpy and phen are in equatorial positions while naphtholate oxygens are in axial positions. The enolate oxygens remain uncoordinated. The dihydrazone ligand is suggested to be coordinated to manganese in the anti-cis configuration in all complexes. This configuration arises due to coordination of both azomethine nitrogens and naphtholate oxygens of the same dihydrazone to the same metal center which introduces steric crowding. As a result, one hydrazone arm remains in the equatorial plane while the other hydrazone arm is axial. In this configuration, axial azomethine absorbs at lower frequency than equatorial azomethine as observed in IR and electronic spectra. The magnetic susceptibility data in all cases support the electronic and EPR data suggesting a high-spin distorted octahedral stereochemistry in all the complexes except for complex (1) which has a low-spin square-planar stereochemistry involving significant metal-metal interaction.

The present npahH₄ is a strong ligand that enables formation of low-spin inner orbital square-planar complex (**1**) after forcible pairing of electrons within the 3d level of the metal centre. Upon coordination in complexes (**2**) to (**7**), pyridine and its substituents stabilize the high-spin Manganese(II)(npahH₂) species in their octahedral geometry and easily reduces the manganese center to lower oxidation states during the redox cycles. Cyclic voltammetry studies show that the metal center cycles among the $Mn^{II} \rightarrow Mn^{0}$ in complexes (**2**) to (**7**) and among $Mn^{II} \rightarrow Mn^{1}$ oxidation states in complex (**1**).

These complexes are promising candidates with potential applications in catalysis [4,26,27].

Structures of the complexes have been presented in Fig. 1.

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