SYNTHESIS, CHARACTERISATION AND CATALYTIC STUDIES OF SALEN-TYPE COMPLEXES OF MANGANESE

DISSERTATION

Submitted in Partial Fulfillment of the Degree of M.Sc

(Organic Chemistry)

By

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To

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STATEMENT

I hereby declare that the matter presented in this dissertation entitled, **'Synthesis, Characterisation and Catalytic studies of Salen-type complexes of Manganese'** is based on the result of the investigations carried out by me in the School of Chemical Sciences,Goa University under the supervision of **Dr. Sandesh Bugde** and **Dr.Sundar Dhuri** and the same has not been submitted elsewhere for the award of a degree or diploma.

Ms. Asmita A. Halarnkar

M.Sc. Part II, Organic Chemistry

School of Chemical Sciences

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CERTIFICATE

This is to certify that the dissertation entitled, **'Synthesis, Characterisation and Catalytic studies of Salen-type complexes of Manganese'**

Herein I confirm that work by **Ms. Asmita A. Halarnkar** under the supervision in partial fulfillment of the requirements for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa university.

Dr. Sandesh Bugde

Project Supervisor

School of Chemical Sciences

Goa University

CERTIFICATE FROM THE HEAD

This is to certify that the dissertation entitled, **'Synthesis, Characterisation and Catalytic studies of Salen-type complexes of Manganese'**

Herein I confirm that the work carried out by Ms. Asmita A. Halarnkar under the supervision of Dr. Sandesh Bugde and Dr. Sundar Dhuri for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.

Prof. V.S Nadkarni

Dean of School of Chemical Sciences

Goa University

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INTRODUCTION

INTRODUCTION

A Schiff base is a compound with the general structure $R_2C=NR'$ ($R' \neq H$). A number of special naming systems exist for these compounds. For example, a Schiff base derived bis-compounds are often referred to as salen-type compounds. These compounds are used commonly as ligands to form coordination complexes with metal ions. Such complexes occur naturally, for instance in corrin, but the majority of them are artificial and are used to form many important catalysts, such as Jacobsen's catalyst. In typical Schiff bases, the imine nitrogen is basic and exhibits pi-acceptor properties. The ligands are typically derived from alkyl diamines and aromatic aldehydes.[1]

Schiff bases are still prepared by modern chemists and nowadays active and well-designed Schiff base ligands are considered ‘‘privileged ligands’’. Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations. P.G Cozzi reviewed that Schiff bases are also able to transmit chiral information to produce non-racemic products through a catalytic process and summarized and introduced some practical guidelines for the preparation and use of Schiff base metal complexes in catalysis. focusing on the different ways of preparing metal complexes and their use in catalytic processes.[2]

Schiff base ligands stabilize different metal ions in solution to yield metal co-ordinate compounds with a various properties and applications. For example, the chelating salen is known by the ability to significantly decrease the Mn(III) /Mn(II) redox potential and the resulting complexes constitute suitable systems to catalyze multiple redox reactions such as asymmetric epoxidation of unfunctionalized olefins, catalase reaction, water photolysis, Diels-Alder cycloaddition, enantioselective cyclopropanation of styrenes and ring opening of epoxides[3-10].

A variety of applications of this type of complexes have also been reported which include biological activities (antibacterial, antifungal, anticancer, antioxidant, anti-inflammatory, etc.).[11-15] The concept of “green chemistry” is becoming increasingly important in synthetic as well as in industrial chemistry.[16] This idea is often accomplished by using catalytic variations of reactions. Salen-type constitute a standard system in coordination chemistry. The investigation of salen complexes has been very active after the discovery of salen-catalyzed enantioselective epoxidation of olefins by the groups of Jacobsen[17] and Katsuki.[18]

Mn-salen complexes have been found to be excellent catalysts for asymmetric epoxidation of simple olefins[19] and to catalyze oxidation of the C-H bond giving a hydroxy group[20] and optically catalyst has been used for kinetic resolution of racemic 1,2-epoxy-3,4-dihydronaphthalene by effecting diastereomeric oxidation of the benzylic C-H bond.[21] Hamachi et al. worked on enantioselective benzylic oxidation using Mn-salen complexes salen-type catalysts.[22]

The coordination chemistry of Manganese(II) has attracted considerable interest due to the crucial role played by the metal in redox and non-redox proteins. Studies involving the synthesis and characterization of manganese complexes are useful towards the understanding of the structure and reactivity of manganese sites in biological systems.[23-25] Manganese(II) ion has a high spin d5 electronic configuration, which gives no crystal field stabilization energies for any coordination geometries. Therefore, various coordination geometries are expected for manganese(II) co-

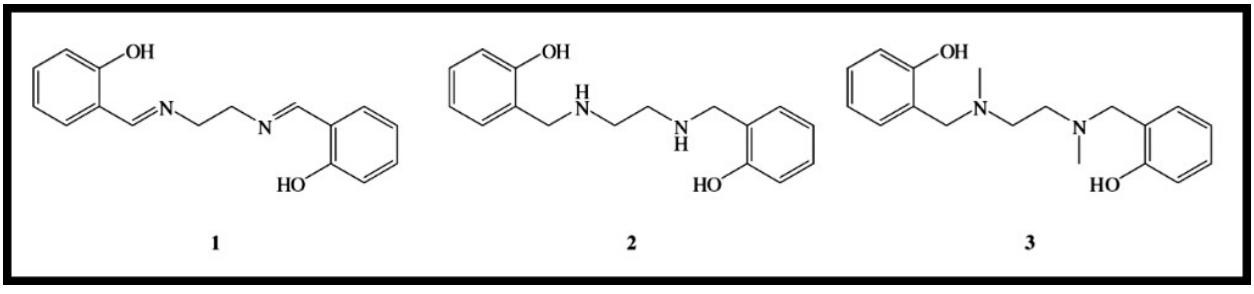
ordinate compounds. However, most manganese(II) co-ordinate compounds take an octahedral geometry and only few examples are known to take other coordination geometries.[26] Coordination numbers exceeding six are uncommon for manganese(II) ion. This metal ion prefers a limited number of coordination geometries, which minimize ligand-ligand repulsions.

Studies of high oxidation state complexes are of special importance because of their potential uses as oxidizing agents, catalysts and electro-catalysts, for the oxidation of compounds such as alcohols, esters, and water. A large number of manganese complexes involving different ligand environments have been structurally characterized and their electron transfer properties have been studied extensively; however, there remains a wider scope to study the chemistry of MnII, MnIII and MnIV oxidation states.[27]

The ligand has multiple roles. As in case of epoxidation, the ligands force the manganese oxo to come closer to incoming olefins. More importantly, the Mn(O)(Salen) is in equilibrium in different forms, while the oxo ligand can coordinate another Mn(Salen). Regarding epoxidation, the dimer is considered inactive. Axial ligands are able to stabilize the monomer form of the complex. Easy catalyst deactivation and irreversible ligand oxidation have prompted recent efforts to stabilize the active form of the catalyst.

The high valent metal-oxo short-lived species have been extensively studied and used in the oxidation of the organic substrates into viable products[28-29]. A large number of reports are available on the biomimetic chemistry of heme and nonheme high valent manganese-oxo species.[30-34] The key intermediate is an Mn(O)(Salen), studied using spectroscopic and theoretical calculations. An analysis of the mechanism of the reactions suggests that a stepped conformation of the Salen is crucial in transmitting chiral information.

In the search for new metal catalysts containing salen-type ligands, a better catalytic behaviour was observed when the substrate molecule can be easily coordinated by the complex and is favoured when the catalyst has either a vacancy in the coordination sphere or a labile ligand. [35-38] and to achieve this, a careful design of the environment around the metal ion is necessary.



Hydrogenation of the imine bond of salen**(1)** compounds produces a new tetradentate ligand, called as salan ($H_2[H_4]$salen; tetrahydrosalen; N,N'-bis(2-hydroxybenzyl)-1,2-diaminoethane(**2**).[57] While the salen ligands feature two sites capable of covalent bonding with an electropositive element, the H_4 salan ligands contain four such sites, and are therefore ideally suited to bind multiple metals.[58]

Tetrahydrosalen, N,N'-dimethylated tetrahydrosalen**(3)** and its derivatives have rarely been studied, and the most common approach for the preparation of these compounds involves isolation of the salan intermediate followed by additional substitution steps on the salan products[59,60], or condensation of salans with formaldehyde/acetic acid followed by in situ sodium borohydride reduction to give the N-methylated salans.[42] Other procedures employ the reductive amination of N,N'-dimethylethylene diamine with $NaBH_3(CN)$.[61,62]

Based on a comparison of the basicity of tetrahydrosalen and salen, where the basicity decreases, we expected that the methyl functionality in tetrahydrosalens would provide the best template for metal binding.[65] On the other hand, it is well known that tetrahydrosalen associated with metal centers displays cis-octahedral coordination geometry, which can form two possible diastereomers (cis *facmer* and cis *fac-fac*). [64] Each of these can exist as a pair of chiral-at-metal enantiomers. [63]

Tetrahydrosalens have also been investigated for the potential use as achiral ligand that can adopt asymmetric conformations and can participate in enantioselective catalysis transferring asymmetry from the catalyst to the substrate.[39-42] Previous syntheses tetrahydrosalens have involved isolation of the salen intermediate and reduction with $NaBH_4$ or $LiAlH_4$, resulting in lower yields.[43] Other procedures employ the reductive amination of N,N'-dimethylethylenediamine with $NaBH_3(CN)$.[44] Tshuva et al. recently published a new method for synthesizing tetrahydrosalens in a single stage via Mannich condensation from primary or secondary diamine, formaldehyde, and a substituted phenol.[45] The tetrahydrosalen complexes show structural properties, chemical and thermal behaviour which is different from those of the corresponding salen complexes.

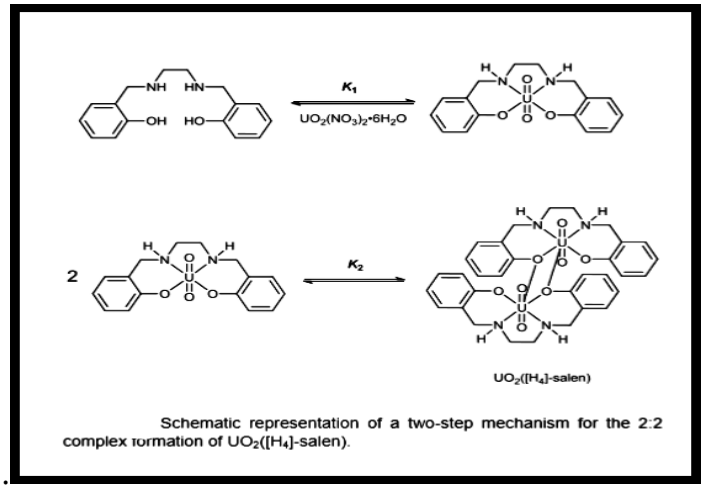
Zhao et al. synthesized and studied a pair of uranyl complexes incorporating tetrahydrosalen and N,N'-dimethyltetrahydrosalen ligands.[46] Compared to the prototype Schiff-base (salen) structure, these new ligands with saturated secondary and tertiary amines exhibited higher chemo-stability, especially under acidic conditions. Apparently, these new molecules containing saturated secondary and tertiary amine moieties are basically inert to hydrolysis and more stable compared to corresponding Schiff-base analogues.[47]

In this report, we report the synthesis of tetrahydrosalen and N,N'-Dimethylated salen ligands and form their Manganese metal complexes for their catalytic studies to be carried out.

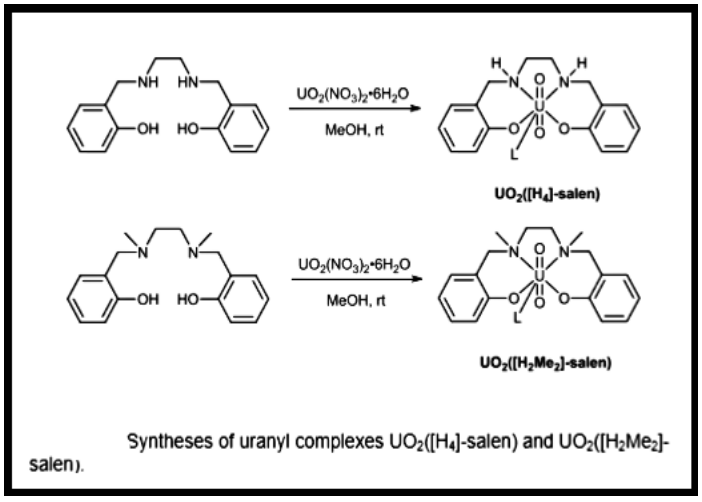
LITERATURE REVIEW

LITERATURE REVIEW

1. Zhao et al. synthesized and studied a pair of uranyl complexes incorporating tetrahydrosalen and N,N-dimethyltetrahydrosalen ligands, considering the fact that in comparison to the prototype Schiff-base (salen) structure, the new ligands with saturated secondary and tertiary amines exhibited higher chemo-stability, especially under acidic conditions.[46] X-ray crystallographic studies reported that the coordination geometry of uranium in these new complexes is a distorted pentagonal bipyramid, with the (dimethyl)tetrahydrosalen wrapped around the equatorial plane of UO_2^{2+}. They also observed that UO_2([H_4]-salen) comprising the tetrahydrosalen ligand forms a dimer structure in the crystals, with two subunits held together by sharing one of the two phenoxy oxygen atoms from each subunits and UO_2([H_2Me_2]-salen) with the N,N'-dimethyltetrahydrosalen ligand is in the monomer state, with a solvent molecule coordinated to uranium to complete the penta-coordination configuration. From UV−vis spectrometry studies, using the colorimetry method, they also inferred that these hydrogenated salen ligands exhibited comparable or even higher binding affinity toward uranyl than the prototype Schiff-base salen ligand in weakly basic solution.



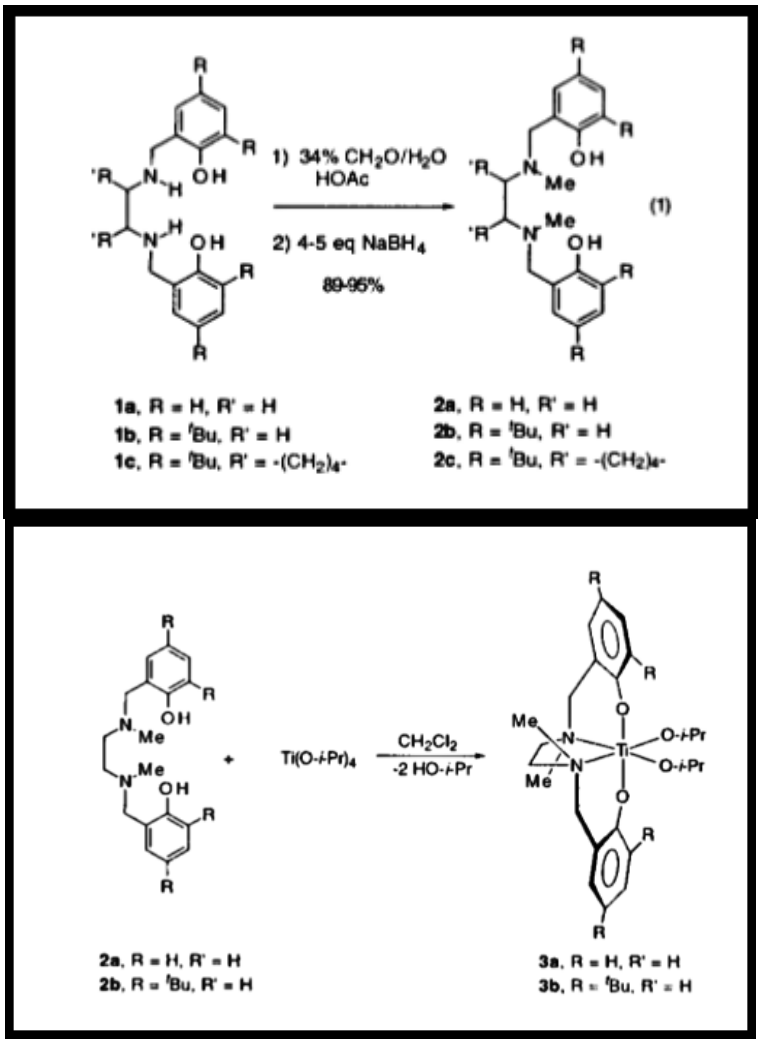
Schematic representation of a two-step mechanism for the 2:2 complex formation of UO_2([H_4]-salen).



Syntheses of uranyl complexes UO_2([H_4]-salen) and UO_2([H_2Me_2]-salen).

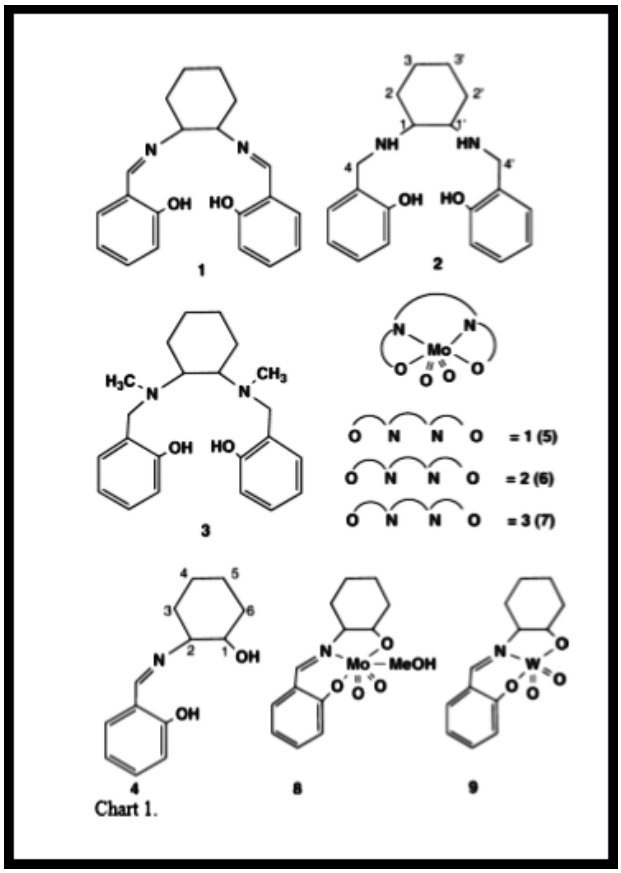
Scheme 1 : Synthesis of Uranyl coordinate compounds

2. Walsh et al. employed an achiral tetrahydrosalen ligands in the synthesis of chiral C_2-symmetric titanium complexes.[48] They combined later with tetrahydrosalen ligands 2a and 2b, titanium tetraisopropoxide which liberated 2 equivalents of isopropyl alcohol and generated the (tetrahydrosalen)Ti(O-i-Pr)$_2$ complexes 3a and 3b. ^{1}H and ^{13}C{^{1}H} NMR spectrometry and X-ray crystallography studies reported showed these complexes to be C_2-symmetric. It was concluded from the X-ray structures of 3a and 3b, that the bonding of the tetrahydrosalen ligand to titanium is different than the bonding of salen ligands to titanium and while salen ligands usually bind to titanium in a planar arrangement, the tetrahydrosalen is bonded with the phenoxide oxygens was mutually trans. When bounded in this fashion, the nitrogens of the tetrahydrosalen ligand and the titanium became stereogenic centers. It was noted that the use of titanium complexes of high enantiopurity in the generation of tetrahydrosalen titanium adducts resulted in a maximum diastereoselectivity of 2:1. It was observed that the diastereoselectivity obtained using chiral titanium alkoxide complexes was greater than the diastereoselectivity observed when a tetrahydrosalen ligand derived from (S,S)-trans-diaminocyclohexane was employed.[55]

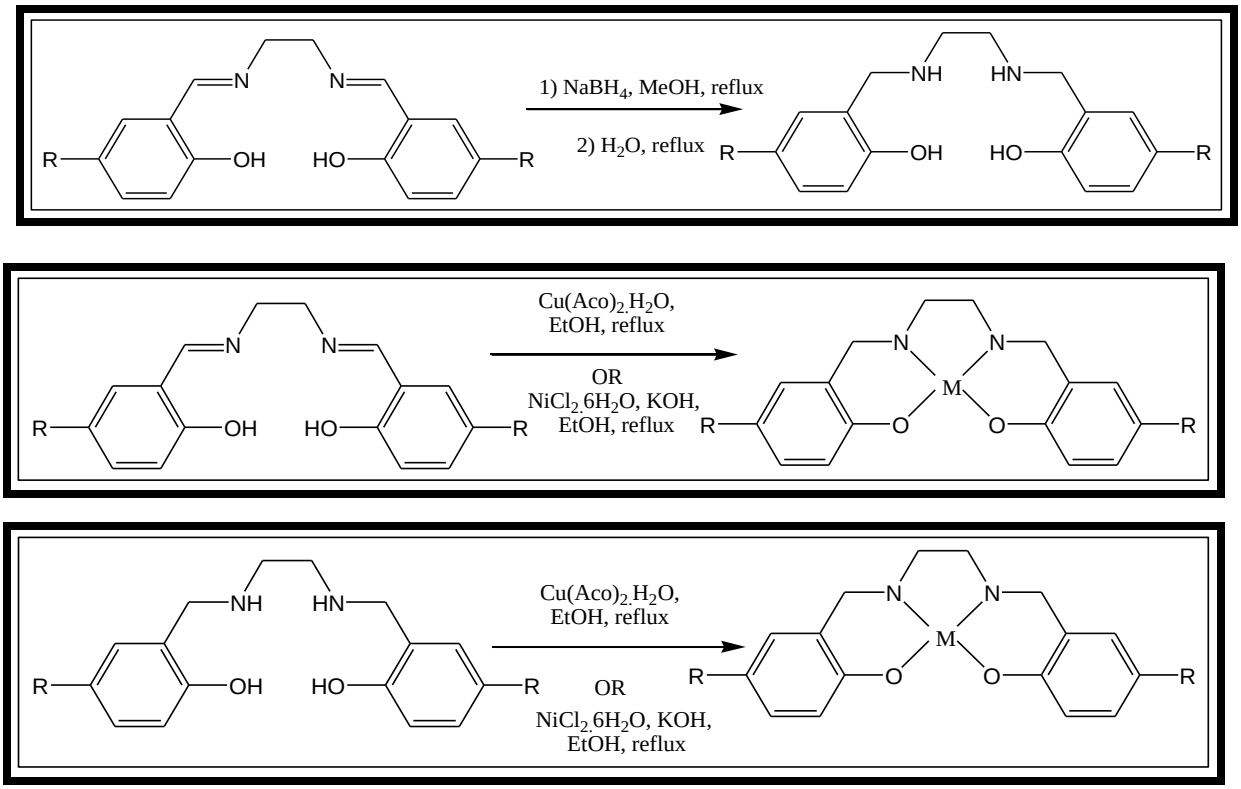


Scheme 2 : Synthesis of Titanium co-ordinate compounds

3. Zhou and his co-workers synthesized and examined three optically active Molybdenum (VI) dioxo complexes with tetrahydro salen and substituted tetrahydro salen derivatives as ligands as catalysts for asymmetric epoxidation.[49] They prepared by the reaction of the ligand L with $MoO_2(acac)2$ or $WO_2(acac)_2$ in alcohols as the solvent and characterized complexes of the type $MoO_2(L)(Solv)$ and $WO_2(L)$ (L = tridentate, trans-2-aminocyclohexanol derived chiral Schiff base, Solv = alcohol) by elemental analysis, NMR and IR spectroscopy. These complexes are found to be applicable as catalysts for olefin epoxidation reactions with tert-butyl hydroperoxide (TBHP) as the oxidizing agent. They reported that in cisβ -methylstyrene moderate enantiomeric excesses of up to 26% reached when the reaction was carried out at 0°C.

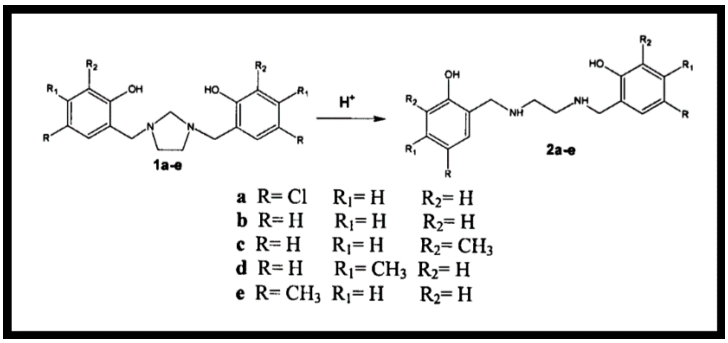


4. Soto-Garrido et al. reported the synthesis and characterization of novel bis-salen complexes, M(salenH_2), N,N'-*bis*-[5(1,1,3,3-tetramethylbutyl)salicylidene]-1,2-diaminoethane complexes, (M = Ni or Cu), and the less studied, bis-tetrahydrosalen complexes, M[H_2(salenH_2)], N,N'-*bis*-[2-hydroxy-5(1,1,3,3-tetramethylbutyl)benzyl]-1,2-diaminoethane complexes, (M = Ni or Cu), with a highly branched substitution pattern at C-5 of the benzene ring.[50] The Schiff bases are found to behave as dibasic tetradentate ligands. It was observed that the tetrahydrosalen complexes show structural properties, chemical and thermal behaviour which is different from those of the corresponding salen complexes. The melting points and decomposition temperatures of these complexes were determined by d.s.c. and t.g.a. (Differential scanning calorimetry and Thermogravimetric analysis).



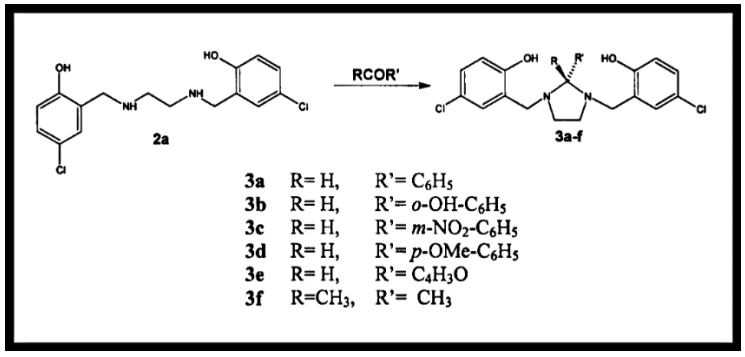
Scheme 3 : Synthesis of tetrahydrosalen Ligand and Copper and Nickel co-ordinate compounds

5. Rivera et al. reported the synthesis of a variety of tetrahydrosalens by hydrolyzing 1,3-bis (20-hydroxy-50-substituted-benzyl) imidazolidines with hydrochloric acid.[51] They carried out the acid hydrolysis of Mannich type bases such as 1,3-bis(20-hydroxybenzyl)-imidazolidine **1a–e** synthesized according to the cited methodology[56], which lead to to tetrahydrosalens **2a–e**, respectively. Wherein they concluded that the nature and position of substituents in the aromatic ring do not influence the course of the reaction, making this a very versatile method for producing unsubstituted tetrahydrosalens with good yield.



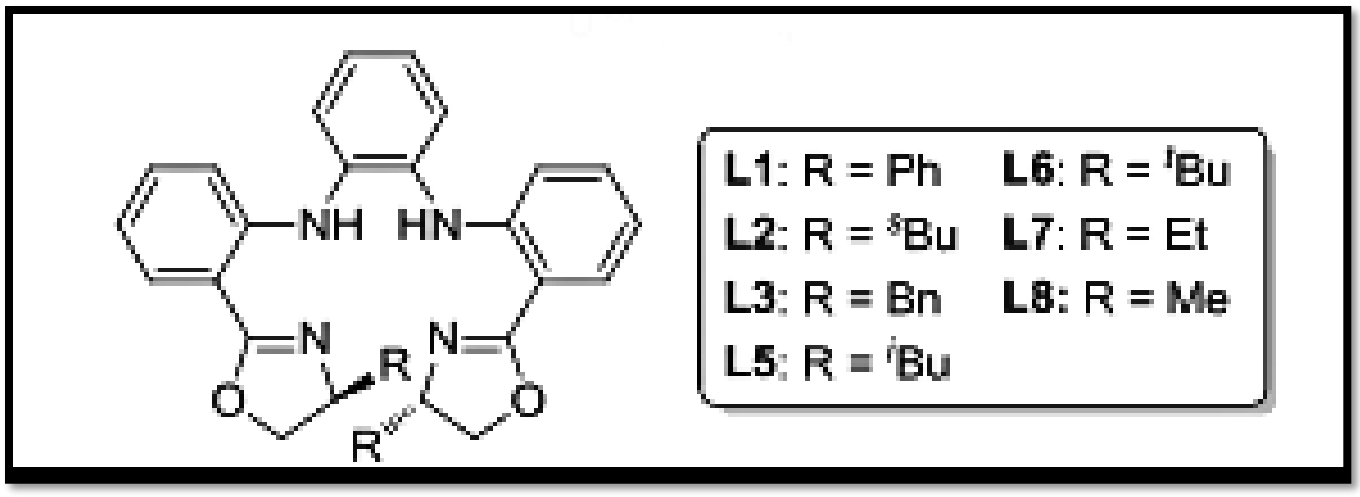
Scheme 4 : Synthesis of tetrahydrosalens by hydrolyzing 1,3-bis (20-hydroxy-50-substituted-benzyl)imidazolidines in presence of acid

Further, they also carried out a reaction of these tetrahydrosalens with aldehydes and yielded 2-substituted-1,3-bis(20-hydroxy-50-substituted-benzyl) imidazolidines **3a–f** depicting its use as base materials in synthesizing new ligands representing a new, convenient asymmetrical tetrahydrosalen synthetic route having good yield for simple reactions and which could be carried out using commercially available reagents. The main advantages of this method over previous ones are the ready availability of reagents, high yields for various carbonyl compounds, and operational simplicity.

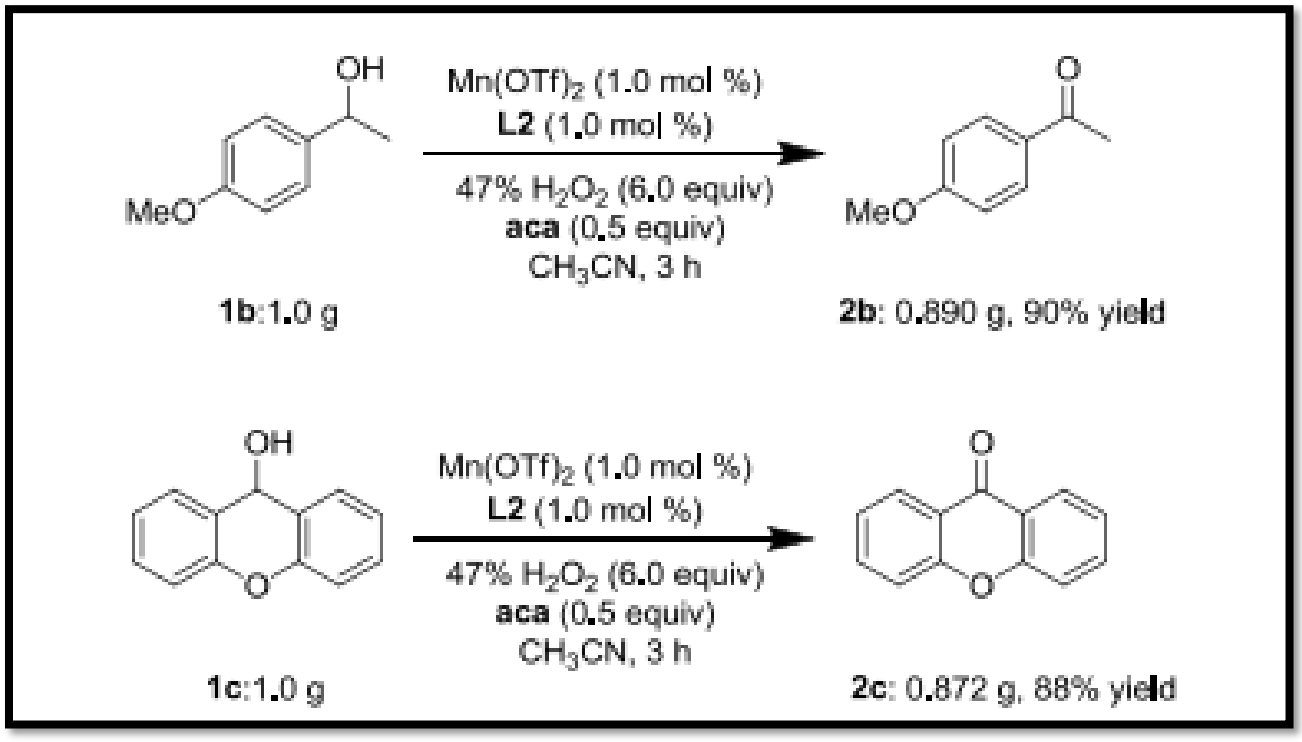


Scheme 5 : Synthesis of new ligands by reaction of aldehydes with tetrahydrosalens

6.Dai and his co-workers performed various studies to illustrate the catalyst system using cinnamyl alcohol as a substrate.[52] It was found that adamantane carboxylic acid (**aca**) when used as an additive provided best results. They found that 6 equiv. of H_2O_2(oxidant) were necessary in order to achieve the best result. They investigated on ligand screening that L2 excelled and the ratio of $Mn(OTf)_2$ and L2 as 1:1 gave best results. They performed successful oxidations on various alcohols (Conjugated and non-conjugated allylic alcohols, benzylic primary and secondary alcohols) and compared the results.

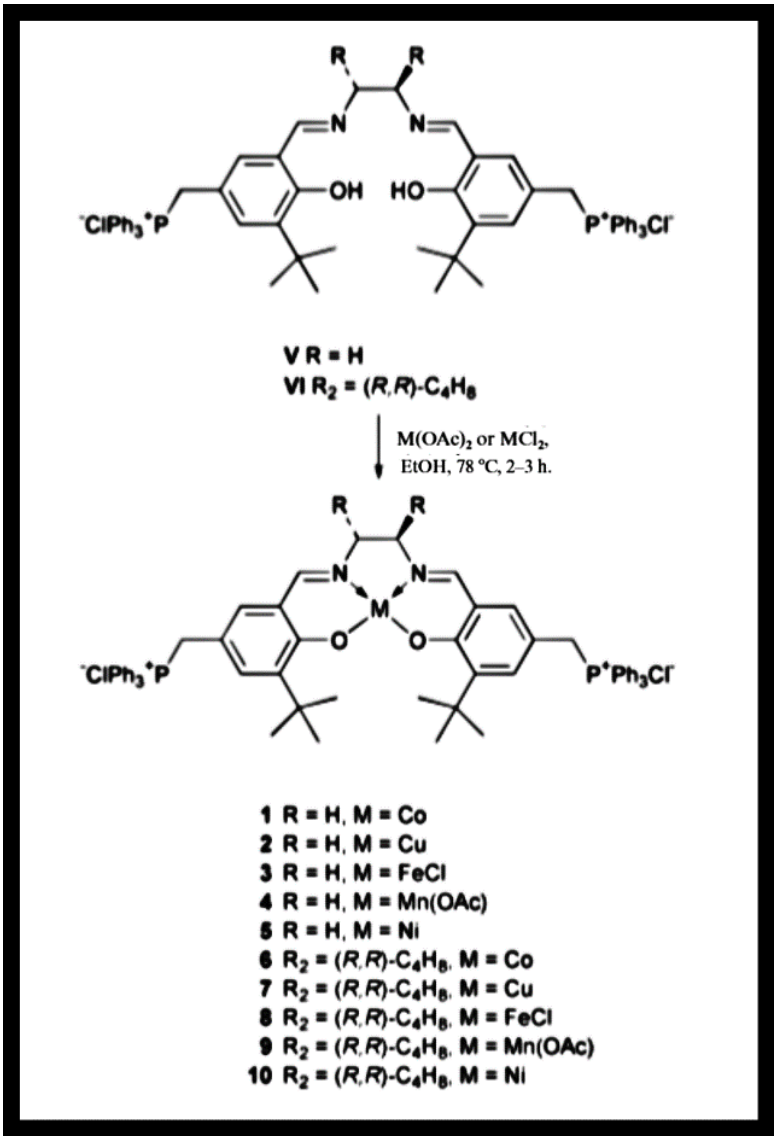


It was inferred from these results that a high-valent Mn-oxo species would be an active intermediate in current catalyst system and carboxylic acid additive may play a key role in the activation of H_2O_2 to form the high-valent Mn-oxo species, although the exact structure of the catalyst is not clear. They further evaluated the practical utility of the catalyst system by the oxidation of 1-(4-methoxyphenyl)ethanol (**1b**) and xanthydrol (**1c)** was carried out on gram scale under the optimized conditions, affording the desired product **2b** and **2c** in 90% yield and 88% yield after a prolonged reaction time, respectively.



Scheme 6 : Ligand $Mn(OTf)_2$ used as catalyst

7. Haikarainen et al. reported the synthesis and characterization of several new bulky salen-type Schiff base ligands and their complexes with first-row transition metals Co, Cu, Fe, Mn and Ni. The drawback of most of the complexes was observed to be in their limited solubility in aqueous solutions.[53] To overcome this limitation, they synthesized a series of complexes with broad solubility properties by introducing both lipophilic and ionic methyl (triphenylphosphonium chloride) substituents in the ligands. The ligands containing tert-butyl and methyl (triphenylphosphonium chloride) substituents in aromatic rings hence provided flexible solubility properties. Crystal structures of some of the complexes were also determined.



Scheme 7 : Synthesis of Cobalt, Copper, Iron, Manganese and Nickel co-ordinate compounds

8. Katsuki et al. reported the benzylic oxidation using a Mn-salen complex **3** as catalyst and iodosobenzene as oxidant which proceeded with moderate enantioselectivity to give the corresponding benzylic alcohol in solvents of high viscosity such as chlorobenzene and

fluorobenzene.[54] The carried out the study with 4 different catalysts and varying solvents and results were reported**.(TABLE 1)** It was observed that the use of solvents of a kind considerably improved enantioselectivity and the highest ee of 64% was achieved when chlorobenzene was used.

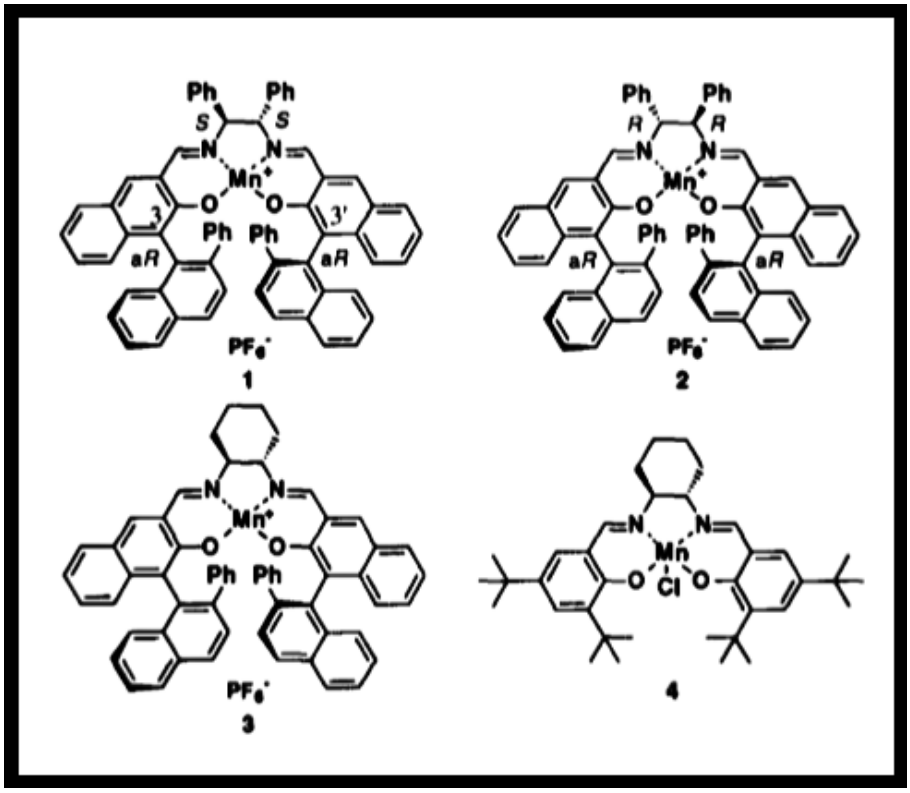


TABLE 1: Asymmetric hydroxylation of 1,1 Dimethylindane using a Mn-Salen Complex as Catalyst

Entry	Catalyst	Solvent	Temp	% ee	Yield (%)	Configuration
1	1	CH_3CN	r.t	36	15	R
2	2	CH_3CN	r.t	15	7	R
3	3	CH_3CN	r.t	36	25	R
4	4	CH_3CN	r.t	1	3	R
5	3	AcOEt	r.t	56	23	R
6	3	Fluorobenzene	r.t	62	21	R
7	3	Chlorobenzene	10°C	64	29	R

They carried out the asymmetric oxidation of different substrates using **3** as a catalyst and results were reported **(TABLE 2).**

TABLE 2 : Asymmetric oxidation using 3 as a catalyst.

Entry	Substrate	% ee	Yield (%)	Configuration	% ee
1	Ethylbenzene	53	22	R	40
2	4-methoxyethylbenzene	53	19	R	66
3	tetrahydronaphthalene	55	19	R	72
4	1,2,3,4-tetrahydro-1,1-dimethylnaphthalene	56	28	Not determined	-

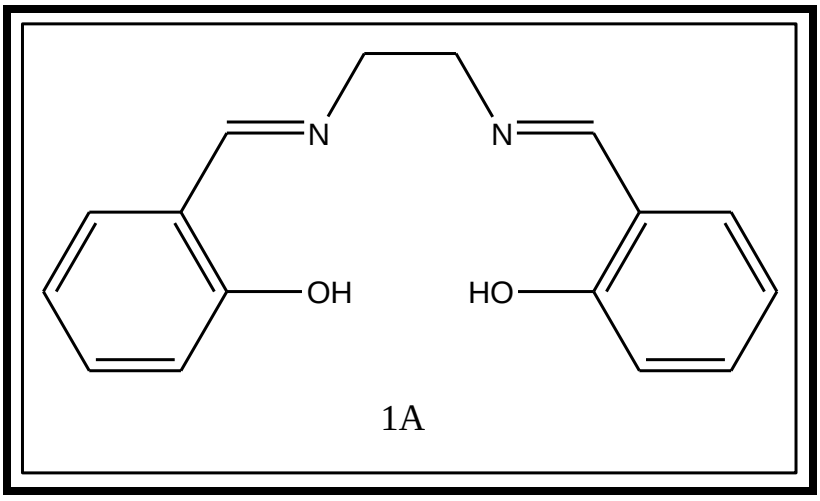
RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

It is seen that the tetrahydrosalen complexes show structural properties, chemical and thermal behaviour which is different from those of the corresponding salen co-ordinate compounds. It is observed that in comparison to the prototype Schiff-base (salen) structure, these new ligands (tetrahydrosalen and N,N'-Dimethyltetrahydrosalen) with saturated secondary and tertiary amines exhibited higher chemo-stability, especially under acidic conditions. It was also seen that these new molecules containing saturated secondary and tertiary amine moieties are basically inert to hydrolysis and more stable compared to corresponding Schiff-base analogues.[47] Based on a comparison of the basicity of tetrahydrosalen and salen, where the basicity decreases, we expected that the methyl functionality in tetrahydrosalens would provide the best template for metal binding. To the best of our knowledge, Manganese complexes of these ligands have not been reported yet and their catalytic studies haven't been explored yet. Further, the synthesis of the ligand N,N'-bis(2'-hydroxy-5'-substituted-benzyl)-N,N´dimethylpropane-1,3-diamines has not been reported yet.

In this work, we planned to synthesize the ligands, N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylethane-1,2-diamine and N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylpropane-1,3-diamine. The compounds were synthesized as per the cited literature.[46] The synthesized compounds were characterized by TLC, IR Spectroscopy and Physical Constant Determination.

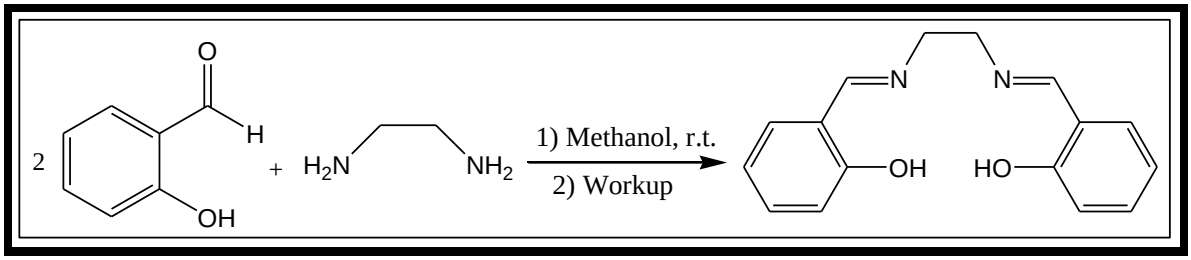
Firstly, to synthesize N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylethane-1,2-diamine, we started with the synthesis of of N,N'-ethylene*bis*(salicylimine). **(1A)**



1A

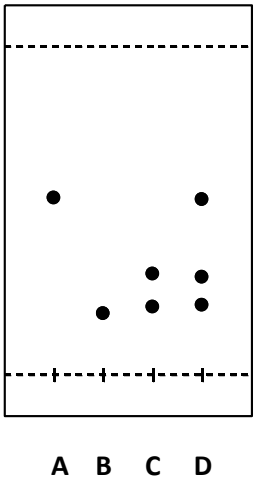
A) Synthesis of N,N'-ethylene*bis*(salicylimine)

The compound was synthesized as per the cited literature as depicted in Scheme A.[46] The synthesized compound was characterized by TLC and Physical Constant Determination.



SCHEME A

TLC of the compound was taken in Petroleum ether:Ethyl acetate (70:30).



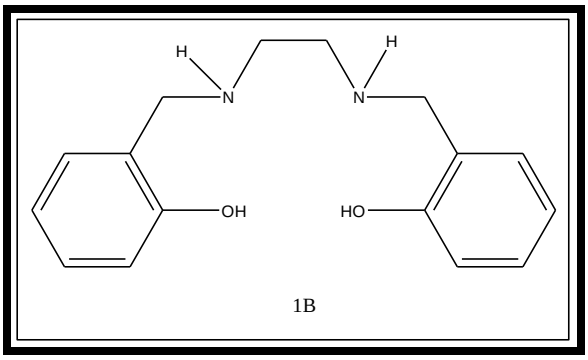
A – Ethylenediamine

B – Salicylaldehyde

C - N,N'-ethylene*bis*(salicylimine)

D – Co

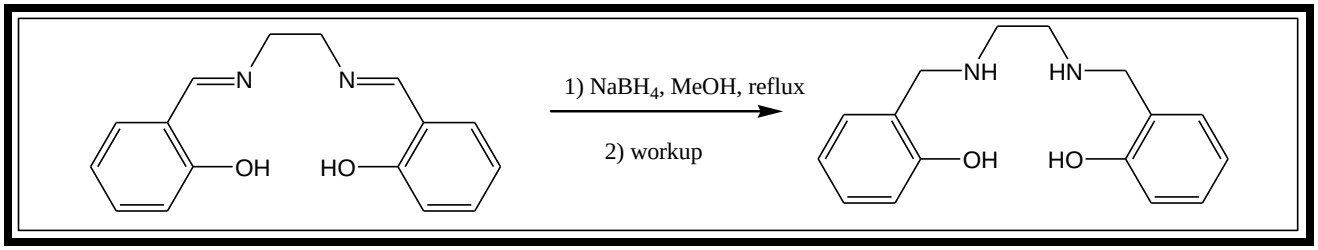
As aldehyde impurity was observed the compound was purified by column chromatography. The Physical Constant of the compound was determined. The melting point was found to be 126°C. The synthesized N,N'-ethylene*bis*(salicylimine) was further subjected to reduction to form N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylethane-1,2-diamine.**(1B)**



1B

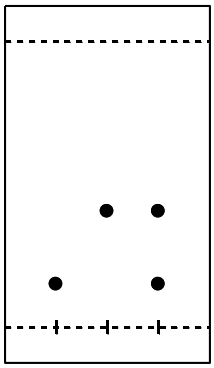
B) Reduction of N,N'-ethylene*bis*(salicylimine)

The compound was synthesized as per the cited literature as depicted in Scheme B.[46] The synthesized compound was characterized by TLC, IR Spectroscopy and Physical Constant Determination.



SCHEME B

TLC was taken in Petroleum ether:Ethyl acetate (70:30).



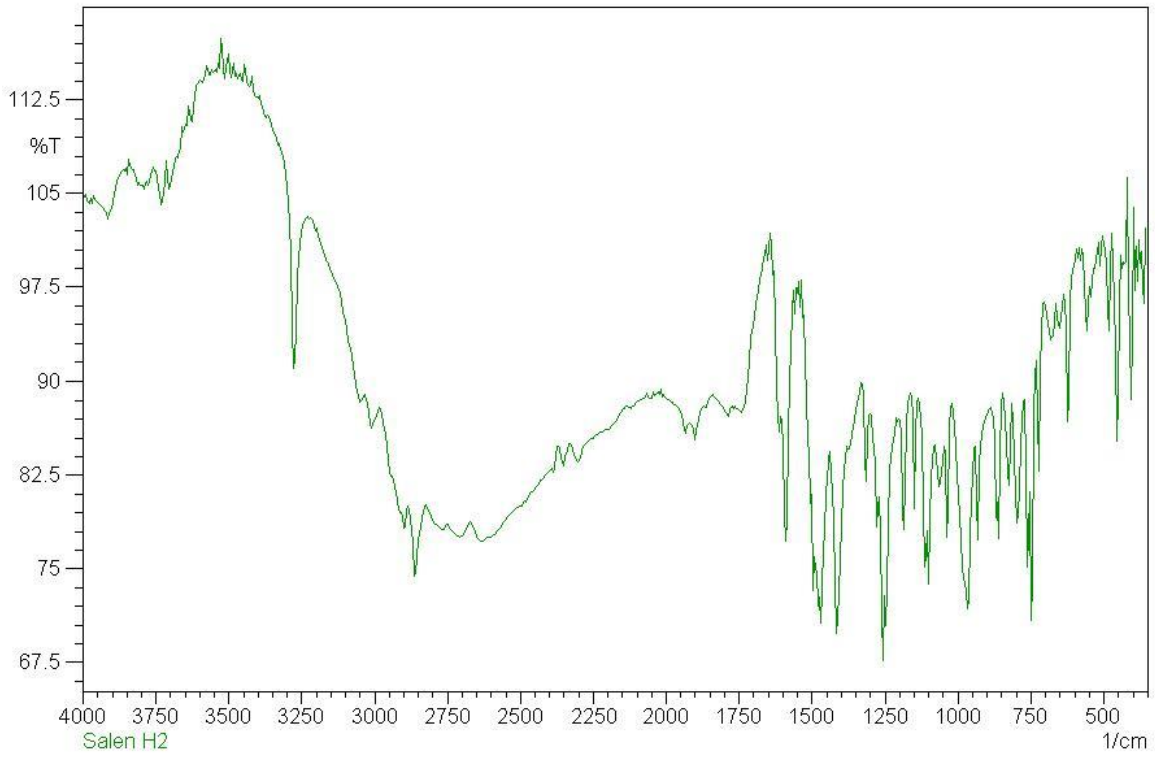
A B C

A - N,N'-ethylene*bis*(salicylimine)

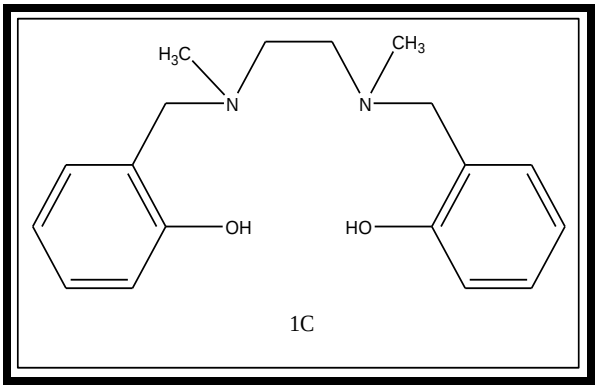
B - N,N'-*bis*(2-hydroxybenzyl)ethylenediamine

C – Co

This compound was purified by column chromatography. The IR Data of the compound is given below:



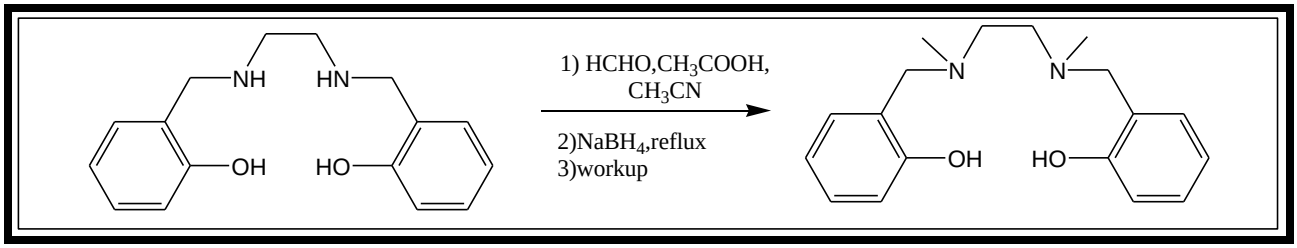
The Physical Constant of the compound was determined. The melting point was found to be 118°C. The reduced compound was further subjected to N-Methylation to yield N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylethane-1,2-diamine.**(1C)**



1C

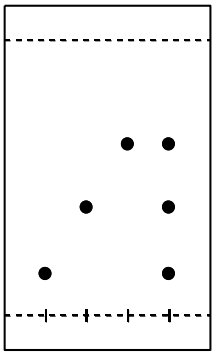
C) Synthesis of N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylethane-1,2-diamine

The compound was synthesized as per the cited literature as depicted in Scheme C.[46] The synthesized compound was characterized by TLC, IR Spectroscopy and ^{1}H-NMR Spectroscopy.



SCHEME C

TLC was taken in Petroleum ether:Ethyl acetate (70:30).



A B C D

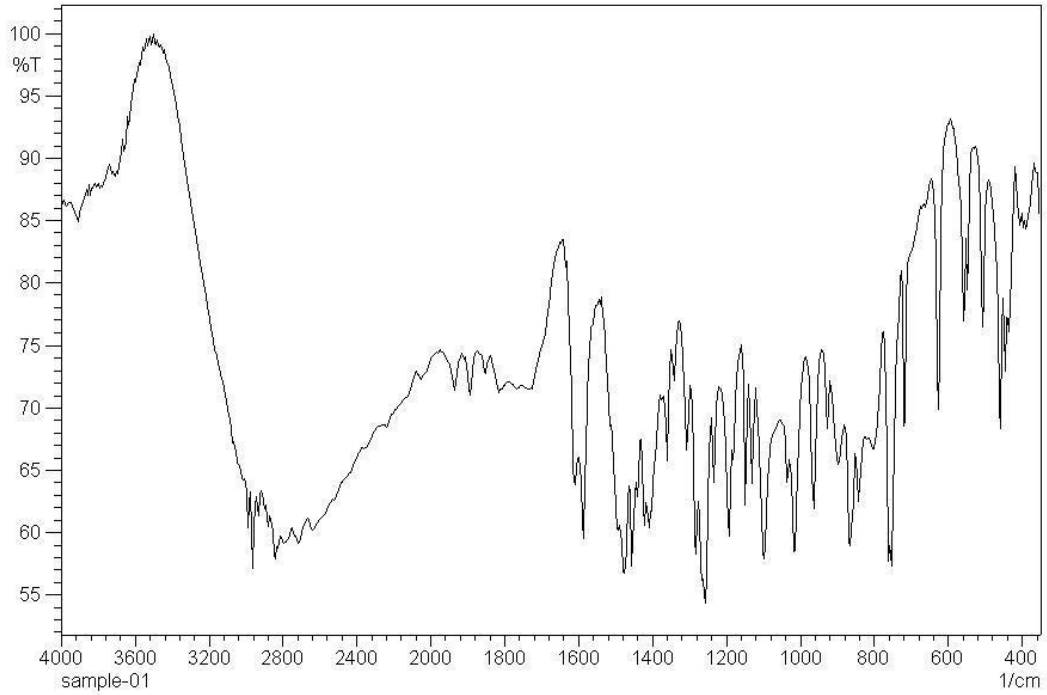
A - N,N'-ethylene*bis*(salicylimine)

B - N,N'-*bis*(2-hydroxybenzyl)ethylenediamine

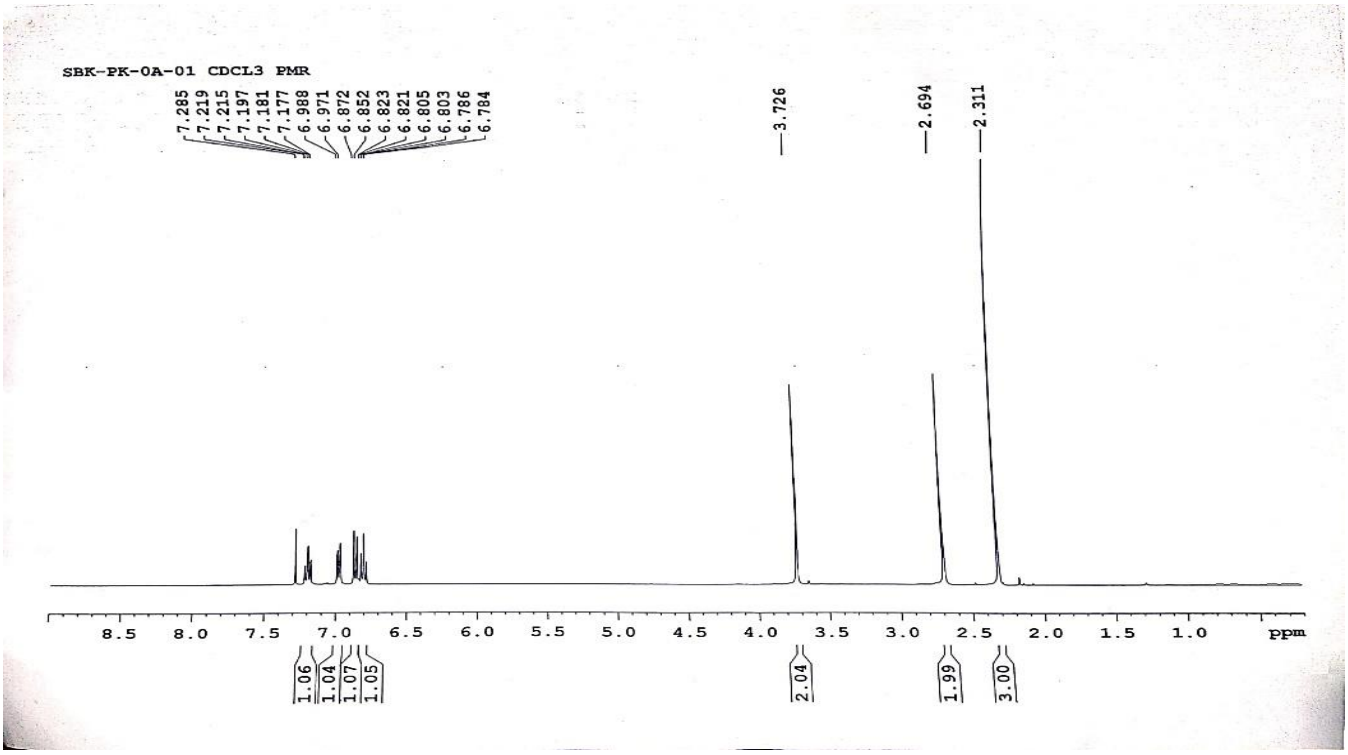
C - N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylethane-1,2-diamine

D – Co

This compound was purified by column chromatography. The IR Data of the compound is given below:

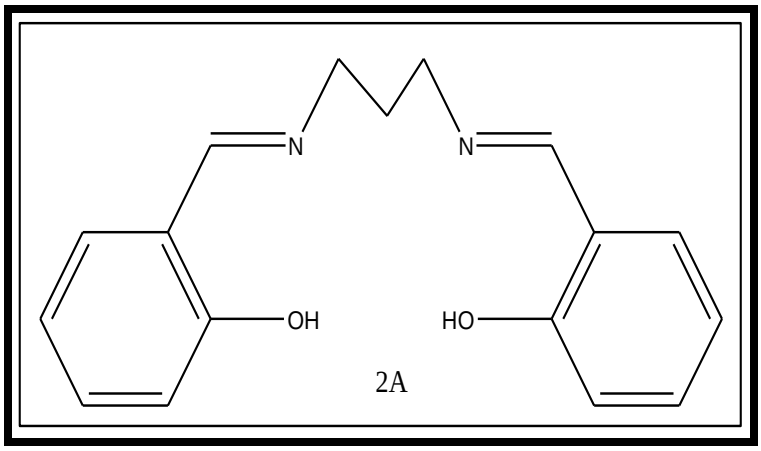


The ^{1}H-NMR Data for N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylethane-1,2-diamine is given below:



^{1}H NMR (400 MHz, CDCl3): δ 2.31 (s, 6H), 2.694 (s, 4H), 3.726 (s, 4H), 6.78 (td, J = 7.0, 1.0 Hz, 2H), 6.86 (dd, J = 8.1, 1.0 Hz, 2H), 6.97 (dd, J = 7.0, 1.6 Hz, 2H), 7.18 (td, J = 8.0, 1.6 Hz, 2H).

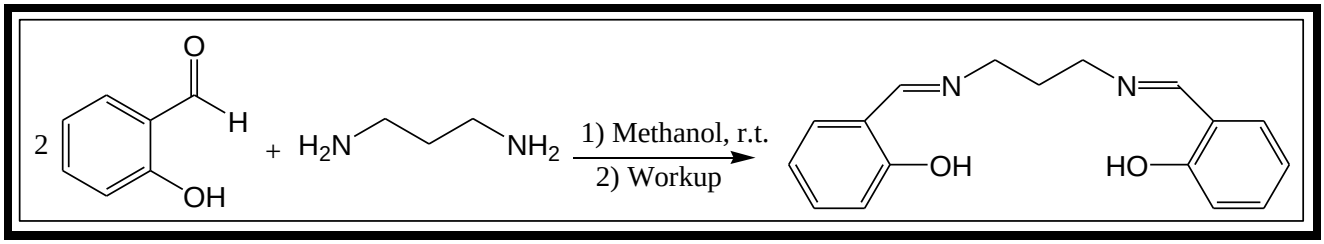
Secondly, to synthesize N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylpropane-1,3-diamine, we started with the synthesis of of N,N'-propylene*bis*(salicylimine).**(2A)**



2A

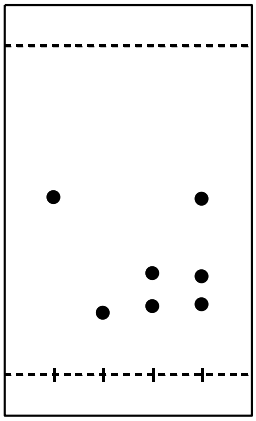
A) Synthesis of N,N'-propylene*bis*(salicylimine)

The compound was synthesized as per the cited literature as depicted in Scheme D.[46] The synthesized compound was characterized by TLC, IR Spectroscopy and Physical Constant Determination.



SCHEME D

TLC of the compound was taken in Petroleum ether:Ethyl acetate (70:30).



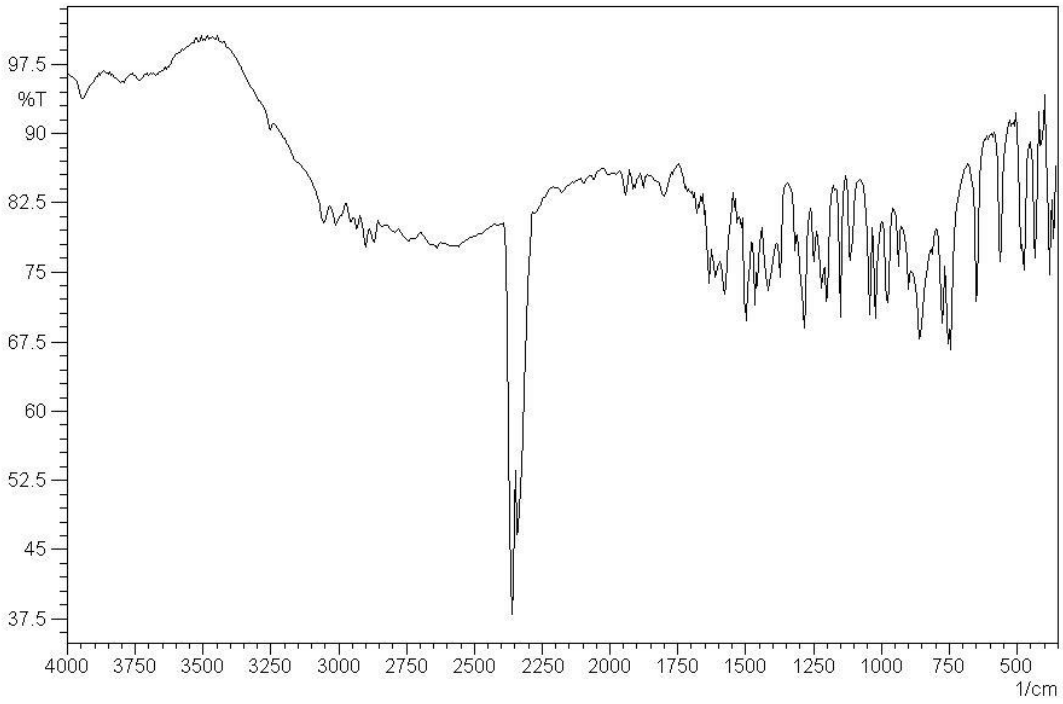
A –Propylenediamine

B – Salicylaldehyde

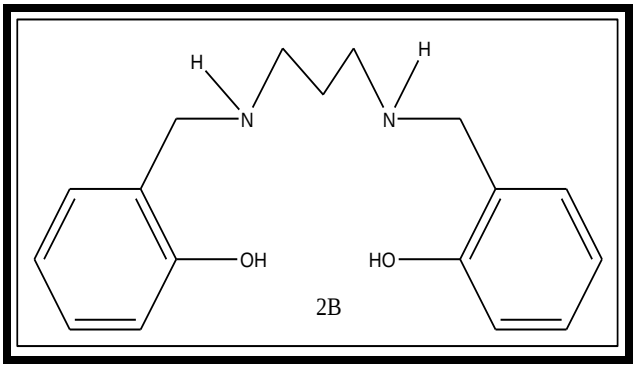
C - N,N'-propylene*bis*(salicylimine)

D – Co

As aldehyde impurity was observed the compound was purified by column chromatography. The IR Data of the compound is given below:



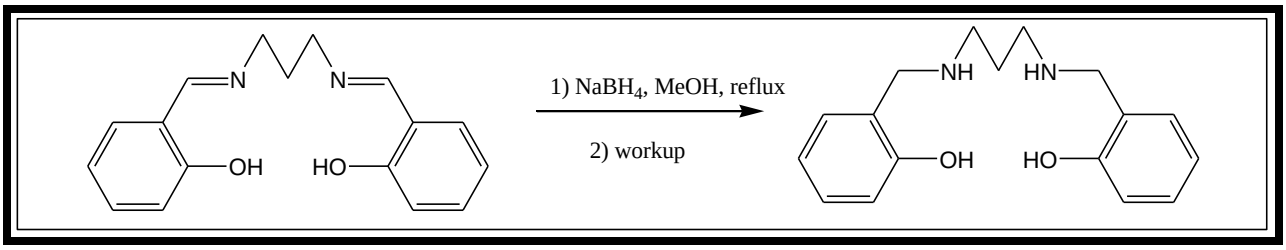
The Physical Constant of the compound was determined. The melting point was found to be 52°C. The synthesized N,N'-propylene*bis*(salicylimine) was further subjected to reduction to form N,N'-*bis*(2-hydroxybenzyl)propylenediamine.**(2B)**



2B

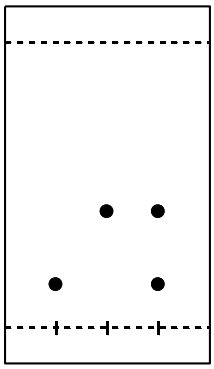
B) Reduction of N,N'-propylene*bis*(salicylimine)

The compound was synthesized as per the cited literature as depicted in Scheme E.[46] The synthesized compound was characterized by TLC, IR Spectroscopy and Physical Constant Determination.



SCHEME E

TLC was taken in Petroleum ether:Ethyl acetate (70:30).



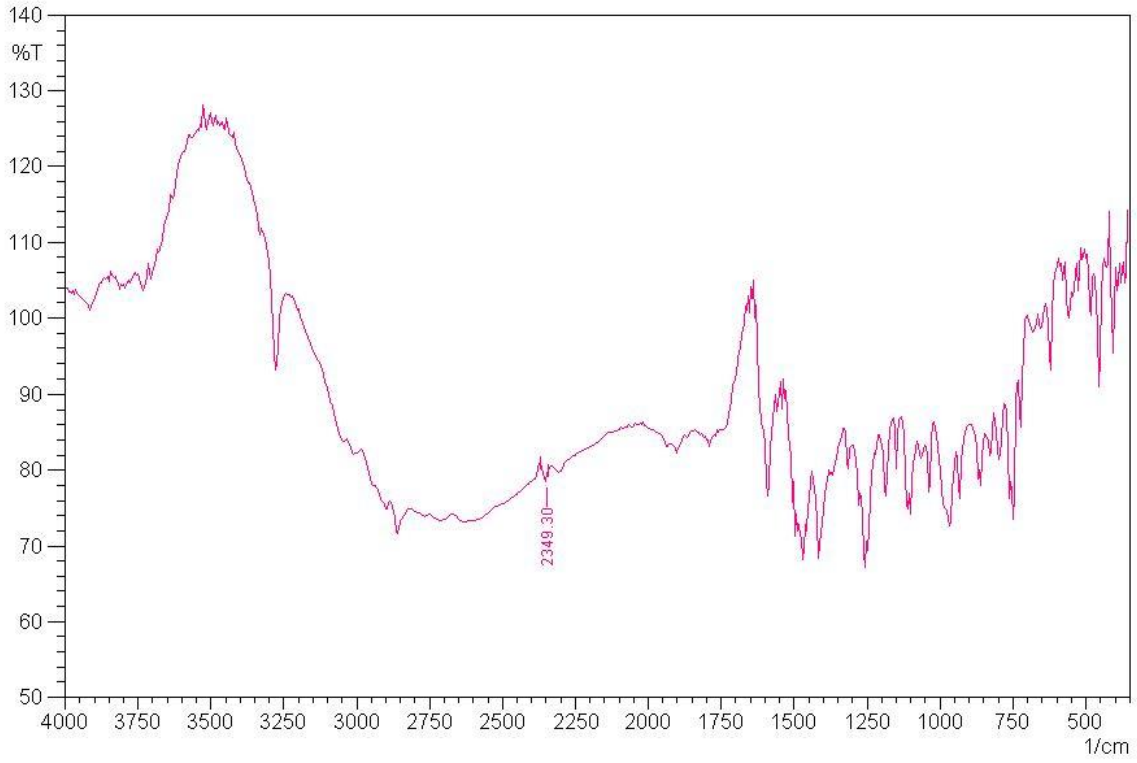
A B C

A - N,N'-propylene*bis*(salicylimine) compound

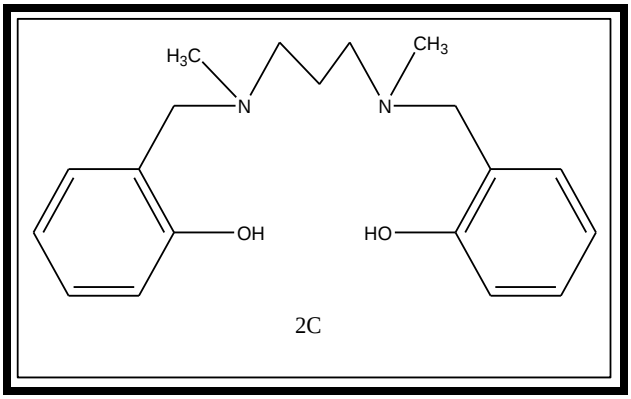
B - N,N'-*bis*(2-hydroxybenzyl)propylenediamine compound

C – Co

This compound was purified by column chromatography. The IR Data of the compound is given below:



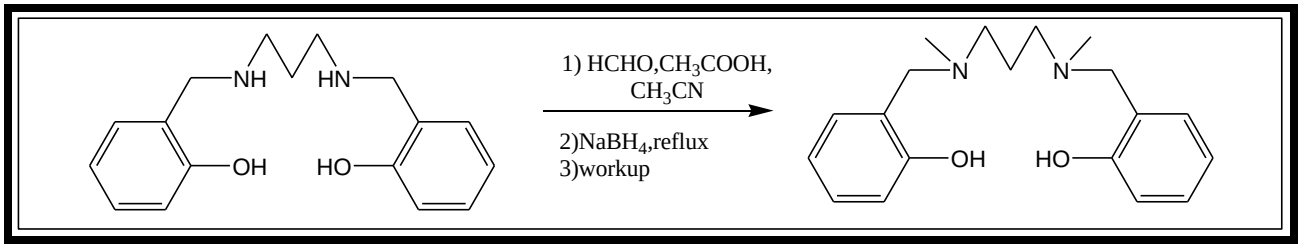
The Physical Constant of the compound was determined. The melting point was found to be 110°C. The reduced compound was further subjected to N-Methylation to yield N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylpropane-1,3-diamine.**(2C)**



2C

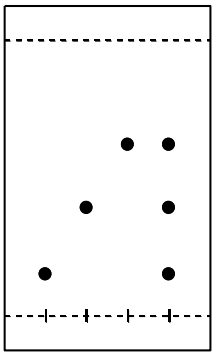
C) Synthesis of N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylpropane-1,3-diamine

The compound was synthesized as per the cited literature as depicted in Scheme F.[46] The synthesized compound was characterized by TLC.



SCHEME F

TLC was taken in Petroleum ether:Ethyl acetate (70:30).



A B C D

A - N,N'-ethylene*bis*(salicylimine)/ N,N'-propylene*bis*(salicylimine) compound

B - N,N'-*bis*(2-hydroxybenzyl)ethylenediamine/N,N'-*bis*(2-hydroxybenzyl)propylenediamine compound

C - N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylethane-1,2-diamine /N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylpropane-1,3-diamine compound

D – Co

This compound was purified by column chromatography.

EXPERIMENTAL WORK

EXPERIMENTAL WORK

IR Spectra were recorded on a Shimadzu FTIR Spectrophotometer using solid KBr pellets. All melting points were measured by normal Thiele's tube. Distilled solvents were used in all cases. Commercial reagents were used without further purification. All solvents and reagents were purified and dried by standard techniques. All the reactions were monitored by Thin Layer Chromatography (TLC) on silica gel. All compounds were purified by column chromatography.

1) Synthesis of N,N'-ethylene*bis*(salicylimine)

To a stirred solution of salicylaldehyde (9.76 g, 80 mmol) in 10 mL of methanol was slowly added a solution of ethylenediamine (2.4 g, 40 mmol) in 10 mL of methanol, and the reaction was monitored by TLC. When the reaction was completed, the precipitate was collected by filtration and washed with cold ethanol. The filtrate was concentrated in vacuo to afford a yellow solid. The melting point of the compound was recorded. Yield = 8.85 g. Melting point =126 ° C.

2) Synthesis of N,N'-*bis*(2-hydroxybenzyl)ethylenediamine

Sodium borohydride (5.52 g, 145.86 mmol) was added in portions to a solution of salen (8.62 g, 36.46 mmol) in MeOH (10 mL). The mixture was poured into 100 mL of water and extracted with ethyl acetate. The combined organic layers were dried, and the solvents were removed in u to offer N,N'-*bis*(2-hydroxybenzyl)ethylenediamine as a white solid. The melting point of the compound was recorded. Melting point = 118°**C** Yield = 5.2 g.

3) Synthesis of N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylethane-1,2-diamine

To a solution of N,N'-*bis*(2-hydroxybenzyl)ethylenediamine (2.5 g, 9.1875 mmol) in acetonitrile (50 mL) and acetic acid (21 mL) was added formaldehyde (7.56 mL, 95.5625 mmol, 37% aqueous solution), and the mixture was stirred for 20 min. Sodium borohydride (3.43 g, 91.78 mmol) was added, and the reaction mixture was stirred at room temperature for 12 h. Acetonitrile was removed in vacuo, and the residue was dispersed in 2 N aq. NaOH. The aqueous phase was extracted with dichloromethane; the organic layer was dried, and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, hexanes/ethyl acetate) to offer N,N-dimethyltetrahydrosalen as a white solid. The melting point of the compound was recorded. Melting point = ° Yield = 1.5g.

4) Synthesis of N,N'-propylene*bis*(salicylimine)

To a stirred solution of salicylaldehyde (9.77g ,80 mmol) in 10 mL of methanol was slowly added a solution of propylenediamine (2.97g,40 mmol) in 10 mL of methanol, and the reaction was monitored by TLC. When the reaction was completed, the precipitate was collected by filtration and washed with cold ethanol. The filtrate was concentrated in vacuum to afford a yellow solid. The melting point of the compound was recorded. Melting point =52°C Yield = 9.27g.

5) Synthesis of N,N'-*bis*(2-hydroxybenzyl)propylenediamine

Sodium borohydride (4.61g, 121.83 mmol) was added in portions to a solution of N,N'-propylene*bis*(salicylimine) (8.6 g, 30.45 mmol) in MeOH (10 mL). The mixture was poured into 100 mL of water and extracted with ethyl acetate. The combined organic layers were dried, and the solvents were removed in vacuum to offer N,N'-*bis*(2-hydroxybenzyl)propylenediamine as a white solid. The melting point of the compound was recorded. Melting point = ° Yield = 4.8g.

6) Synthesis of N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylpropane-1,3-diamine.

To a solution of N,N'-*bis*(2-hydroxybenzyl)propylenediamine(2.5 g, 8.7 mmol) in acetonitrile (50 mL) and acetic acid (18 mL) was added formaldehyde (7 mL, 91 mmol, 37% aqueous solution), and the mixture was stirred for 20 min. Sodium borohydride (3.303g, 87.32 mmol) was added, and the reaction mixture was stirred at room temperature for 12 h. Acetonitrile was removed in vacuo, and the residue was dispersed in 2 N aq. NaOH. The aqueous phase was extracted with dichloromethane; the organic layer was dried, and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, hexanes/ethyl acetate) to offer N,N-dimethyltetrahydrosalen as a white solid. Yield = 1.12 g.

7) Synthesis of Manganese perchlorate

15 mL Perchloric acid was added dropwise to 10g of Mn_2CO_3 with continuous stirring. Mixture was concentrated on a water bath and filtered to obtain light pink coloured crystals.

8) Metal complexation of N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylethane-1,2-diamine

A solution of Manganese perchlorate (301 mg, 0.833 mmol) in acetonitrile (5 mL) was added dropwise to acetonitrile solution (5 mL) of N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylethane-1,2-diamine (250 mg, 0.833 mmol) with constant stirring. The resulting reaction mixture was stirred overnight in inert conditions at room temperature and the colour was turned to dark green. To this solution, 10 mL diethyl ether was added to obtain solid. It was then isolated by filtration, washed with diethyl ether and air dried. Further, recrystallized from acetonitrile to afford a crystalline solid.

9) Metal complexation of N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylpropane-1,3-diamine

A solution of Manganese perchlorate (290 mg, 0.78 mmol) in acetonitrile (5 mL) was added dropwise to acetonitrile solution (5 mL) of N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylpropane-1,3-diamine (250 mg, 0.78 mmol) with constant stirring. The resulting reaction mixture was stirred overnight in inert conditions at room temperature and the colour was turned to dark green. To this solution, 10 mL diethyl ether was added to obtain solid. It was then isolated by filtration, washed with diethyl ether and air dried. Further, recrystallized from acetonitrile to afford a crystalline solid.

CONCLUSION

CONCLUSION

In summary, we have synthesized a novel ligand N,N'-bis(2'-hydroxy-5'-substituted-benzyl)-N,N´dimethylpropane-1,3-diamine, synthesis of which has not been reported yet. The IR Data of the compound is reported and further characterization is yet to be carried out. Additionally, we have also synthesized the ligand previously reported, N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylpropane-1,3-diamine. Furthermore, we have synthesized Manganese complexes of these two ligands namely, N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylethane-1,2-diamine and N,N'-bis(2'-hydroxybenzyl)-N,N´dimethylpropane-1,3-diamine, which have not been previously reported. These Coordinate compounds can be studied as catalysts for variety of organic transformation.

FUTURE SCOPE

SCOPE FOR FUTURE

The applications of such complexes as catalysts are very well studied, and undoubtedly new catalytic processes will continue to emerge. Bearing in mind the scope that exists for changing the metal-centre and the detailed ligand structure, it is perhaps not surprising that such versatility exists in the catalytic processes available. Potentially such complexes could emerge as unique important group of catalysts in technological as well as scientific terms. Such species, if also capable of re-use or continuous operation, would in turn further improve the importance of this group of catalysts, and offer a more cost-effective use of these species in a larger number of circumstances. It seems that this area of catalysis will remain a fertile one for scientific research and development for some time to come.

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