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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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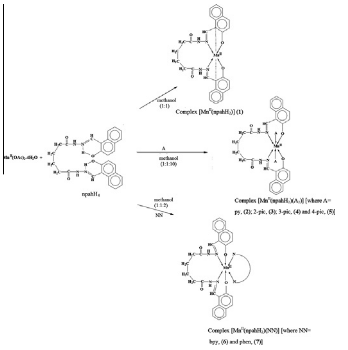
HIGHLIGHTS

- Low and high spin manganese(II) complexes have been synthesized from bis(2-hydroxy-1-naphthaldehyde)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.

GRAPHICAL ABSTRACT

Reactions and structures of the Mn(II) complexes.



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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 ($npahH_4$) 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 (npahH_4). 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 npahH_4 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 low-spin 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 (npahH_4) 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%).