

Synthesis, characterization and electrochemical study of manganese(II) complexes derived from polyfunctional adipoyldihydrazone

Debajani Basumatary^{1*}, Arvind Kumar² and Ram Ashray Lal³

1Department of Chemical Science, Gauhati University, Guwahati-781014, Assam, India, email:debbasumatary@gmail.com;

2Department of Chemistry, The University of the West Indies, St. Augustine campus, Trinidad and Tobago, West Indies, e-mail:

arvind72@gmail.com; **3**Department of Chemistry, North-Eastern Hill University, Shillong-793022, Meghalaya, India, email:ralal@rediffmail.com

ABSTRACT

Manganese(II) complexes $[Mn^{II}(\text{slahH}_2)]$ (1), $[Mn^{II}(\text{slahH}_2)(A)_2]$ and $[Mn^{II}(\text{slahH}_2)(NN)]$ (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 disalicylaldehyde adipoyldihydrazone (slahH₄). The complexes have been characterized by physical, spectral and analytical data. The synthesized Schiff base act as tetradentate ligand for the complexation reaction with Mn(II) ions and the compounds show octahedral geometry. Cyclic voltammetry show the metal center cycles among $Mn^{II} \rightarrow Mn^I$ oxidation states in complexes.

Keywords: Manganese(II); Disalicylaldehyde adipoyldihydrazone; Stereochemistry; Redox activity

1 INTRODUCTION

There is continuous interest in the chemistry of manganese complexes due to its occurrence in many biological systems, its capabilities as potential biomimics for various manganese enzymes [1, 2] and its ability to catalyze oxidation and oxo-transfer reactions [3].

The present work constitutes the exploration of the coordination chemistry of manganese with ligand disalicylaldehyde adipoyldihydrazone (slahH₄). The ligand is rich and versatile but has not yet been fully explored with transition metals.

In view of the meagre amount of work on manganese complexes of the title dihydrazone, monometallic complexes of manganese(II) have been synthesized and characterized here. The composition of the isolated complexes have 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 are used as a probe to study the molecular distortions caused by pyridine and its derivatives (pyridine (py, 2); 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.

2. Experimental

2.1 Materials and spectral measurements:

The metal salts manganese acetate tetrahydrate ($Mn(OAc)_2 \cdot 4H_2O$), diethyladipate ($(CH_2)_4(COOEt)_2$), hydrazine hydrate ($N_2H_4 \cdot H_2O$), and salicylaldehyde were E-Merck or equivalent grade reagents. Adipoyldihydrazone was prepared by reacting diethyl adipate (4.94 mM) with hydrazine hydrate

(10.89 mM) in 1:2 molar ratio and crystallized from methanol. Disalicyladehyde adipoyldihydrazone (slahH₄) was prepared by treating a solution of adipoyldihydrazone (5.75 mM) in ethanol with salicylaldehyde (11.48 mM) in hot ethanol. The white precipitate obtained on cooling the solution was thoroughly washed with ethanol and purified by column chromatography (m.p. > 300 °C).

Determination of manganese was done following the standard procedure [5]. ¹³C, H and N were determined microanalytically. The molar conductances of the complexes (10⁻³ molL⁻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 [6]. 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. FAB mass spectra of the complexes were recorded on a JEOL SX102/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 compound in DMSO (10⁻³ M) were done 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. 0.1 M TBAP was used as the supporting electrolyte.

2.2 Synthesis of complexes

[Mn^{II}(slahH₂)] (1)

Mn(OAc)₂·4H₂O in methanol (20 mL) was added to lig-

and solution in methanol in 1:1 molar ratio and refluxed for 2 hrs. The yellow-brownish compound obtained was filtered, washed with hot methanol and air dried. The residue was further purified by column chromatography to give the desired compound (Yield: 71%).

[Mn^{II}(slahH₂)(A)₂] and [Mn^{II}(slahH₂)(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·H₂O and slahH₄ maintaining Mn(OAc)₂·4H₂O:slahH₄:pyridine molar ratio at 1:1:10 in case of pyridine bases and 1 : 1 : 2 in case of 2,2'-bipyridine and 1,10-phenanthroline (Yield: 60 % (2); 57 % (3), (4); 55 % (5); 51 % (6) and 48 % (7)).

3. Results and discussion

The complexes with their composition, colour, decomposition point, analytical and magnetic moment data given in table 1. The complexes are air-stable and insoluble in water and common organic solvents such as ethanol, acetone etc 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.

3.1 Molar Conductance:

The molar conductance values for the complexes lie in the range 1.5–2.8 ohm⁻¹cm²mole⁻¹ in DMSO (table 1) indicate their non-electrolytic nature in this solvent [7].

3.2 Thermal studies:

All these complexes decompose above 300 °C without melting, indicating that the metal-ligand bonds have higher ionic character. The complex (1) shows weight loss corresponding to two water molecules at 180 °C accompanied by change in colour,

Table 1: Colour, Decomposition Point, Analytical, Magnetic Moment and Molar Conductance Data for complexes of Disalicylaldehyde adipoyldihydrazone (slahH₄)

Ligand/Complex	Colour	D.P (°C)	Analysis: Found(Calcd)%				μ_B (B.M)	Molar Conductance Δm (ohm ⁻¹ cm ² mol ⁻¹)
			Mn	C	H	N		
[Mn ^{II} (slahH ₂)(H ₂ O) ₂]	Light-brown	> 300 °C	12.30 (11.677)	50.52 (50.955)	5.10 (5.096)	12.73 (11.890)	5.87	1.5
[Mn ^{II} (slahH ₂)(py) ₂].H ₂ O	Light-brown	> 300 °C	8.895 (9.002)	60.94 (58.919)	5.34 (5.237)	14.40 (13.748)	6.02	1.5
[Mn ^{II} (slahH ₂)(2-pic) ₂].H ₂ O	Dull-brown	> 300 °C	9.63 (8.634)	57.91 (60.283)	6.50 (5.337)	14.78 (13.187)	5.86	2.8
[Mn ^{II} (slahH ₂)(3-pic) ₂].H ₂ O	Dull-brown	> 300 °C	10.13 (8.634)	56.98 (60.283)	6.40 (5.338)	15.43 (13.187)	5.79	1.7
[Mn ^{II} (slahH ₂)(4-pic) ₂].H ₂ O	Dull-brown	> 300 °C	10.15 (9.87)	57.13 (57.45)	6.51 (6.46)	15.31 (15.08)	5.89	2.5
[Mn ^{II} (slahH ₂)(bpy)]	Light-brown	> 300 °C	9.67 (9.31)	61.40 (60.91)	4.70 (4.74)	13.91 (14.21)	5.95	1.9
[Mn ^{II} (slahH ₂)(phen)]	Dull-brown	> 300 °C	9.59 (8.94)	62.44 (62.45)	4.51 (4.55)	13.39 (13.66)	5.98	2.2

hence, these water molecules are considered to be present in the first coordination sphere around the metal centre [8]. In the complexes (2) to (5), water molecules are lost at 110 °C without change in colour. Hence, these water molecules are suggested to be present in the lattice structure of the complexes [9]. Complexes (2) to (5) also show further 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 centre.

3.3 Magnetic Moment:

The μ_B values for complexes lie in the range 5.86 – 6.02 B.M. fall within the range reported for Mn(II) complexes in the high-spin state ($t_{2g}^3 e_g^2$, $S = 5/2$) in octahedral geometry [10] ruling out the possibility of any spin-spin coupling in the solid state between

unpaired electrons belonging to different Mn(II) centres in the structural unit of the complexes .

3.4 Electronic Spectra:

The free ligand slahH₄ shows three bands at 284 (4308), 320 (2808) nm (table 2). The band at 284 nm are assigned to intraligand $\pi - \pi^*$ transitions while the bands in the region 313 - 363 nm are assigned to $n-\pi^*$ transitions. The bands in the region 313-363 nm are characteristic of salicylaldehyde part of the ligand as has been reported in several monoacyl hydrazones [11]. The first band in slahH₄ are split into two components 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 in anti-cis configuration as concluded from IR spectroscopic studies. The first ligand band in the complexes (1) and (6) undergo blue shift by 8 nm while red shift by 2 - 6 cm⁻¹ in the remaining complexes. The slahH₄ band

observed at 320 nm due to salicylaldehyde fraction shifts to longer wavelength by 2-10 nm. This shows the effect of complexation. The ligand bands in the electronic spectra of the complexes have almost the same splitting patterns as in the uncoordinated ligands. This suggests that the conformation of the ligands in the complexes remains essentially the same as in those of the free

ligands i.e. the ligands are coordinated to the metal in anti-cis configuration [12].

The d-d transition in the Mn (II) complexes are very weak because they are both spin as well as laporte forbidden. Hence, these bands generally, they do not appear in the visible region [13] of the electronic spectra of the complexes.

Table 2: Important Electronic spectral bands and EPR data for Manganese (II) Complexes of Disalicylaldehyde adipoyldihydrazone

Ligand/Complex	$\lambda_{max}(nm)$	$(\epsilon_{max} dm^3 mol^{-1} cm^{-1})$ for conc $10^{-2} M$ soln	Temp	solid/ soln	g-value	A_{Mn} (G)
slahH ₄	284(4308)	320(2808)				
[Mn ^{II} (slahH ₂)(H ₂ O) ₂]	276 (7670)	324(3450)	LNT LNT RT	SOLID DMSO DMSO	2.019 2.007 1.924	- 96 -
[Mn ^{II} (slahH ₂)(py) ₂].H ₂ O	290(9450)	325(3800)	LNT LNT RT	SOLID DMSO DMSO	2.045 2.019 1.935	- 96 96
[Mn ^{II} (slahH ₂)(2-pic) ₂].H ₂ O	287(8670)	330(4055)	LNT LNT RT	SOLID DMSO DMSO	2.032 2.038 1.924	- 96 -
[Mn ^{II} (slahH ₂)(3-pic) ₂].H ₂ O	287(6313)	322 (4423)	LNT LNT RT	SOLID DMSO DMSO	2.032 2.045 1.924	- 94 94
[Mn ^{II} (slahH ₂)(4-pic) ₂].H ₂ O	290 (9270)	328(4950)	LNT LNT RT	SOLID DMSO DMSO	2.044 2.050 1.950	- 94 92
[Mn ^{II} (slahH ₂)(bpy)]	276(9266)	323(6420)	LNT LNT RT	SOLID DMSO DMSO	2.045 2.032 -	- - -
[Mn ^{II} (slahH ₂)(phen)]	286(8790)	330(5680)	LNT LNT RT	SOLID DMSO DMSO	2.045 2.032 -	- - -

3.5 EPR Spectra:

The EPR spectra of the complexes in the solid state are essentially similar to one another at LNT and show an isotropic signal with g-value in the region 1.924-2.045. This shows that these complexes have similar octahedral stereochemistry [14]. 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 otherhand, in DMSO solution at RT, six line spectrum is obtained with ⁵⁵Mn hyperfine splitting constant falling in the range 94-104 G [15]. This ⁵⁵Mn hyperfine splitting constant is characteristic of Mn(II) complexes rather than for Mn(IV) complexes. The overall intensity of the split component

of the signal due to ⁵⁵Mn hyperfine splitting at LNT is weak as compared to that at RT. This might be attributed to the effect of strong coordination of DMSO molecules to the metal centre. The total width of the central isotropic resonance in the case of the complexes (2) to (7) falls in the region 470-520 G at X-band. Such an isotropic resonance has been related to the absence of any exchange narrowing phenomenon, where Mn(II) ions are not coupled to any other ion [16].

3.6 Infrared Spectra:

The IR spectral bands for the dihydrazone show a strong band at 1679 cm⁻¹ (table 3) which are assigned to νC=O band [17].

These bands on an average shifts to lower frequency by 2-26 cm⁻¹ and appear in the region 1640-1664 cm⁻¹. Such a lower shift rules out the possibility of coordination of >C=O groups to the metal centre but involvement in strong intramolecular H-bonding with secondary NH group in the complexes. This is also corroborated from the observation as the band in the region 500-400 cm⁻¹ which could be assigned to νM-O(carbonyl) is absent ruling out the possibility of coordination of carbonyl oxygen atom to the metal centre either as such or enol form. This suggests that the dihydrazone is coordinated to the metal centre in keto form. The band observed at 1620 cm⁻¹ in free

Table 3: Structurally Significant Infrared Spectral Bands of Disalcylaldehyde adipoyldihydrazone (slahH₄) and its Monometallic Manganese(II) Complexes

Ligand/Complex	ν(OH) +ν(NH)	ν(C=O)	ν(C=N)	Amide(II) + ν(CO) phenolic/naphtholic	β(C-O) (phenolic/naphtholic)	ν(N-N)	ν(M-O) phenolic/naphtholic	ν(M-N) py/bpy/phen vibration in plane
slahH ₄	3300-3600(sbr) 3436(m) 3204(s) 3065(s)	1679(s)	1620(s)	1560(s)	1275(s)	1036(m)		
1	3000-3600(sbr) 3432(s)	-	1605(s)	1541(s)	1270(w)	1038(w)	582(m)	-
2	3000-3600(sbr) 3449(s)	-	1606(s)	1540(s)	1270(w)	1043(m)	592(m)	671(m)
3	3000-3600(sbr) 3430(s)	-	1605(s)	1535(msh)	1260(w)	1050 (w)	580(w)	-
4	3000-3600(sbr) 3432(s)	-	1605(vs)	1541(s)	1277(m) 1250(m))	1038(m)	581(m)	660(m)
5	3000-3600(sbr) 3431(s)	-	1605(vs)	-	1270(m)	1050(w)	580(mbr)	680(w)
6	3445(s) 3202(s) 3068(s)	1667(s) 1680(m)	1611(s)	1559(m)	1277(s) 1250(msh)	1050(w)	580(w)	680(w)
7	3430(s) 3202(s) 3067(s)	1667(m) 1675(s)	1607(s)	1560(s)	1277(w) 1250(msh)	1035(m)	582(w)	696(w)

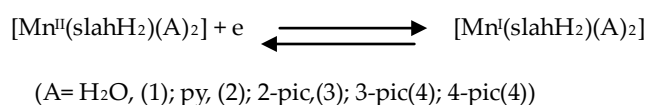
dihydrazone is assignable to $\nu\text{C}=\text{N}$ band [18]. This band on an average shift to lower frequency by $9\text{-}15\text{ cm}^{-1}$ indicating coordination of $>\text{C}=\text{N}$ group to the metal centre. This arises due to coordination of both the azomethine nitrogen atoms and phenolate oxygen atoms of the same dihydrazone molecule to the same metal centre. This should introduce steric crowding in the molecule. So one dihydrazone arm remains in the equatorial plane while the other hydrazone arm attains axial position. In this configuration, axial azomethine proton absorb at lower frequency as compared to equatorial azomethine protons which absorb at higher frequency. In the IR spectra of the complexes (1) to (7), both $\nu\text{C}=\text{N}$ band merge into one another giving rise to a single band only. At the same time, this also suggests that there is less steric crowding in these metal complexes. A band at 1275 cm^{-1} is assignable to $\beta(\text{C}-\text{O})(\text{phenolic})$ in the free dihydrazone. This band undergoes splitting into two bands in the IR spectra of the complexes (4), (6) and (7) which appears to be the effect of bonding of phenolic C-O group to the metal centre. This shifts to lower frequency by $5\text{ to }15\text{ cm}^{-1}$ in the complexes and is associated with involvement of phenolic C-O group in coordination. Another weak broad band appearing at $580\text{-}582\text{ cm}^{-1}$ is assigned to $\nu\text{M}-\text{O}(\text{phenolic})$ that indicates π -electron density flows of aromatic ring to metal centre through phenolic oxygen atom. Pyridine bases absorb at around $\sim 604\text{ cm}^{-1}$ due to in-plane ring deformation mode [19]. In the complexes (2) to (7), a new medium to weak band is observed in the region $660\text{-}696\text{ cm}^{-1}$ is assigned to arise due to in-plane ring deformation mode of pyridine bases indicating their coordination to the metal centre. A distinct band

appearing in 635 cm^{-1} in the complex (1) arises due to rocking mode of coordinated water molecules to the metal centre [20]. The broad band appearing in the region $3432\text{-}3449\text{ cm}^{-1}$ in the complexes (2) to (5) are assigned to antisymmetric and symmetric stretching vibrations of lattice water molecules while the band in the above region in the complex (1) is assigned to coordinated water molecule.

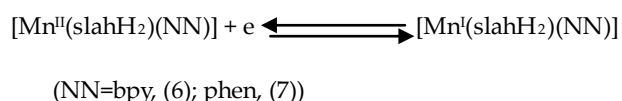
3.7 Cyclic Voltammetry:

The cyclic voltammograms of 2 mmol solutions of the ligand and complexes in DMSO solution under nitrogen with 0.1 molL^{-1} TBAP as a supporting electrolyte were run at several scan rates. The data have been set out in table 4 at scan rate of 100 mV/s .

The free ligand exhibits one quasi-reversible redox couple at $+0.275\text{ V}(E_{1/2})$ ($\Delta E = 150\text{ mV}$) 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. The complexes show metal centered redox processes, that may be shown as below



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



The manganese centre exhibits stable one electron chemical reversibility in the complexes. The oxidation potential at $+0.45\text{ V}$ in complexes (6) and (7) suggest the ease in removal of electron

from the valence shell of the ligand. Pyridine bases play important role in shifting the oxidation potentials values that increases in going from complex (1) without pyridine base to complexes (2) to (5) with monodentate methyl pyridine bases to complexes (6) and (7) with bidentate bases.

Table 4: The Electrochemical Parameters for Monometallic Manganese(II) Complexes (Pot vs SCE)

Complex	E_{pa}/V	E_{pc}/V
$[Mn^{II}(slahH_2)(H_2O)_2]$	+0.05	-0.25
$[Mn^{II}(slahH_2)(py)_2].H_2O$	+0.32	+0.25
$[Mn^{II}(slahH_2)(2-pic)_2].H_2O$	+0.35	+0.05
$[Mn^{II}(slahH_2)(3-pic)_2].H_2O$	+0.35	+0.05
$[Mn^{II}(slahH_2)(4-pic)_2].H_2O$	+0.35	-0.17
$[Mn^{II}(slahH_2)(bpy)]$	+0.45	-0.18
$[Mn^{II}(slahH_2)(phen)]$	+0.45	+0.26

4. CONCLUSION

This article reports the synthesis, characterization of Mn(II) complexes of ligand disalicyladehyde adipoyldihydrazone, their stereochemistry and redox activity upon coordination of various mono and bidentate nitrogen donor ligands. The dihydrazone coordinates to Mn(II) through azomethine nitrogen and phenolate oxygen with manganese occupying the NNOO coor-

dination chamber. The dihydrazone donors are arranged around manganese in the equatorial plane while the axial positions are occupied by water /pyridine/2-picoline/3-picoline/4-picoline in complexes (1) to (5). In complexes (6) and (7), the nitrogen from azomethine of dihydrazone and bpy or phen are in equatorial positions and phenolate 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 phenolate 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 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.

Cyclic voltammetry show that the metal center cycles among $Mn^{II} \rightarrow Mn^I$ oxidation in the complexes.

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

Acknowledgments

The authors are grateful to the Head, SAIF, North-Eastern Hill University, Shillong-793022, Meghalaya, India for elemental analyses and mass spectral studies, the Head, SAIF, CDRI, Lucknow, Uttar Pradesh, India for FAB mass spectral data, and the Head, SAIF, IIT Mumbai, India for EPR spectroscopic studies.

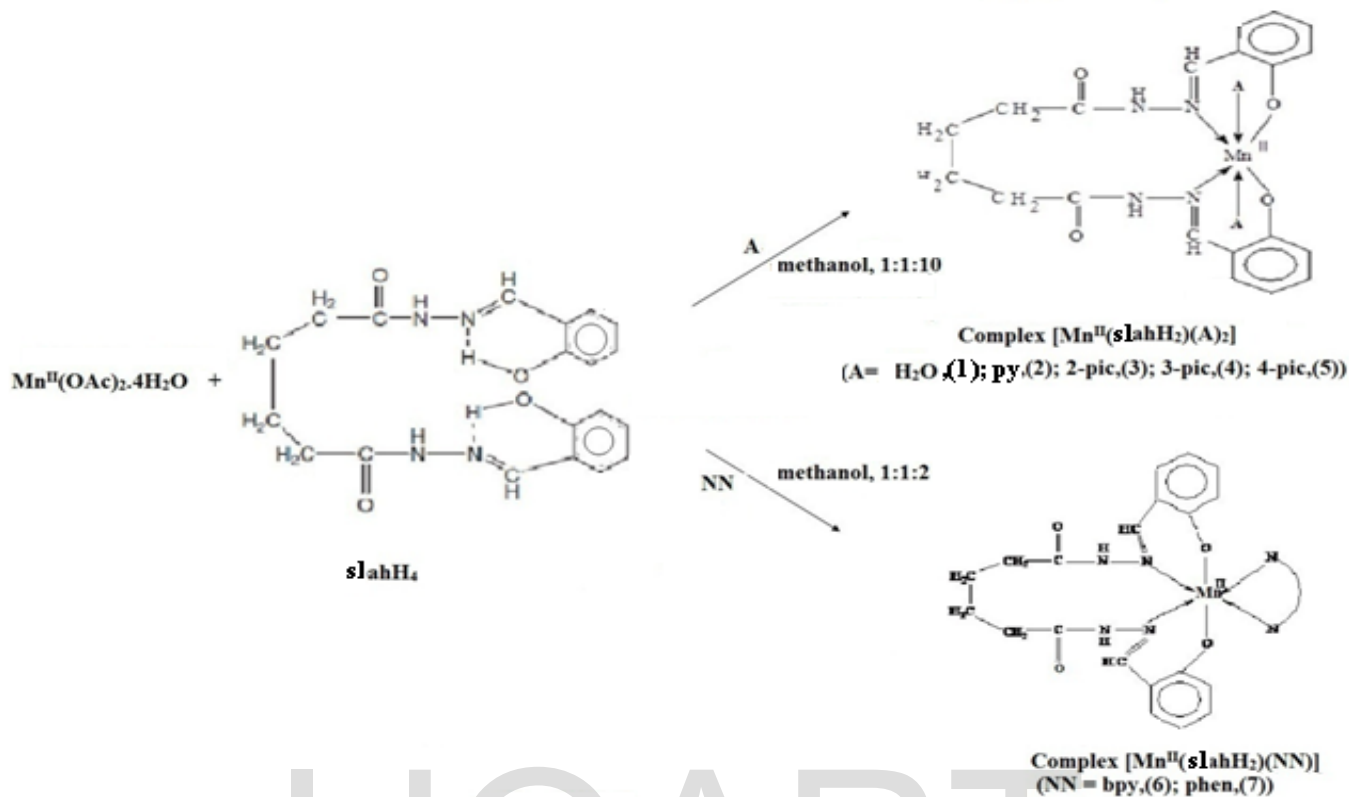


Figure 1: Reactions and structures of the Mn(II) complexes

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