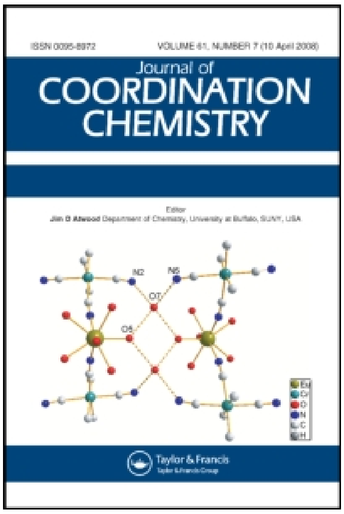

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Synthesis, characterization, reactivity, and electrochemical studies of manganese(IV) complexes of *bis*(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone

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Synthesis, characterization, reactivity, and electrochemical studies of manganese(IV) complexes of *bis*(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone

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Manganese(IV) complexes $[Mn^{IV}(npah)(H_2O)_2]$ (**1**) and $[Mn^{IV}(npah)(A)_2]\cdot nH_2O$ (where A = py (**2**), 2-pic (**3**), 3-pic (**4**), 4-pic (**5**)) and $Mn^{IV}(npah)(NN)]$ (NN = bpy (**6**) and phen (**7**)) have been synthesized from *bis*(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone in methanol. The composition of the complexes has been established by elemental analyses. Complex **3** has been characterized by mass spectral data also. Structural assessment of the complexes has been based on data from molar conductance, magnetic moment, electronic, electron paramagnetic resonance, and infrared (IR) spectral studies. Molar conductances of the complexes in DMSO suggest non-electrolytes. Magnetic moment and EPR studies suggest +4 oxidation state for manganese in these complexes. Electronic spectral studies suggest six-coordinate octahedral geometry around the metal ions. IR spectra reveal that H_4npah coordinates to the metal in enol form. Reaction of the complexes with benzyl alcohol and SO_2 has been investigated. Cyclic voltammetric studies of the complexes have also been carried out.

Keywords: "EPR of Mn (IV)" complexes; *Bis*(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone; Magnetic moment; Electrochemical studies; Spectral studies

1. Introduction

Manganese shares an essential role in electron and oxygen transfer processes in nature with iron and copper [1]. Manganese-containing enzymes are involved in a number of fundamental biological processes, such as photosynthesis [2], the regulation of oxidative stress [3], and bacterial virulence [4] including delignification [2] and superoxide dismutase [3].

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

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oxygen-evolving complex [2, 3] and as Mn(III) in manganese superoxide dismutase [4]. Further, manganese is found in a variety of enzymes as mononuclear [5], binuclear [6], or multinuclear [7]. High oxidation state manganese moieties have long been accepted as the reactive intermediates in reactions, such as water oxidation for oxygen evolution. Oxomanganese(V) reactive units are believed to serve as key intermediates in oxygenation mediated by synthetic manganese complexes [8]. The oxygen-evolving center of photosystem II, where water is split into dioxygen and protons, remains a mysterious reaction [9, 10]. Its active site is proposed to consist of four manganese ions in a "3+1" tetranuclear complex fashion in which a trimer is linked to a monomer [11]. X-ray absorption and electron paramagnetic resonance (EPR) spectroscopy have established that the Mn ions are present in the +2, +3, and +4 oxidation states [12, 13]. Polynuclear Mn-oxo complexes have been studied as models for this active site [14]. Further, higher oxidation state manganese complexes serve as oxidizing agents, catalysts, and electrocatalysts for oxidation of alcohols, ethers, and water [15]. A number of reports [16] deal with Mn(III) and Mn(IV) complexes as oxidizing agents. Higher oxidation oxo-bridged dinuclear manganese complexes have been reported in aliphatic and aromatic C–H activation and oxygen insertion reactions [11]. This has attracted attention to trinuclear, binuclear, and mononuclear complexes of manganese in +3 and +4 oxidation states as structural and functional models for enzymes as well as for a variety of catalytic reactions.

Schiff base and oxo-bridged manganese complexes have been of particular interest because they seem to mimic the coordination environment of Mn in PSII which does not contain a porphyrinic system and is thought to be made up of O and N donors only [17, 18]. An interesting feature associated with ligands containing phenolate/naptholate donors is their ability to stabilize higher oxidation state and their tendency to form phenyl radical. Dihydrazones derived from condensation of acyldihydrazines, aroyldihydrazines, and pyridoyldihydrazines with *o*-hydroxy aromatic aldehydes and ketones are potential polyfunctional ligands possessing as many as eight or nine bonding sites, such as phenolic/naptholic–OH, azomethine, secondary-NH, and carbonyl oxygen in duplicate and pyridyl nitrogen in their molecular skeleton [19, 20]. They are capable of giving mononuclear and polynuclear complexes [20].

A survey of literature reveals that although work on metal complexes of monohydrazide-based ligands and their Schiff bases has been carried out in some detail [21–25], metal complexes of dihydrazones are quite meager [19, 20, 26–31]. Although some Cu(II), Ni(II), Co(II) [19, 28, 29], uranyl complexes [30], and a few zinc-uranyl heterobimetallic complexes [31] of disalicylaldehyde adipoyldihydrazone have been synthesized and characterized, those of *bis*(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone are absent. Moreover, the metal complexes of dihydrazones in higher oxidation state are almost non-existent. In view of the significant role played by manganese in biological systems and its compounds in higher oxidation states in catalysis and the meager amount of work done on its metal complexes with dihydrazones containing bulky fragments, we have set a goal of synthesizing manganese(IV) and manganese(V) complexes either from preformed dihydrazones containing bulky fragments in their molecular skeleton or *in situ* [27]. The ligand *bis*(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone (H_4npah) is a multidentate ligand containing two hydrazones joined together through four intervening methylene groups (figure 1). Further, it contains bulky naphthyl fragment in its molecular skeleton and is capable of giving complexes possessing discrete molecularity.

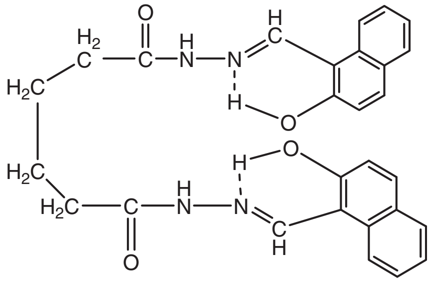

Figure 1. Structure of *bis*(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone (H_4npah).

This article reports the synthesis, characterization, reactivity, and electrochemical studies of manganese(IV) complexes derived from reaction of *bis*(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone in alkaline methanol.

2. Experimental

2.1. *Materials and methods*

The metal salts $Mn(OAc)_2 \cdot 4H_2O$, diethyladipate $[(CH_2)_4(COOEt)_2]$, hydrazine hydrate $(N_2H_4 \cdot H_2O)$, 2-hydroxy-1-naphthaldehyde, and KOH were E-Merck or equivalent grade reagents. Adipoyldihydrazone was prepared by reacting diethyl adipate (10.0 g, 49.50 mmol) with hydrazine hydrate (4.95 g, 99.00 mmol) and crystallizing from methanol. *Bis*(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone was prepared by reacting a solution of adipoyldihydrazone (10.37 mmol) in ethanol with 2-hydroxy-1-naphthaldehyde (25.93 mmol) in hot ethanol. The yellow precipitate obtained on cooling the solution was thoroughly washed with ethanol and air dried (m.p. >300°C).

2.2. *Preparation of the complexes*

2.2.1. Preparation of $[Mn^{IV}(naph)(H_2O)_2]$ (1). A methanol solution (20 mL) of $Mn(OAc)_2 \cdot 4H_2O$ (0.51 g, 2.08 mmol) was added to a suspension of dihydrazone (1.00 g, 2.07 mmol) in methanol (20 mL) accompanied by vigorous stirring for 10 min at 50°C. To the resulting yellow solution, KOH (0.47 g, 8.21 mmol) in methanol (20 mL) was added accompanied by gentle stirring. The resulting solution was stirred for another half an hour. The solution was then kept for 2 days, which precipitated a shiny black compound. This was suction filtered, washed with methanol, and air dried. The complex was finally dried in an electric oven maintained at 90°C (yield: 60%).

2.2.2. Preparation of $[Mn^{IV}(naph)(A)_2] \cdot nH_2O$ and $[Mn^{IV}(naph)(NN)]$ (where A = pyridine (py, 2); 2-picoline (2-pic, 3); 3-picoline (3-pic, 4); 4-picoline (4-pic, 5); NN = 2,2′-bipyridine (bpy, 6); 1-10 phenanthroline (phen), (7); (n = 0,1)). These complexes were also prepared by following essentially the above method and adding pyridine bases to the reaction mixtures obtained by mixing $Mn(OAc)_2 \cdot H_2O$ and H_4naph maintaining $Mn(OAc)_2 \cdot 4H_2O : H_4\text{naph} : KOH$ molar ratio at 1 : 1 : 4 : 10 in case of pyridine bases and 1 :1 : 4 : 3 in case of 2,2′-bipyridine and 1,10-phenanthroline. (Yield: 70% (**2**), (**3**); 67% (**4**); 58% (**5**); 50% (**6**); and 48% (**7**)).

2.3. *Elemental analyses*

Determination of manganese was done following the standard procedure [32]. C, H, and N were determined microanalytically. The molar conductances of the complexes (10^{-3} mol L^{-1} in DMSO) were measured on a Systronics Direct Reading Conductivity meter-303 with 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 [33]. Infrared (IR) spectra were recorded on a Bomen DA-8FT-IR spectrophotometer from 450 to 4000 cm^{-1} in KBr disks. Electronic spectra were recorded from 200 to 1000 nm in DMSO on a Perkin-Elmer Lambda 25 UV-Vis spectrophotometer. EPR spectra of the complexes as powders 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. A FAB mass spectrum of one of the complexes was 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 of the compounds in DMSO were done using a CH Instruments' Electrochemical analyzer under nitrogen. The electrolytic cell comprised of three electrodes, the working electrode was a Pt disk, while the reference and auxiliary electrodes were Ag/AgCl separated from the sample solution by a salt bridge; 0.1 mol L^{-1} TBAP was used as the supporting electrolyte.

3. Results and discussion

The complexes with their color, decomposition point, and analytical and magnetic moment data given in table 1 are of composition $[Mn^{IV}(naph)(A)_2] \cdot nH_2O$ and $[Mn^{IV}(naph)(NN)]$ (where $A = H_2O$ (**1**); py (**2**); 2-pic (**3**); 3-pic (**4**); 4-pic (**5**); NN = bpy (**6**); phen (**7**); ($n = 0$, 1)). All the complexes are shiny black, air stable, and decompose above 300°C without melting, indicating that the metal–ligand bonds have ionic character. The complexes were insoluble in water and common organic solvents such as ethanol, acetone, chloroform, carbon tetrachloride, ether, and benzene, sparingly soluble in methanol, acetonitrile, and dichloromethane, and completely soluble in DMSO and DMF. The solutions are black brown in color. Complexes **2**, **4**, and **5** show weight loss corresponding to one water molecule at 110°C suggesting water in the lattice structure, while **1** shows loss corresponding to two water molecules at 180°C, indicating they are coordinated to the metal. Complexes **2**–**5** show weight loss at 220°C corresponding to two pyridine or substituted pyridine molecules; **6** and **7** show weight loss corresponding to one bipyridine and one 1,10-phenanthroline, respectively.

Table 1. Color, decomposition point, analytical, magnetic moment, molar conductance, electronic, and EPR data of manganese(IV) complexes of *bis*(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone.

				Analysis: found (Calcd), %							EPR parameters (LNT)		
No.	Complex	Color	Decomposition point (°C)	Mn	C	H	N	μ_B (BM)	Molar conductance, Λ_m (Ω^{-1} cm^2 mol^{-1})	Electronic spectral bands, λ_{max} (nm) (E_{max} (dm^3 mol^{-1} cm^{-1}))		Solid	DMSO
1	[Mn^{IV}(npah)(H$_2$O)$_2$]	Shiny black	>300	10.11 (9.65)	58.82 (59.06)	4.47 (4.50)	9.52 (9.84)	3.83	2.1	313(5302) 368(4210) 433(458) 615(4250)	$g_\parallel$ $g_\perp$	2.008 4.335	1.947 4.064
2	[Mn^{IV}(npah)(py)$_2$] · H$_2$O	Shiny black	>300	8.21 (7.75)	64.71 (64.32)	4.79 (4.82)	12.13 (11.85)	4.18	2.5	310(3379) 360(2700) 437(650) 610(3750)	$g_\parallel$ $g_\perp$	– –	 –
3	[Mn^{IV}(npah)(2-pic)$_2$]	Shiny black	>300	7.60 (7.63)	66.38 (66.80)	5.53 (5.53)	11.79 (11.68)	3.85	3.7	310(3100) 362(2500) 430(630) 625(33,400)	$g_\parallel$ $g_\perp$	– –	– –
4	[Mn^{IV}(npah)(3-pic)$_2$] · H$_2$O	Shiny black	>300	7.47 (7.45)	65.17 (65.13)	5.18 (5.19)	11.18 (11.40)	4.10	1.9	310(3187) 358(5785) 436(1714) 620(3200)	$g_\parallel$ $g_\perp$	– –	– –
5	[Mn^{IV}(npah)(4-pic)$_2$] · H$_2$O	Shiny black	>300	7.67 (7.45)	64.63 (65.13)	5.23 (5.19)	11.39 (11.40)	4.11	2.2	315(7070) 357(5785) 436(1714) 630(4150)	$g_\parallel$ $g_\perp$	2.007 4.335	2.032 4.335
6	[Mn^{IV}(npah)(bpy)]	Shiny black	>300	8.02 (7.97)	66.01 (66.19)	4.42 (4.38)	11.95 (12.19)	4.02	3.5	310(2800) 356(2300) 470(3200) 627(5000)	$g_\parallel$ $g_\perp$	2.036 4.780	2.007 4.223
7	[Mn^{IV}(npah)(phen)]	Shiny black	>300	7.61 (7.50)	66.10 (65.60)	4.41 (4.40)	11.71 (11.48)	4.39	2.8	305(3671) 360(2000) 465(1000) 620(43,500)	$g_\parallel$ $g_\perp$	1.988 5.000	2.058 5.000

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. Both saturated and dilute solutions of the complexes in various solvent systems such as DMSO, DMF, DMSO–CH_3CN, DMSO–CH_2Cl_2, and DMF–CH_2Cl_2 each were kept for half, 1, and 2 months at ambient temperature to grow crystals. Also, solutions were gently evaporated at 40°C, 50°C, and 60°C in an electric oven to promote crystal growth. Solvent diffusion methods were also used to grow crystals. Unfortunately, in all our efforts, only amorphous compounds precipitated preventing analysis by X-ray crystallography.

3.1. *Mass spectra*

Complex **3** was characterized by FAB mass spectroscopy as a representative sample. The mass spectrum shows a signal at *m/z* 536, probably from the formation of $[Mn(npah)]^+$. $[Mn(npah)]^+$ results from loss of both 2-picoline molecules. The mass spectrum of the complex shows its monomeric nature.

3.2. *Molar conductance*

The complexes have molar conductance values in the range 1.9–3.7 $\Omega^{-1}\,cm^2\,mol^{-1}$ in DMSO at $10^{-3}\,mol\,L^{-1}$, indicating non-electrolytes [34].

3.3. *Magnetic moment*

The μ_B values for the complexes lie in the range 3.83–4.30 BM, consistent with manganese(IV) complexes in a d^3 high-spin electronic configuration [17]. The μ_B values rule out the possibility of spin–spin coupling in the solid state between unpaired electrons belonging to different Mn(IV) centers in the structural unit of the complexes.

3.4. *Electronic spectra*

The free ligand shows three bands at 290 (2041), 313 (2800), and 363 (1352) in DMSO, assigned to intra-ligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The band at 363 nm is characteristic of naphthyl of dihydrazone as reported in several monoacylhydrazones [25]. Bands at 290 and 313 nm in the free ligand are shifted by 20–25 and 45–55 nm in the complexes, 305–315 and 356–368 nm, respectively. Such a big red-shift of the ligand bands in spectra of the complexes indicates strong bonding between metal and ligand. The ligand band at 363 nm remains almost unshifted in the complexes and is merged with the band in the region 356–368 nm. In addition to the intra-ligand bands, the complexes show new bands at 430–470 and 610–630 nm, respectively. For octahedral manganese(IV) complexes, three spin-allowed d–d transitions $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$, and $^4A_{2g} \rightarrow {}^4T_1g(P)$ are expected. The manganese(IV) complex, $[MnF_6]^{2-}$, shows absorptions at 360 and 450 nm assignable to $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{2g}(F)$ transitions, respectively [35, 36], while the third band arising from $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ is obscured either by charge transfer or ligand bands. Sawyer *et al.* [37] and Pecoraro *et al.* [38] reported a band at 545–575 nm in mononuclear *tris*(glucarato), *tris*(gluconato), *tris*(sorbitolato) manganese(IV) complexes and manganese(IV) complexes of 1-hydroxy-2-(salicylideneamino)ethane and related hydroxyl ligand with molar extinction coefficients in the 1508–2380 $dm^3\,mol^{-1}\,cm^{-1}$ region. They assigned this band to the d–d transition. The higher value of molar extinction coefficient was attributed to the presence of adjacent charge-transfer band which contributed to its intensity. Cooper *et al.* [36] reported an intense band at 585 nm with molar extinction of $\sim$4500 $dm^3\,mol^{-1}\,cm^{-1}$ in manganese(IV) complexes derived from catecholato ligands. They assigned this band to a catechol → Mn(IV) LMCT band on the basis of its high molar extinction coefficient. Okawa *et al.* [39] reported a band at $\sim$650 nm with molar extinction coefficient of 2090–3020 $dm^3\,mol^{-1}\,cm^{-1}$ in manganese(IV) complexes derived from 2-substituted (salicylideneamino) phenol, assigned to charge-transfer transition from phenolic oxygen to manganese(IV). The molar extinction coefficient of the band at 430–470 nm is 458–3280 $dm^3\,mol^{-1}\,cm^{-1}$. These values are in the same region in which the d–d transition ${}^4T_{2g} \leftarrow {}^4A_{2g}$ in manganese(IV) complexes has been assigned albeit with some charge-transfer contribution from ligand-to-metal [37–41]. Hence, this band is assigned to arise from ${}^4T_{2g} \leftarrow {}^4A_{2g}$ transition for manganese(IV). However, slightly higher values of molar extinction coefficients of this band than those expected for d–d bands in the manganese(IV) complexes may be attributed to arise from contribution due to LMCT bands. The band observed at 610–630 nm has molar extinction coefficient of 3200–5000 $dm^3\,mol^{-1}\,cm^{-1}$; almost the same ϵ_{max} values have been reported by Cooper *et al.* [36] and Okawa *et al.* [39] in manganese(IV) complexes and have been attributed to LMCT transitions. Hence, it is suggested that the band in the region 610–630 nm in the present complexes arises from LMCT transitions, most probably, from naphtholate oxygen to the metal.

3.5. *Electron paramagnetic resonance*

Only **1** and **5**–**7** have been analyzed by EPR spectroscopy. These complexes exhibit highly anisotropic EPR spectra in polycrystalline state as well as in the glassy state at LNT. EPR spectra for **1** in the powder form and for **6** in powder as well as in solution at LNT are shown in Supplementary material as representative examples. Complexes **1** and **5** show two resonances with $g_\perp \approx 4$ and $g_\parallel \approx 2.0$ in the solid state and in solution. The former resonance is more intense in the solid state than the latter, but in the glassy state both resonances are almost of the same intensity. Complexes **6** and **7** also show resonances at $g_\perp \approx 5.0$ and $g_\parallel \approx 2.0$. The signal at $g_\perp \approx 5.0$ is of low intensity compared to the signal at $g_\parallel$ in both crystalline and glassy states. For both complexes, the polycrystalline phase and magnetically dilute glassy state spectra are well-resolved, with the hyperfine coupling ($S = 3/2$) of ^{55}Mn nucleus well-resolved in the glassy state [41, 42] with six clean hyperfine lines at $g \approx 2$, suggesting that they retain the same structures in solution and solid state. The EPR signal at $g \approx 2$ shows ^{55}Mn hyperfine splitting equal to 80 G in **6** and **7** nearer to Mn(IV) hyperfine splitting constant of 77 G than Mn(II) hyperfine coupling constant of 87 G.

In a crystal field of strict octahedral symmetry, a d^3 ion has ${}^4A_{2g}$ ground state leading to an isotropic resonance at $g \approx 2.0$. Distortion and spin-orbit coupling split the ground state quartet into two Kramer's doublets separated by $2(D^2 + E^2)$, where D and E are, respectively, axial and rhombic zero field splitting parameters [43]. The complexity of EPR spectra of a d^3 ion in an axial field ($E/D = 0$) is dependent on the magnitude of zero-field splitting parameters [44]. Two limiting cases are when the value of axial zero-field splitting parameter $2D$ is either much larger than or much smaller than $h\nu$ ($0.31\,\mathrm{cm}^{-1}$ X-band frequencies). In the first case, when $2D$ is much larger than $h\nu$, the feature at low field is strong and $g \approx 2$ component is weak. This is the observation for *tris*(catecholato) manganese(IV) [45] and *tris*(sorbitolato) manganese(IV) complexes [46]. In the second case, when D is small, the $g \approx 2$ component should dominate with relatively weak signals in the low-field region. This is observed for *tris*(thiohydroxamato) manganese(IV) [47] and thiocarbamato complexes [48]. Spectra for **1** and **5** do not fit either limit. Instead, they exhibit marked rhombic distortion. Complexes **6** and **7** spectra correspond to a Mn(IV) in octahedral field with axial distortion $2D \gg h\nu$. EPR spectra reveal that the ligand provides effective electronic environment for the metal that is highly distorted in the ground state in **1** and **5** but only slightly distorted in the ground state in **6** and **7**. The distortion is sensitive to geometrical orientation of the donors. The effective environment of Mn(IV) lies close to ideally pseudo-octahedral environment.

The EPR spectra of **1**, **6**, and **7** in solution at LNT remain essentially the same as in the solid state, but **5** is entirely changed on dissolution in DMSO, attributed to replacement of water and 4-picoline by DMSO. While water and DMSO provide the same donor atom (oxygen) in bonding to the metal center which leads to almost unchanged EPR spectral features of **1** in solution state as compared to that in the solid state. The replacement of 4-picoline by DMSO molecules in **5** significantly changes the coordination environment around the metal which changes the spectral features significantly. Essential EPR spectral features of **6** and **7** remain the same in the solid state and DMSO solution, indicating that the solvent molecules are unable to replace coordinated bipyridine and 1,10-phenanthroline. The contrasting EPR spectral features of **1** and **5** as compared to those of **6** and **7** suggest that nitrogen donors from bipyridine and 1,10-phenanthroline in **6** and **7** occupy *cis*-position while donors from co-ligands in **1** and **5** occupy *trans*-positions.

3.6. *IR spectra*

Some structurally significant IR bands along with the assignments for free dihydrazone and complexes are given in table 2. Comparison of IR spectra of the complexes with that of the free ligand suggests that the dihydrazone is coordinated to the metal in enol form in all complexes.

The uncoordinated ligand shows a strong band at $1666\,\mathrm{cm}^{-1}$ assignable to ν(C=O) which disappears in the complexes, indicating collapse of amide structure and coordination of the ligand in enol form. This is also corroborated from observation that ν(NH) at $3224\,\mathrm{cm}^{-1}$ in uncoordinated dihydrazone is absent in IR spectra of the complexes. The ligand shows strong to medium intensity bands at 1630 and $1593\,\mathrm{cm}^{-1}$ assigned to stretching vibration of azomethine [19]. On an average, these bands shift to lower frequency by $3\text{–}11\,\mathrm{cm}^{-1}$ in complexes. The free dihydrazone shows a weak band at $1530\,\mathrm{cm}^{-1}$ from mixed contributions of amide II and ν(C–O) (naphtholate). In IR spectra of the complexes, this band is replaced by a strong band at $1503\text{–}1560\,\mathrm{cm}^{-1}$ assigned to stretching vibration of newly created NCO^- group produced as a result of deprotonation of the enolized carbonyl. In the dihydrazone, a medium intensity band at $1281\,\mathrm{cm}^{-1}$ is similar to other ligands containing phenol [49] and assigned to

Table 2. Structurally significant IR spectral bands for *bis*(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone and its manganese complexes.

Ligand/ complex	ν(OH) + ν(NH)	ν(C=O)	ν(C=N)	Amide(II) + ν(C–O) naptholic	ν(C–O)	ν(N–N)	ν(M–N) in-plane ring deformation	ν(M–O) (naptholic)	ν(M–O) (enolate)	ν(M–N) (azomethine)	ν(M–N) py
H_4npah	3300–3600(sbr) 3469(s) 3430(sbr) 3224(s) 3051(sbr)	1666(s)	1630(s) 1593(m)	1530(w)	1281(m)	1050(w)	–		–	–	–
1	3000–3600(sbr)	–	1619(s) 1586(s)	1513(s)	1285(w)	1029(m)	–	526(s)	430(s)	353(w)	–
2	3200–3600(sbr)	–	1621(s) 1604(s)	1515(s)	1282(m)	1029(m)	–	524(w)	432(s)	375(w)	277(w)
3	3000–3600(sbr)	–	1620(s) 1598(vs)	1583(s)	1299(w)	1029(m)	660(m)	509(s)	435(m)	360(w)	279(w)
4	3000–3600(sbr)	–	1600(s)	1560(s)	1290(s)	1029(wbr)	650(mbr)	525(s)	440(m)	355(w)	280(w)
5	3000–3600(sbr)	–	1615(s) 1599(vs)	–	1295(s)	1029(m)	650(w)	510(s)	436(s)	370(w)	274(w)
6	3000–3600(sbr) 3420(s)	–	1620(s) 1597(s)	1540(s)	–	1029(w)	–	510(w)	–	358(w)	270(w)
7	3000–3600(sbr) 3392(s)	–	1617(m) 1586(m)	1503(s)	1280(w)	1029(w)	660(w)	520(w)	–	360(w)	265(w)

β(C–O) (naptholic). This band shifts to higher frequency by 2–18 $\mathrm{cm^{-1}}$ in the complexes, 1283–1299 $\mathrm{cm^{-1}}$, indicating bonding of naptholate oxygen to the metal. Free pyridine bases absorb at ~604 $\mathrm{cm^{-1}}$ due to in-plane ring deformation [50]. In **3**–**5**, a new medium to weak band is observed at 650–660 $\mathrm{cm^{-1}}$ assigned to in-plane ring deformation of pyridine bases indicating their coordination. Complex **7** also shows a weak band at ~660 $\mathrm{cm^{-1}}$ assigned to in-plane ring deformation of 1,10-phenanthroline indicating coordination. In metal complexes, new bands at 509–526 and 353–375 $\mathrm{cm^{-1}}$ are assigned to ν(M–O) (naptholate) and ν(M–N) indicating coordination of naptholate oxygen and azomethine nitrogen, respectively [50]. New bands at 274–280 $\mathrm{cm^{-1}}$ are assigned to ν(M–N) due to coordinated pyridine bases/bipyridine/1,10-phenanthroline. Complexes **2**–**5** show a new non-ligand, medium to strong band at 430–440 $\mathrm{cm^{-1}}$ assigned to ν(M–O)(enolate), indicating coordination of carbonyl oxygen to manganese(IV) [50].

3.7. *Reactivity*

When **1** and **3** were allowed to react with benzyl alcohol either under ambient condition or at 50°C for 4 h in CH_3OH under stirring, no reaction was observed. The unreacted components were recovered from the reaction mixture by filtration and fractional distillation. IR spectra and the magnetic moment of the residue matched with those of the original complexes, signifying that the complexes did not react. The boiling point of the last fraction matched with that of the reported value for benzyl alcohol, b.p. 203°C (202–205°C in the literature) [51]. Dioxygen gas was also passed through the above reaction mixture without any reaction. When SO_2 gas was passed through the suspension of the complexes in CH_3OH, a vigorous exothermic reaction occurred. The color of the solution changed from shining black to light brown to colorless, giving a white precipitate. The precipitate was recovered by filtration and washed with methanol. Its melting point, IR and ^{1}H-NMR matched with that of the uncoordinated dihydrazone. The presence of SO_4^{2-} in the filtrate was confirmed by chemical tests. The results indicated that SO_2 was oxidized to SO_4^{2-} ion with reduction to Mn^{2+}, evident from the light pink color of the filtrate. The dihydrazone did not suffer any degradation with SO_2.

3.8. *Cyclic voltammetry*

Cyclic voltammograms (CV) of 2 mmol solutions of the ligand and complexes in DMSO under nitrogen with 0.1 $\mathrm{mol\,L^{-1}}$ TBAP as supporting electrolyte were run at a scan rate of 100 $\mathrm{mV\,s^{-1}}$. The free ligand exhibits a single quasi-reversible redox couple at +0.27 V ($E_{1/2}$) ($\Delta E = 90$ mV) against Ag/AgCl electrode. The CV of **1**, **5**, and **6** are provided in Supplementary material as representative examples.

All complexes except **6** and **7** show two oxidative and two reductive waves (table 3). The oxidative and reductive waves are well-separated from those associated with free dihydrazone. Hence, these waves may be attributed to metal-centered electron-transfer reactions. Both redox couples in **4** and **6** are reversible as the separation between oxidative and reductive waves is around 59 mV. However, in **5** and **7**, the separation between the cathodic and anodic peaks is more than 59 mV. Hence, the redox couples in

Table 3. Electrochemical parameters for the dihydrazone and its manganese(IV) complexes (potential *vs.* Ag/AgCl).

Ligand/complex	E_{pa}/V	E_{pc}/V	ΔE_p(mV)
H_4npah	+0.32	+0.23	90
1	−0.06	−0.18	120
	−0.65	−1.00	350
2	+0.70	+0.43	240
	−0.50	−0.85	350
3	+0.65	+0.43	220
	−0.58	−0.80	220
4	+0.25	+0.19	60
	−0.56	−0.62	60
5	+0.15	+0.07	80
	−0.24	−0.36	120
6	−0.60	−0.66	60
	−0.79	−0.85	60
	–	−0.96	–
7	+1.10	+0.97	130
	–	+0.25	–
	−0.20	−0.35	150

these complexes are quasi-reversible. Thus, the two waves observed in these complexes may be attributed to the following redox processes (from the positive side).

$$[Mn^{IV}(L)(H_2O)_2] + e \rightleftharpoons [Mn^{III}(L)(A)_2]^{-1} + e \rightleftharpoons [Mn^{II}(L)(A)_2]^{-2}$$

Separation between oxidative and reductive waves of the redox couples in **1**–**3** is more than 200 mV except for the first redox couple ($E = 120$ mV) in **1**. This separation is much higher than that for an uncomplicated one-electron redox process (59 mV). Hence, the redox couples in these complexes are irreversible. The separation between the oxidative and reductive waves probably originates from a slow heterogeneous electron exchange rather than intervening homogenous reaction [52]. Complex **6** shows an irreversible wave at −0.96 V, attributed to electron transfer centered on bipyridine. Complex **7** shows an irreversible wave at +0.25 V in the forward scan which is not visible in return scans. Evidently, some transient species is produced in the forward scan which is not stable and reverts back to the original species. This irreversible process may be attributed to reduction of phenanthroline in the complex. Examination of table 3 shows regular decrease in reduction potential as well as oxidation potential in going from pyridine to 2–picoline to 3-picoline to 4-picoline complexes for first redox couple Mn^{IV}/Mn^{III} (from positive side). This is attributed to the increasing removal of electron density toward the metal in going from pyridine to 2-picoline to 3-picoline to 4-picoline. A necessary criterion for model systems for water oxidation in PSII is that they must have redox potential more positive than the minimum of 0.6 V *versus* NHE required to oxidize water to dioxygen at pH 7 in the biomembrane. Manganese complexes **2** and **3** with their oxidation potentials at +0.70 and +0.65 against Ag/AgCl may thus be an appealing model system to simulate water-oxidizing complex (WOC) of PSII in plant photosynthesis [53]. Complex **7** also shows very high quasi-reversible redox behavior at +0.97 V. Hence, this complex might be another candidate to simulate the WOC of PSII.

4. Conclusion

This article reports synthesis and characterization of seven Mn(IV) complexes derived from *bis*(2-hydroxy-1-naphthaldehyde)adipoyldihydrazone. The dihydrazone coordinates to Mn(IV) in enol form through azomethine nitrogen and naptholate oxygen 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 H_2O/pyridine/2-picoline/3-picoline/4-picoline in **1**–**5**. In **6** and **7**, the nitrogen from azomethine of dihydrazone and bpy and phen are in equatorial positions

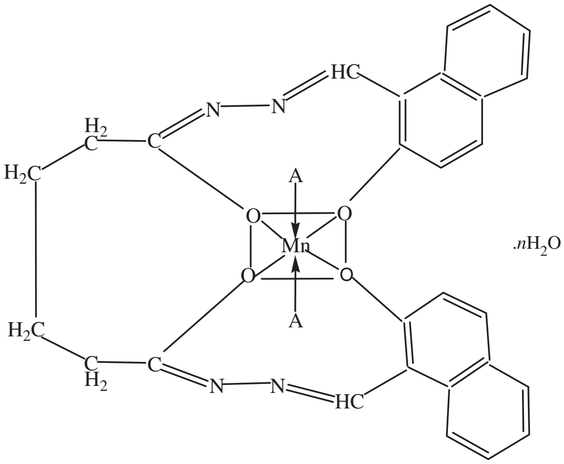

Figure 2. Suggested structure of the complexes $[Mn^{IV}(naph)(A_2)]\cdot H_2O$ (where $A = H_2O$ (**1**); py (**2**), 2-pic (**3**); 3-pic (**4**); and 4-pic (**5**)).

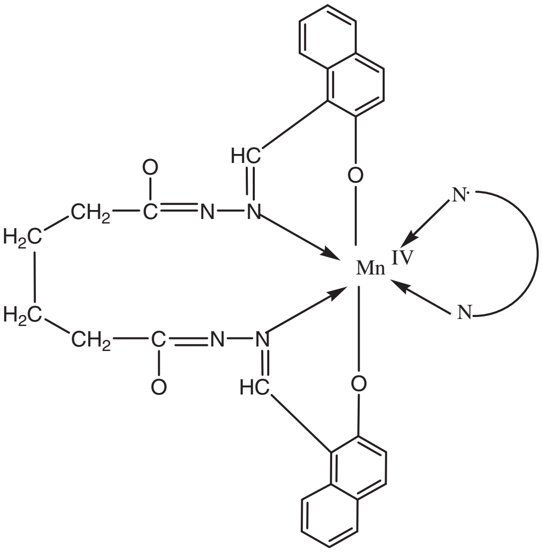

Figure 3. Suggested structure of the complexes [Mn(naph)(NN)] (where NN = bpy (**6**) and phen (**7**)).

and naptholate 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 nitrogen and naptholate oxygen 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 in IR spectra. The complexes are proposed to have distorted octahedral stereochemistry. Cyclic voltammetry shows that the metal center cycles among the $\mathrm{Mn^{IV}} \rightarrow \mathrm{Mn^{III}} \rightarrow \mathrm{Mn^{II}}$ oxidation states in all the complexes. Structures of the complexes have been proposed as shown in figures 2 and 3.

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