

**ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUTE STUDIES
DEPARTMENT OF CHEMISTRY**

Graduate Project

Chem. 774



**METAL COMPLEXES OF A PENTADENTATE
LIGAND STRUCTURAL INVESTIGATION**

BY

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July 2010

**METAL COMPLEXES OF A PENTADENTATE LIGAND
STRUCTURAL INVESTIGATION**

A Graduate project Submitted to the school of Graduate Studies of Addis Ababa University in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry

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Fe (III) COMPLEXES OF A PENTADENTATE LIGAND
STRUCTURAL INVESTIGATION

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Acknowledgement

I am grateful to my advisor prof.V.J.T.Raju for his endless help in correcting, editing, critical assessment and his endless constructive comments and encouragement. I also like to appreciate his patience in following up this work from the very beginning to the end. I pay special respect to him, for his advice in all aspects for achieving today's success.

I also appreciate Dr.Yonas Chebude for his helpful suggestions and encouragement and for his patience in running spectroscopic experiments. I am also thanks to Dr.Ignacio V. Garcia for his encouragements and inexhaustible patience in running spectroscopic experiments.

I also thank my friends for sharing the finer points of science, discussion and their practical efforts and contributions to the preparation of Schiff base complexes.

I would also thank Addis Ababa University, chemistry department for providing materials and chemicals necessary to accomplish my study.

I am grateful to the Amhara Education Bureau and Debre Markos preparatory school for their generous financial support.

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List of Abbreviations

DHIO	1, 3-dihydrazone-indene-2-one
BNSDHIO	Bis-(N-Salicylaldehyde)- 1,3-dihydrazone-indene-2-one
Salen	Salicylic aldehyde ethylenediamine
TLC	Thin Layer Chromatography
B.M	Bohr Magneton
EDTA	Ethylenediamine tetraceticacid
Fe-L ^D	Iron ligand complex prepared by direct method
Fe-L ^T	Iron ligand complex prepared by template method
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxamide
UV-Vis	Ultraviolet-visible region
AAS	Atomic absorption spectroscopy
μS	micro Siemens
μ _{eff}	Effective magnetic moment
LMCT	Ligand metal charge transition

ABSTRACT

Two new Fe (III) complexes of two different geometries were synthesized from a pentadentate ONONO donor ligand. The Schiff base ligand, BNSHIO, Bis-(N-Salicylaldehyde)-1,3-inden-2-one was prepared and analyzed from our laboratory [7, 9, 10]. Ninhydrin, hydrazine hydrate, and salicylaldehyde were the precursors used in ligand synthesis. This ligand, by direct condensation with Fe(III) resulted in the formation of a new high spin complex, $\text{Fe(III)L}^{\text{D}}$. Another new $\text{Fe(III)L}^{\text{T}}$ was synthesized by template method using the same precursors. Initially 1,3-Dihydrazono-inden-2-one (DHIO) was prepared by condensing ninhydrin with hydrazine hydrate, which was treated with Fe(III) and salicylaldehyde and refluxed. This resulted in a low spin complex, $\text{Fe (III)L}^{\text{T}}$. The ligand to metal ratio was found to be 1:1 in both complexes. $\text{Fe (III)L}^{\text{T}}$ was found to be a cationic complex and $\text{Fe(III)L}^{\text{D}}$ was found to be a neutral complex. Based on the analytical, conductance, spectral, magnetic susceptibility, AAS, and UV-Vis, data, $\text{Fe (III)L}^{\text{D}}$ was proposed to have an octahedral geometry and $\text{Fe(III)L}^{\text{T}}$ was proposed a trigonal bipyramidal geometry. In both complexes, the ligand behaves as a pentadentate ONONO donor.

Key words: Schiff bases, Ninhydrin, hydrazine hydrate, Salicylaldehyde, pentadentate ONONO donor, Bis-(N-salicylaldehyde)-1,3-dihydrazono-inden-2-one (BNSDHIO), 1,3-dihydrazono-inden-2-one (DHIO)

Declaration

I the undersigned confirm that this project is my original work and has not been presented for a degree in any other university, and that all sources of material used for the project work have been duly acknowledged.

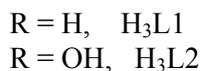
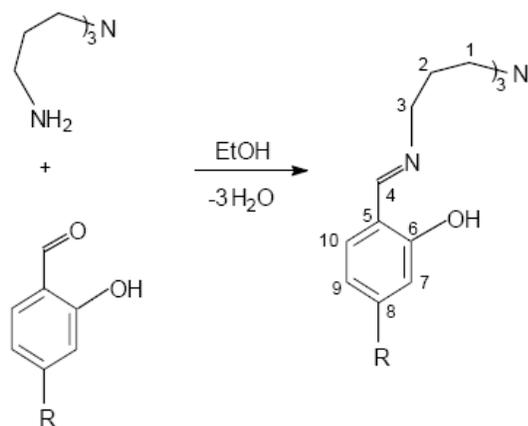
Name : Abebe Asratie Nigussie

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This project work has been submitted for examination with my approval as a university advisor.

Advisor: _____

Signature _____



Scheme.2. The procedure of heptadentate ligand synthesis

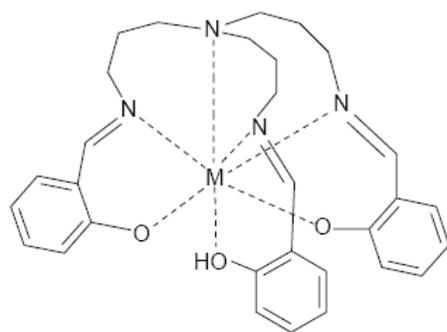
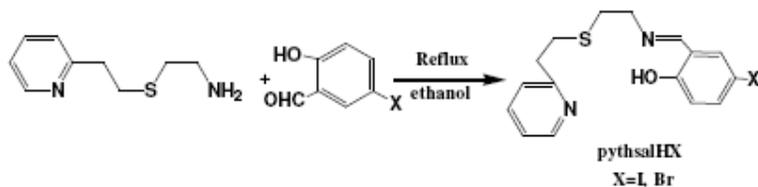
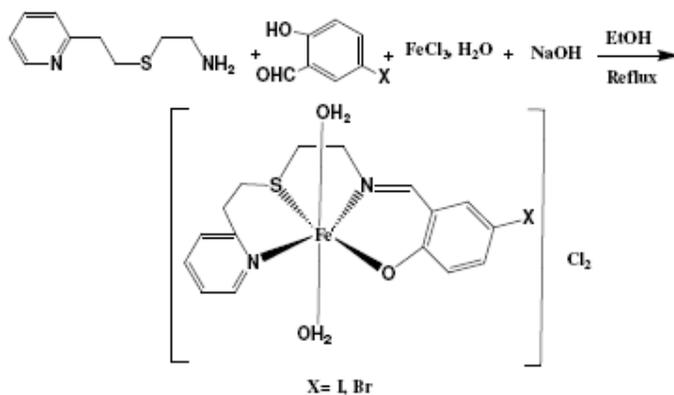


Figure.1. The chemical structure for the complexes.

Reports on four tetradentate monoanionic ligands pythsalHX (X = I, Br) all having an NSNO donor atom set synthesized by the 1:1 condensation reaction 1-(2-pyridyl)-3-thia-5-aminopentane with respective salicylaldehyde derivative in purified ethanol (Scheme 3) are known to behave as antitumour agents. Iron complex of these ligands are reported as shown in Scheme 3 and 4 (31).



Scheme 3. Schematic representation of Schiff base ligands formation.

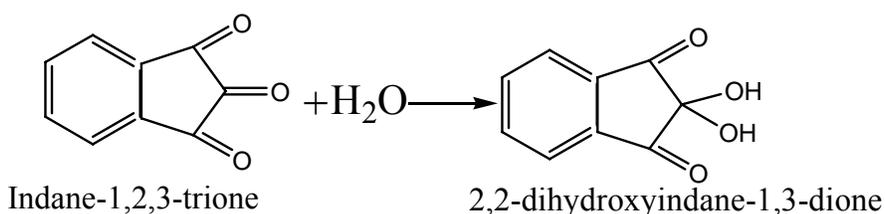


Scheme 4. Schematic representation of iron (III) Schiff base complexes formation.

A number of nitrogen, sulfur and oxygen donor derivatives of Schiff bases have long been used in analytical, industrial and medical applications. Schiff bases compounds are interesting ligand system because they are good chelates for metal anions and neutral molecules. The metal-ion and the chemistry of Schiff bases compounds are very useful in fundamental studies. In a previous study, the synthesis and characterization of Schiff base complexes of Fe(III), Ni(II), Zn(II), Cu(II) and Co(II) derived from ninhydrin, hydrazine and salicylaldehyde was reported from our laboratory [7,8,9,10]

1.2. The chemistry of ninhydrin (2,2-Dihydroxyindane-1,3-dione)[9,11,12]

Ninhydrin was first prepared in 1910 by the English chemist, Siegfried Ruhemann, who also investigated the formation of the violet compound (Ruhemann's Purple, or RP), produced by reaction of ninhydrin with amino acids.

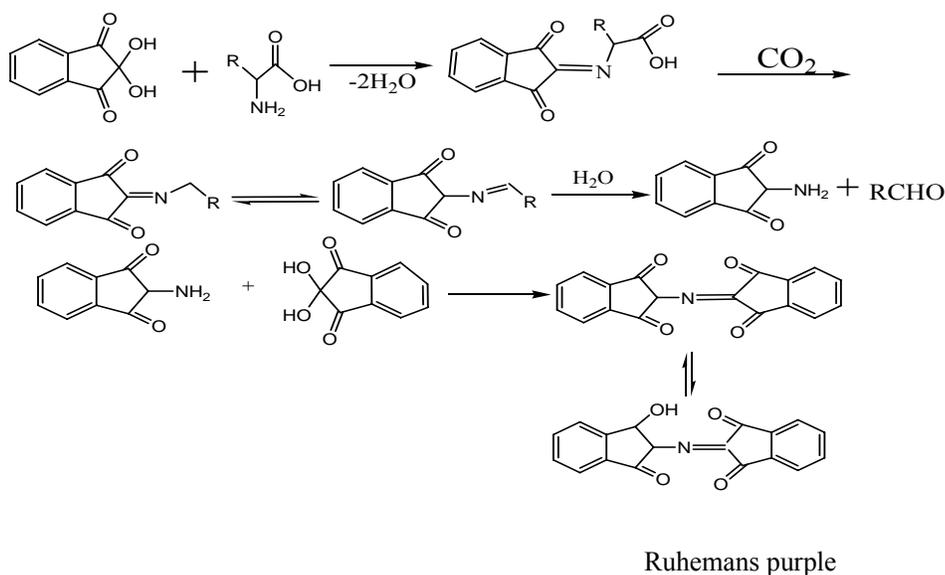


Scheme 5. Conversion of 1, 2, 3-indantrione to ninhydrin (2,2-dihydroxy-1,3-indanedione).

To generate the ninhydrin chromophore, the amine is condensed with a molecule of ninhydrin to give a Schiff base. Thus only ammonia and primary amines can proceed past this step. The reaction of ninhydrin with secondary amines gives an iminium salt, which is generally yellow-orange in color. The high sensitivity of the ninhydrin reaction can be fully understood in ethanol. Ethanol also largely obviates any interference likely to be caused by the pH of the

solution to be analyzed, except in extreme cases. Solutions containing the amino acid to be determined may vary from pH 4.5 to 8. When ammonia or amines are present, care should be taken to neutralize them completely.

The chemistry of the reaction between ninhydrin and amino acids has been extensively studied by several workers. Ninhydrin reacts with amino acids to form a Schiff base and the resultant Schiff base on decarboxylation followed by hydrolysis results in an amine. This amine further condenses with ninhydrin to form Ruhemans purple [34].



Scheme 6. The reaction of ninhydrin with α -amino acids

The Schiff base formed from ninhydrin and amino acids can have metal binding sites as shown in the figure below [9,11].

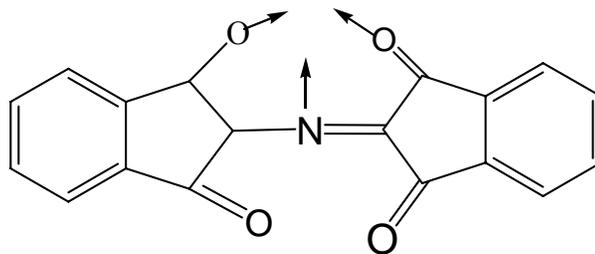


Fig 2. Possible metal binding centers of a Schiff base derived from ninhydrin and amino acid.

In Co (II), Ni (II), and Zn (II) complexes of a Schiff base derived from ninhydrin and glycine (indae-1,3-dione-2-imine-N-acetate, IDLA) are reported[9,11], to exhibit tridenticity with the ligand behaving as an ONO donor.

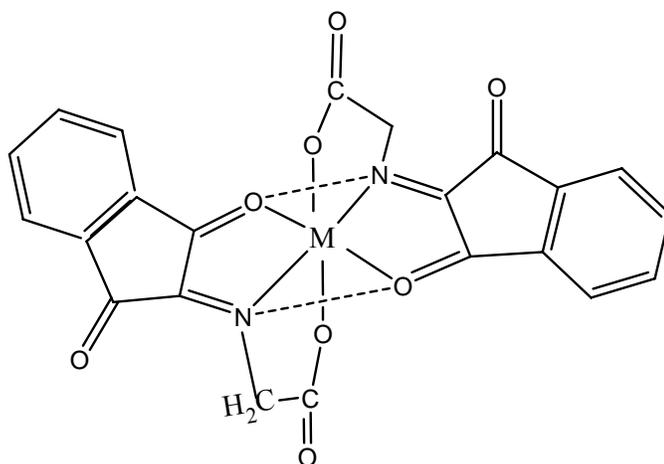
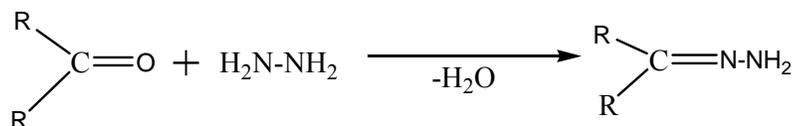


Fig 3. Metal complexes of IDLA, M = Co (II), Ni (II), and Zn (II)

1.3. Hydrazones [13, 14]

Hydrazine is a chemical compound with the formula N_2H_4 . It is a colorless liquid with an ammonia-like odor. Hydrazine can arise via coupling a pair of ammonia molecules by the removal of one hydrogen per molecule. Each H_2N-NH_2 subunit is pyramidal in shape.

When aryl ketone is heated with hydrazine hydrate and a base, usually NaOH or KOH, hydrazone is produced. A hydrazone has the structure $R_1R_2C=NNH_2$ [8].



Scheme 7. Preparation of hydrazone from hydrazine and carbonyl

Being bifunctional, with two amines, hydrazine is a key building block for the preparation of many heterocyclic compounds via condensation with a range of difunctional electrophiles. Hydrazines are part of many organic syntheses, often those of practical significance in pharmaceuticals, such as the antituberculosis medication Isoniazid and the antifungal fluconazole, as well as in textile dyes and in photography.

Hydrazones have been demonstrated to possess, among other, antimicrobial, anticonvulsant, analgesic, anti-inflammatory, antiplatelet, antitubercular and antitumoral activities. For example, isonicotinoyl hydrazones are antitubercular; 4-hydroxybenzoic acid[(5-nitro-2-furyl)methylene]-hydrazide (nifuroxazide) is an intestinal antiseptic; 4-fluorobenzoic acid[(5-nitro-2-furyl)methylene]-hydrazide&2,3,4-pentanetrione-3-[4-[[[(5-nitro-2-furyl)methylene]hydrazino]carbonyl]phenyl]-hydrazone which have antibacterial activity against both *Staphylococcus aureus* ATCC 29213 and *Mycobacterium tuberculosis* H37Rv. Hydrazones

have been demonstrated to possess, among other, antimicrobial, anticonvulsant, analgesic, anti-inflammatory antiplatelet, antitubercular antitumoral activities.

Forexample, isonicotinoylhydrazonesareantitubercular;4-hydroxybenzoic-acid[(5-nitro-2-furyl)methylene]-hydrazide (nifuroxazide) is an intestinal antiseptic; 4-fluorobenzoic acid[(5-nitro-2-furthylene)-hydrazide and 2,3,4-pentanetrione-3-[4-[(5-nitr furyl) methylene] hydrazino] carbonyl]phenyl]-hydrazone, which have antibacterial activity against both Staphylococcus aureus ATCC 29213 and Mycobacterium tuberculosis H37Rv.

N1-(4 Methoxybenzamido)benzoyl]-N2-[(5-nitro-2-furyl)methylene]hydrazine, which was also synthesized have antibacterial activity. Isonicotinic acid hydrazide (isoniazid, INH) has very high in vivo inhibitory activity towards M.tuberculosis H37Rv. Sah et al synthesized INH hydrazide-hydrazones by reacting INH with various aldehydes and ketones.

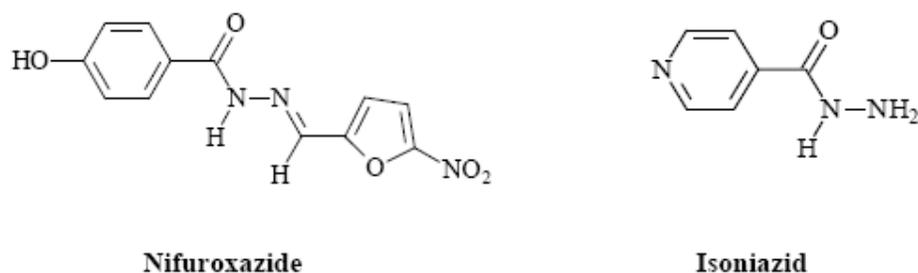
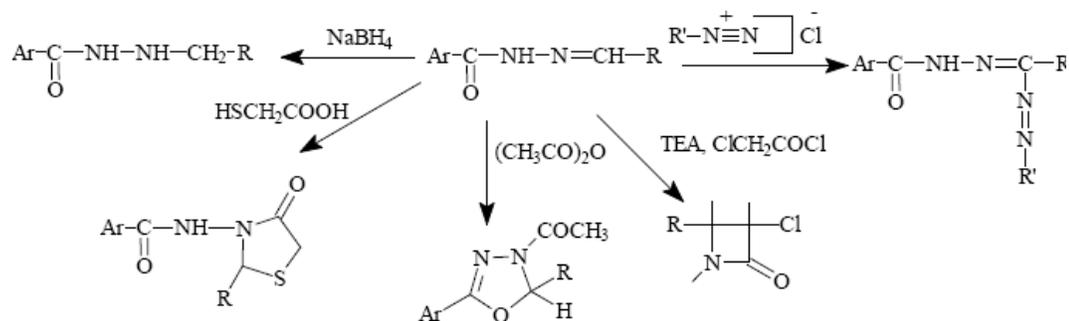


Fig.4. Structure of hydrazide-hydrazones compounds.

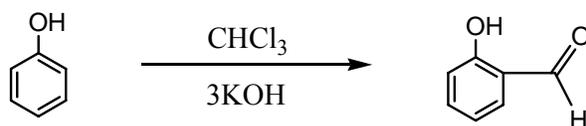
Hydrazones containing an azometine $-NHN=CH-$ proton are synthesized by heating the appropriate substituted hydrazines/hydrazides with aldehydes and ketones in solvents like ethanol, methanol, tetrahydrofuran, butanol, glacial acetic acid, ethanol-glacial acetic acid. Another synthetic route for the synthesis of hydrazones is the coupling of aryldiazonium salts with active hydrogen compounds. Hydrazone-hydrazones compounds are not only intermediates but they are also very effective organic compounds in their own right. N-Alkylhydrazides can be synthesized by reduction of hydrazones with $NaBH_4$, substituted 1,3,4-oxadiazolines can be synthesized when hydrazones are heated in the presence of acetic anhydride. 2-Azetidinones can be synthesized when hydrazones react with triethylamine chloro acetylchloride. 4-Thiazolidinones are synthesized when hydrazones react with thioglycolic acid/thiolactic acid.



Scheme.8. Reaction of hydrazone

1.4. The chemistry of Salicylaldehyde [1,3,15,16]

Salicylaldehyde is a key precursor to a variety of chelating agents. It can be prepared from phenol and chloroform by heating with sodium hydroxide or potassium hydroxide.



Scheme 9. Preparation of Salicylaldehyde

Schiff bases derived from the Salicylaldehydes are well known as Polydentate ligands coordinating in neutral forms. The interaction of these donors' ligands and metal ions give complexes of different geometries and these complexes are potentially biologically active.

When two equivalents of salicylaldehyde are combined with a diamine, a particular chelating Schiff base is produced. The so-called Salen ligands, with four coordinating sites and two axial sites open to ancillary ligands, are very much like porphyrins, but more easily prepared. Although the term Salen was used originally only to describe the tetradentate Schiff bases derived from ethylenediamine, the more general term Salen-type is used in the literature to describe the class of [O,N,N,O] tetradentate bis-Schiff base ligands (fig.5). Basic guidelines for the design, synthesis and application of metal Schiff base complexes in catalysis will thus be surveyed with the emphasis on the relevant problems in producing active and useful complexes [1].

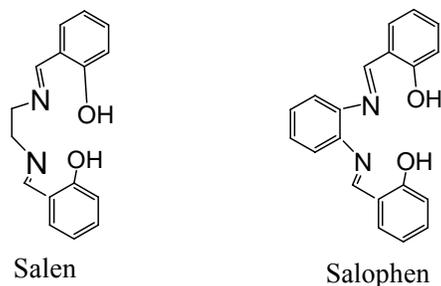


Fig.5. Different salen ligands

SalenH₂ forms complexes with most transition metals. In many cases, the metal adopts square pyramidal or octahedral coordination sphere with stoichiometry M(salen)L and M(salen)L₂. Illustrative examples include VO(salen) and Co(salen)Cl(pyridine). With d⁸ metal ions, low-spin square planar complexes form, such as Ni(salen) was reported [1,15,16].

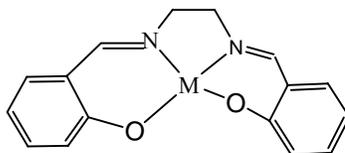


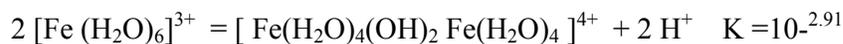
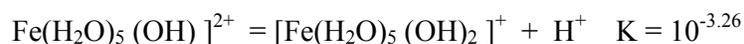
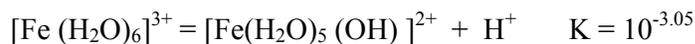
Fig.6. A square planar M(salen) complex

Salicylaldehyde is a common highly-functionalized arene that has often been exploited as a precursor to still other chemicals

1.5. The chemistry of Fe (III)

The chemistry of Fe (III) is well researched and among many commercial available starting materials are the chlorides, perchlorate, sulfate and nitrate. Most of the chemistry of iron involves Fe(II) or Fe(III) compounds with Fe(IV) and Fe(VI) known in small number of compounds. Lower formal oxidation states occur with π -acceptor ligands. One of the most conspicuous features of ferric ion in aqueous solution is its tendency to hydrolyze and/or to form complexes [14,17,18,19,20]

The Fe (III) ion is strongly acidic:



Ferric ion in aqueous solution is rather readily reduced by many reducing agents, such as I⁻. Ferric ions [Fe(III)] forms a large number of complexes, mostly octahedral ones, and the octahedron may be considered its characteristics coordination polyhedron. Fe (III) does also form a few tetrahedral complexes with halide ions and SCN⁻ ions. The complexes with SCN⁻

ions are intense red and used as a sensitive qualitative and quantitative test for ferric ion; $\text{Fe}(\text{SCN})_3$ and/or $\text{Fe}(\text{SCN})_4^-$. The affinity of Fe (III) for amine ligands is very low. No simple amine complex exists in aqueous solution. Addition of aqueous NH_3 only precipitates the hydrous oxide. Chelating amines, forexample, EDTA do form some definite complexes among which is the seven-coordinate $\text{Fe}(\text{EDTA})\text{H}_2\text{O}^-$ ion. The $\text{Fe}(\text{EDTA})\text{H}_2\text{O}^-$ dimerizes and the dinuclear species $\text{Fe}(\text{EDTA})_2\text{O}^{4-}$ is formed. Fe (III) ion has its greatest affinity for ligands that coordinate by oxygen viz phosphate ions, polyols such as glycerol, sugars etc, with β -diketones the neutral $[\text{Fe}(\text{dike})_3]$ complexes are formed. Formation of complexes with β -diketones is the cause of the intense color that develops when they are added to solutions of ferric ion and serves test for them [21]. For example, the red complex $[\text{Fe}(\text{acac})_3]$, can be extracted from an aqueous solution of Fe(III)ion and acetylaceton(e) forms an octahedral complex [14]

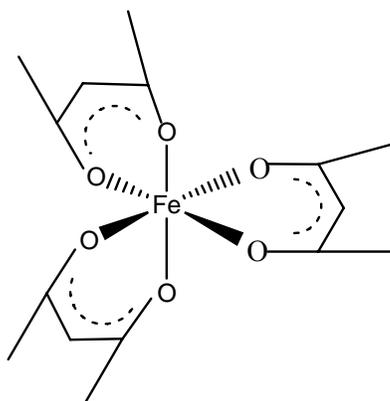
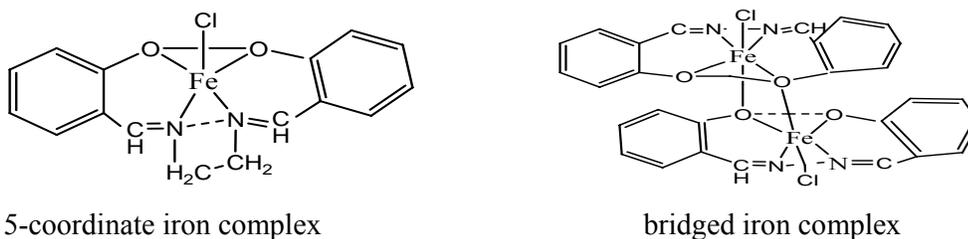


Fig 7. The structure of $\text{Fe}(\text{acac})_3$ octahedral complex

$\text{Fe}(\text{salen})\text{Cl}$ has the interesting property of forming two differently structured crystals depending on the solvent from which it is crystallized. One contains five-coordinate monomer with magnetic moment close to 5.9 BM, while the other contains the bridged binuclear species and exhibits marked anti ferromagnetic coupling between the iron atoms [21].



5-coordinate iron complex

bridged iron complex

Fig.8. Structure of 5-coordinate and bridged iron complexe

1.6. Literature review

Metal complexes of Schiff base ligands derived from ninhydrin and some amino acids were synthesized and characterized [8,18,23]. The coordination chemistry of Schiff bases derived from amino acids has received much attention and interest. Ninhydrin and its related compounds are very useful reagents for the spectrophotometric determination of amino acids, peptides, proteins, primary amines and ammonia, particularly in biological systems. The work reported in this paper describes the synthesis as well as the elucidation of the chemistry and structures of a new series of Fe(III) complexes of Schiff bases derived from ninhydrin with glycine, α -alanine and serine.

The analyses of the chelates show their formulae to be $MLX_2 \cdot nH_2O$ of the ternary 1: 1: 1 M: ninhydrin : amino acid stoichiometry where $M = Fe(III)$, $X = Cl$ for Fe(III). L stands for the anion of the formed ninhydrin-amino acid Schiff base ligands. The NH_2 group of the amino acids has taken part in the in situ condensation reaction, where the proton is liberated during this process. This reaction takes place with the higher reactive $-CHO$ function of ninhydrin leading to formation of the corresponding Schiff bases (Fig. 9).

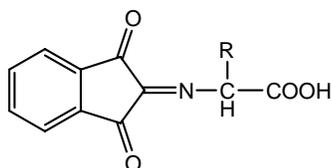


Fig.9. Structure of the Schiff base ligand

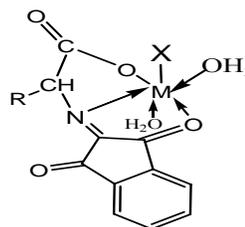


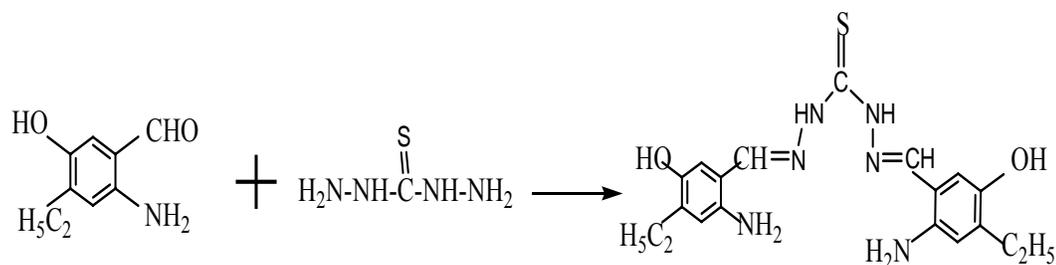
Fig.10. Structure of Metal Complex

Where, $R = H$ (gly), CH_3 (α -anal), CH_2OH (ser) and $M = Fe(III)$, $X = Cl$

M (III) complexes are presumably one coordinated chloro ligand, and one coordinated water molecule in the complex as shown in Fig.10.

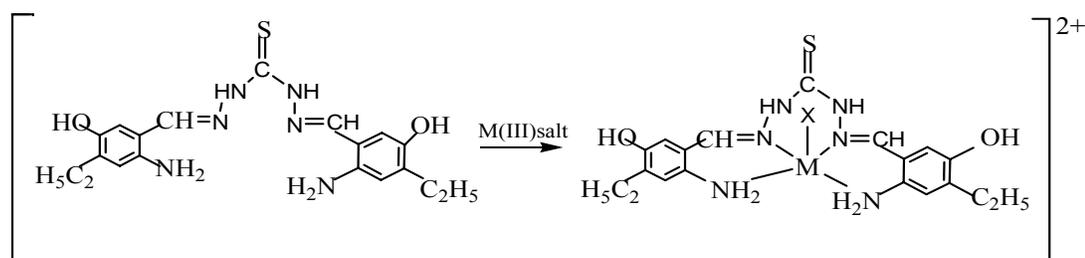
The field of Schiff base complexes is fast developing because of the wide variety of possible structures for the ligands, depending on the aldehyde and amine used [22]. Many Schiff bases and their complexes have been widely studied because of their industrial and biological applications. Some Schiff bases were tested for fungicidal activity, which is related to their chemical structure. The cross-linking agents can also be derived from metal complexes with O, N or S ligands. For example, an intracoordination salt such as salicylates or anthranilates and aliphatic or aromatic amines can form strong five- or six membered chelate rings which are able to produce metal containing cross-linking agents with the required properties. Recently, M(III) complexes of Cr, Mn and Fe with a Schiff base derived from 2-amino-4-ethyl-5-hydroxybenzaldehyde and thiocarbohydrazide were reported. The ligand HL and its $M(III)O$

complexes have antibacterial and antifungal activity against the bacteria: *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Bacillus megaterium*, and the fungi: *Kluyveromyces fragilis*, *Rhodotorula rubra*, *Candida albicans*



Scheme 10. Synthesis of Schiff base ligand from 2-amino-4-ethyl-5-hydroxybenzaldehyde and thiocarbohydrazide.

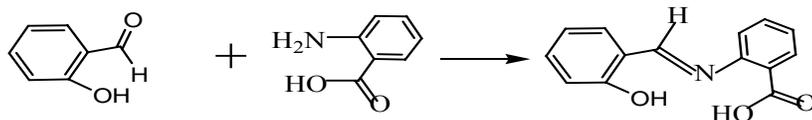
The complexes were prepared by mixing the Schiff base in ethanol and trivalent chromium, manganese or iron chlorides salts and refluxed (Scheme.2).



Scheme11. Synthesis of M(III) Schiff base complexes

Salicylaldehyde and anthranilic acid compounds are capable to form chelates with transition metal ions in the form of Schiff bases [16]. Co (II) and Fe (III) chelates of Schiff base derived from Isatin with some amino acids also synthesized and identified on the basis of their chemical analysis using infrared and electronic spectra. The Schiff base from salicylaldehyde and anthranilic acid was prepared by adding salicylaldehyde ethanolic solution to ethanolic solution of anthranilic acid.

The condensation of salicylaldehyde and anthranilic acid in ethanol yields one product as shown:



Salicylaldehyde

Anthranilic acid

Schiff base

Scheme 12. Synthesis of Schiff base derived from Salicylaldehyde and Anthranilic acid.

M (III) Chelate was Prepared by mixing the Schiff base in ethanol and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in the same amount of the same solvent and refluxed. The formation of the chelates in the ratio of 1:1[M:

L]. The stoichiometric ration of the chelates predicted the formula of the type $[ML(OH(H_2O)_2)] \cdot nH_2O$.

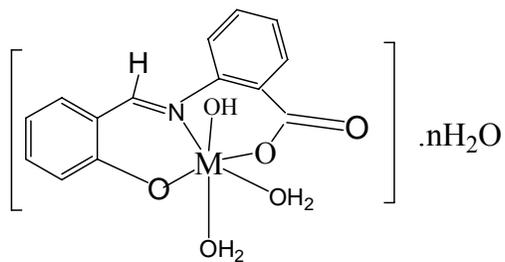


Fig.11. structure of the M(III) complexes

Where M represents Fe(III) ions [n=2] and Os(III) ions [n=1] chelates

1.7. The objective of the present study

The aim of this work is to synthesize and characterize two new Fe(III) complexes from Schiff base derived from the precursors, ninhydrin, hydrazine hydrate and salicylaldehyde. Two methods have been proposed for synthesis, which include direct and template procedures. For the direct method, reported procedure of ligand synthesis (7,9,10) will be followed. Then the ligand will be reacted with Fe(III) to obtain the metal complex Fe-L^D. In template synthesis, DHIO (1,3-dihydrazono-inden-2-one) and Fe(III) ion will be reacted initially and then the resultant product in solution will be treated with salicylaldehyde. The prepared complexes will be characterized by elemental analysis, molar conductance, magnetic susceptibility, UV-Vis and AAS studies. Characterization studies of the ligands DHIO (1,3-dihydrazono-inden-2-one) and BNSDHIO (Bis-(N-Salicylaldehyde)-1,3-dihydrazono-inden-2-one) will be repeated and the data obtained will be compared with the reported data.

2. Materials and Methods

2.1. Materials

Ninhydrin, Hydrazine Hydrate, Salicylaldehyde, Ethanol, Methanol, and Methanolic Ammonia solution, Metal salt (Anhydrous FeCl_3), NaOH methanolic solution, AgNO_3 solution, Concentrated HNO_3 , Ammonium thiocyanate solution, DMF, DMSO, CH_3CN , CHCl_3

2.2. Instruments

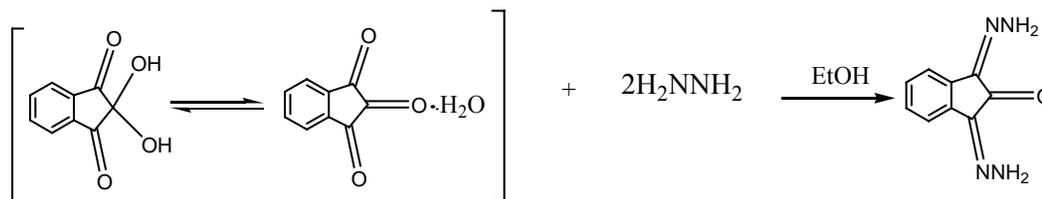
Melting point was determined using electro thermal IA 92000 digital apparatus; UV-Vis spectra were recorded on GENESYS 2PC spectroscopy; magnetic susceptibility were measured on MSB-AUTO Sherwood balance; C, H and N analysis was carried out with Flash EA-1112 elemental analyzer; conductance were measured on EC-214 conductometry apparatus; metal ion estimation was done on Atomic absorption using BUCK MODEL SCIENTIFIC 210 VGB flame spectrophotometer.

2.3. Experimental Method

2.3.1. Synthesis of 1,3-dihydrazono-inden-2-one (DHIO) [7,10]

The preparation was carried out according to a previously reported method. 2.0 g (16.85 mmol) of hydrated ninhydrin was weighed and dissolved in 100 ml of hot ethanol into a round bottom flask. The solution was allowed to cool to room temperature. A freshly prepared hydrazine hydrate solution (containing 3.8 ml) was added slowly by micropipette while stirring continuously with magnetic stirrer for two hours. 100 ml of distilled water was then added to the contents and allowed to stand for 24 hours. The brown yellow compound formed was then filtered by suction, and washed repeatedly with cold ethanol. The solid is preserved and dried in dessiccator. The purity was confirmed by the TLC technique. Yield: 61.54%.

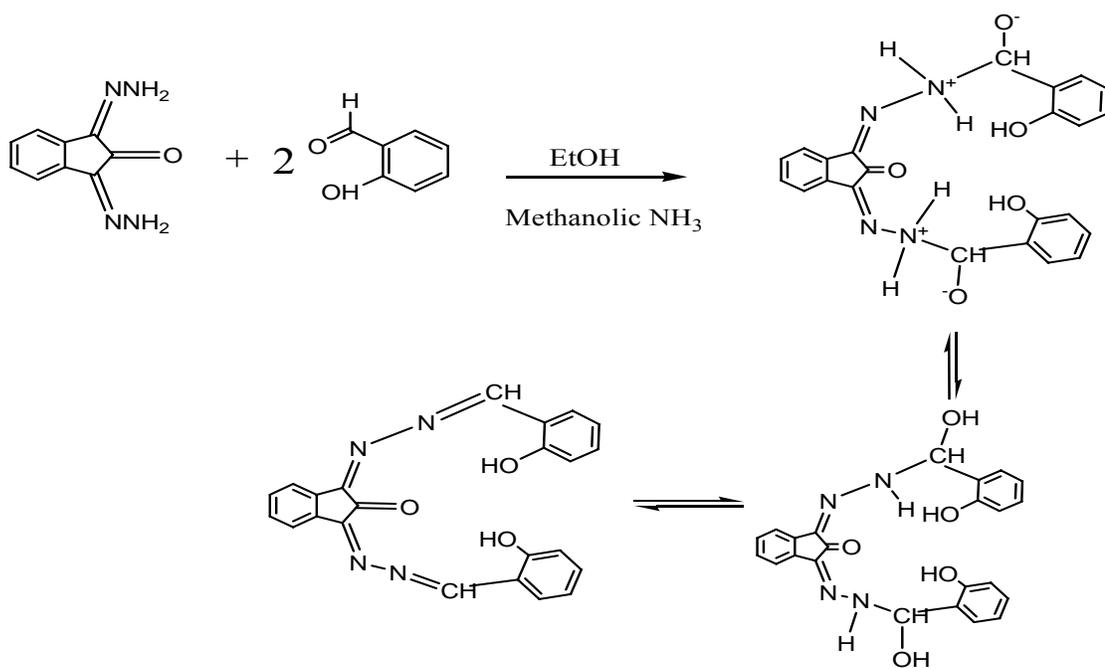
Possible reaction:



Scheme.13. Synthesis of 1,3-dihydrazono-inden-2-one

2.3.2. Synthesis of Bis-(N-Salicylaldehyde)- 1,3-dihydrazone-inden-2-one, (BNSDHIO)

The preparation was carried out according to a previously reported method [7,10]. A 0.5 g (2.66 m mol) DHIO was taken in a round bottom flask and dissolved in a 40 ml of hot ethanol and a clear solution was obtained. Then excess of Salicylaldehyde (0.7ml, 5.35 m mol) diluted with 5 ml of hot ethanol was added to DHIO, and the pH was adjusted to 6, with 5 % methanolic ammonia solution. After that the solution was refluxed for about 8 hours. A brown compound separated. It was then filtered by suction and washed repeatedly with cold ethanol and preserved and dried in desiccator. The purity was confirmed by the TLC technique. Yield: 56.0%.

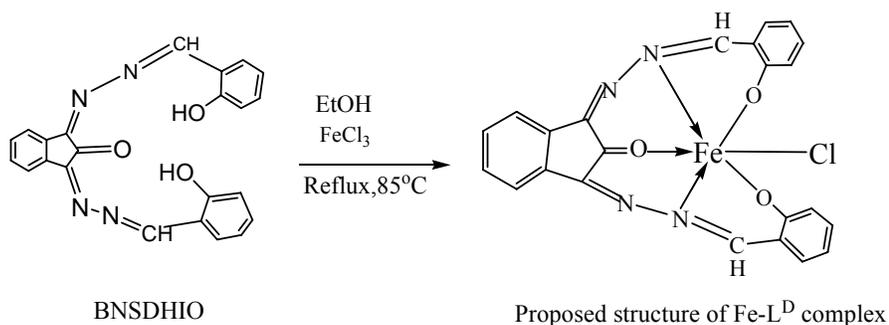


Scheme14. Synthesis of BNSDHIO

2.3.3. Synthesis of Metal Complexes

i) By direct method:

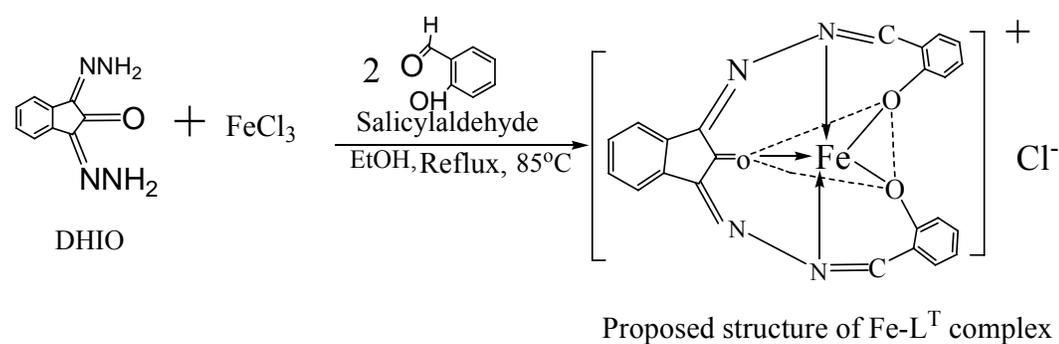
An ethanolic solution ferric chloride, FeCl_3 (0.055 g, 0.337 mmol) was prepared in a round bottom flask. To this solution an ethanolic solution of the ligand (BNSDHIO) (0.2g, 0.505 mmol) was added. The pH was adjusted to 6, by adding a 5 % methanolic ammonia solution in a dropwise manner.. Then reaction mixture was refluxed on water bath for about 12 hours. A dark brown complex separated. It was filtered off and washed with cold ethanol and dried, preserved in dessiccator. The purity of the complex was checked by TLC technique. Yield: 32%.



Scheme.15. Synthesis of Fe-L^{D} complex

ii) By template method

A 0.2 g, 0.505 mmol of DHIO was taken in a round bottom flask and dissolved in 80 ml of hot Ethanol. 0.055g (0.337 mmol) of an Ethanolic solution anhydrous ferric chloride (FeCl_3) was added. The reaction mixture was refluxed for 30 min in a water bath. Then a 0.3 ml of Salicylaldehyde solution in 5 ml of hot Ethanol was added to the reaction mixture. The pH was adjusted to 6, with NaOH solution. Then the reaction mixture was refluxed for about 18 hours. The obtained dark brown compound was filtered off and washed with cold Ethanol and dried, preserved in dessiccator. The purity of the complex was checked by TLC technique. Yield: 80%



Scheme.16. Synthesis of Fe-L^{T} complex

3. Result and Discussion

3.1. Physical characteristics

The details of physical characterization of the ligand and metal complexes are tabulated in table 1.

Table 1. Physical characteristics of the ligands and the complexes

Compound	Yield (%)	Color	M.P(°C)	Physical Appearance	Solubility
DHIO	61.54	Yellow	214=215	Powder	Soluble: DMSO, DMF, THF, CHCl ₃ , hot EtOH, CH ₃ CN, hot MeOH
BNSDHIO	56	Brown	200-201	Powder	Soluble: DMSO, DMF, THF, CHCl ₃ , hot EtOH, CH ₃ CN, hot MeOH
Fe-L ^D	42	Dark Brown	> 350	Powder	Soluble: DMSO, DMF, CHCl ₃ , CH ₃ CN, THF
Fe-L ^T	80	Dark Brown	> 350	Powder	Soluble: DMSO, DMF, CHCl ₃ , CH ₃ CN, THF

3.2. Elemental analysis of DHIO and BNSDHIO:

The experimental and the calculated values of the elemental composition of C, H, and N of DHIO and BNSDHIO data is presented in table 2, which is concurrent with the reported literature data [7, 10].

Table 2. Elemental analysis data of DHIO and BNSDHIO

Compound	Calculated (%)			Found (%)		
	C	H	N	C	H	N
DHIO	57.45	4.25	29.78	57.62	4.32	31.25
BNSDHIO	69.69	4.40	14.40	65.80	4.30	13.71

3.3. Qualitative and quantitative chemical tests

3.3.1. Chloride tests [25,26]

0.01g of each the complex was digested separately in concentrated nitric acid. It was tested in 0.5 M solution of AgNO₃. White precipitate was observed, which indicates the presence of chloride in the complexes. The precipitate was filtered through dried and pre-weighed sintered crucible and washed with 0.1N HNO₃. Then the precipitate was dried in an oven at 110⁰C to constant weight. The percentage of chloride was found to be the same in both complexes. The value supports the presence of one chloride per metal ion in each complex. The amount of chloride ion in the complex is as follows:

Table 3. Percentage of Chloride in the complex

Complex	% of chloride	
	Experimental	calculated
Fe-L ^I	7.71	7.31
Fe-L ^D	7.00	7.31

3.3.2. Iron test [27,34]

This was performed by digesting the complexes with concentrated nitric acid and adding ammonium thiocyanate solution. It was observed that a reddish-brown precipitate of iron thiocyanate was formed which confirms the presence of iron in the sample [30].

3.3.3. Quantitative determination of metal content of the complexes by AAS

A 0.01 g of each metal complex was dissolved in 20 ml of conc.HNO₃ and digested. Then 100ml standard solution of de-ionized water has prepared and analyzed by AAS. The results are tabulated in table 4.

Table 4. AAS data for the Fe-L complexes

Metal complex	Percentage of metal in the complex		Metal to ligand ratio
	Calculated	Found	
Fe-L ^D	11.53	12.32	1:1
Fe-L ^I	11.53	13.14	1:1

From table 3 and table 4 the metal percentage along with chloride percentage reveal M : L:Cl ratio as 1 : 1: 1 in both complexes. The composition of both the complexes is FeLCl.

3.4. Molar Conductance Measurements

The molar conductance of iron complexes was measured in 10^{-3} M solution in DMF as solvents at room temperature (24°C). The complex Fe-L^D showed a lower molar conductivity values in the range 16.2-17.3 Scm² mol⁻¹, and therefore concluded to be a non-electrolyte. Whereas the Fe-L^T complex showed a molar conductivity value in the range 72.6-73.4 Scm² mol⁻¹ which indicates the complex is 1:1 electrolyte. This data suggests the position of chloride in coordination sphere in the Fe-L^D complex and the same in the ionization sphere in Fe-L^T complex. The results are tabulated in table 5.

Table.5. Conductivity data for the Fe-L complexes

Complex	Solvent	Molar conductance (Ohm ⁻¹ cm ² mol ⁻¹)	types of electrolyte
Fe-L ^D	DMF	16.2 – 17.3	Non electrolytes
Fe-L ^T	DMF	72.6 – 73.4	Electrolytes

This shows the presence of one chloride, counter ion, in the complex. That is conductance studies differentiate Fe-L^D and Fe-L^T complexes. Fe-L^D is a non-electrolyte, while Fe-L^T is a 1 : 1 electrolyte.

3.5. Magnetic Susceptibility Measurements [28]

The gram magnetic susceptibility values, the magnetic moment in BM are calculated and presented in table 6. From the obtained result, Fe-L^D is concluded to be a high spin complex and Fe-L^T as a low spin complex (7).

Table 6. magnetic susceptibility data for Fe-L complexes

Complex	χ_g (grams)	Magnetic moment(μ_{eff}),(BM)		Number of unpaired electrons
		Experimental	spin only	
Fe-L ^D	3.365×10^{-5}	6.21	5.92	5
Fe-L ^T	1.537×10^{-5}	4.19	3.87	3

3.6. Electronic Spectra [7,29,30]

The UV-Vis spectral data of the ligands and the complexes were recorded in acetonitrile in the wavelength range from 800 – 200 nm at room temperature. The electronic spectra data of the ligand BNSDHIO exhibit three bands centered at 283, 316, and 399 nm. The first and second bands were attributed to benzene $\pi \rightarrow \pi^*$ and imino $\pi \rightarrow \pi^*$ transition, respectively. The third intense band is attributed to the $n \rightarrow \pi^*$ transition of the thioxo group. The electronic Spectrum of Fe-L^D shows bands at 215, 305, and 356 nm and that of Fe-L^T shows bands at 213, 302, and 354nm, in which the bands of the complexes was shifted to a shorter wavelength along with an increase in its intensity. Bands in the visible region can be attributed to ligand to-metal charge transfer (LMCT) transitions O (2P) \rightarrow Fe (3d) or the ultraviolet bands in the regions of 210 - 300 nm and 300 - 350 nm is of ligand origin assignable to the intraligand transitions ($\pi \rightarrow \pi^*/n \rightarrow \pi^*$) localized predominantly on the phenyl rings and on C=N fragments of the N₂O₂-ligands, respectively [7,30,31]. However, the d-d transition in the spectrum could not be resolved. In general, the electronic transitions for iron (III) systems are spin forbidden and hence weak, and are often marked by charge transfer bands . The data is presented in table 7.

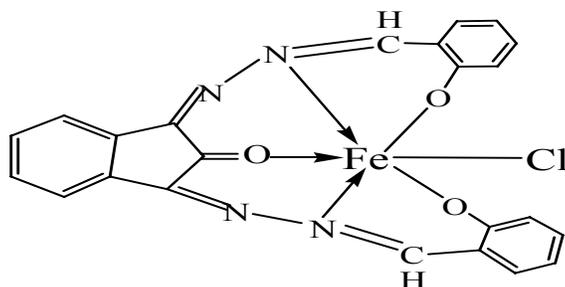
Table7. Electronic spectrum of BNSDHIO and Fe-L complexes

Compound	Absorption band ,nm(cm ⁻¹)	Transition
BNSDHIO	283 (35335.68)	$\pi \rightarrow \pi^*$
	316 (31645.56)	$\pi \rightarrow \pi^*$
	399 (25062.65)	$n \rightarrow \pi^*$
Fe-L ^D	215 (46511.62)	$\pi \rightarrow \pi^*$
	305 (32786.88)	$\pi \rightarrow \pi^*$
	356 (28089.88)	$n \rightarrow \pi^*$
Fe-LT	213 (46948.35)	$\pi \rightarrow \pi^*$
	304 (32894.73)	$\pi \rightarrow \pi^*$
	354 (28248.58)	$n \rightarrow \pi^*$

4. CONCLUSION

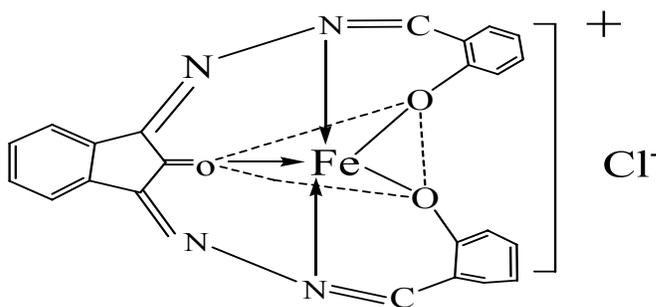
A pentadentate ONONO ligand BNSDHIO was synthesized by the 1:1 condensation reaction of the precursor DHIO with salicylaldehyde in purified ethanol. The Iron complexes were synthesized by direct and template methods. In direct method, BNSDHIO and Fe(III) ions were condensed. In template method, DHIO and Fe(III) ions first refluxed and then salicylaldehyde was added and further condensed, and various data were procured. Based on elemental analysis, magnetic susceptibility, conductivity, UV-Vis, AAS studies it is concluded that the ligand bonds to the metal ion through two azomethine nitrogen, carbonyl oxygen (-C=O), and two phenolic oxygen atoms.

The newly synthesized Fe-L^D complex is concluded to have an octahedral geometry with the sixth coordination site being fulfilled by Cl⁻ ion. For the Fe-L^T complex, a trigonal bipyramidal geometry was proposed based on magnetic data and conductance results. Based on these data the conclusions arrived at, the proposed structures are given in fig.12 and 13.



Proposed structure of Fe-L^D complex

Fig12. Octahedral Fe-L^D complex



Proposed structure of Fe-L^T complex

Fig13. Trigonal-bipyramidal Fe-L^T complex

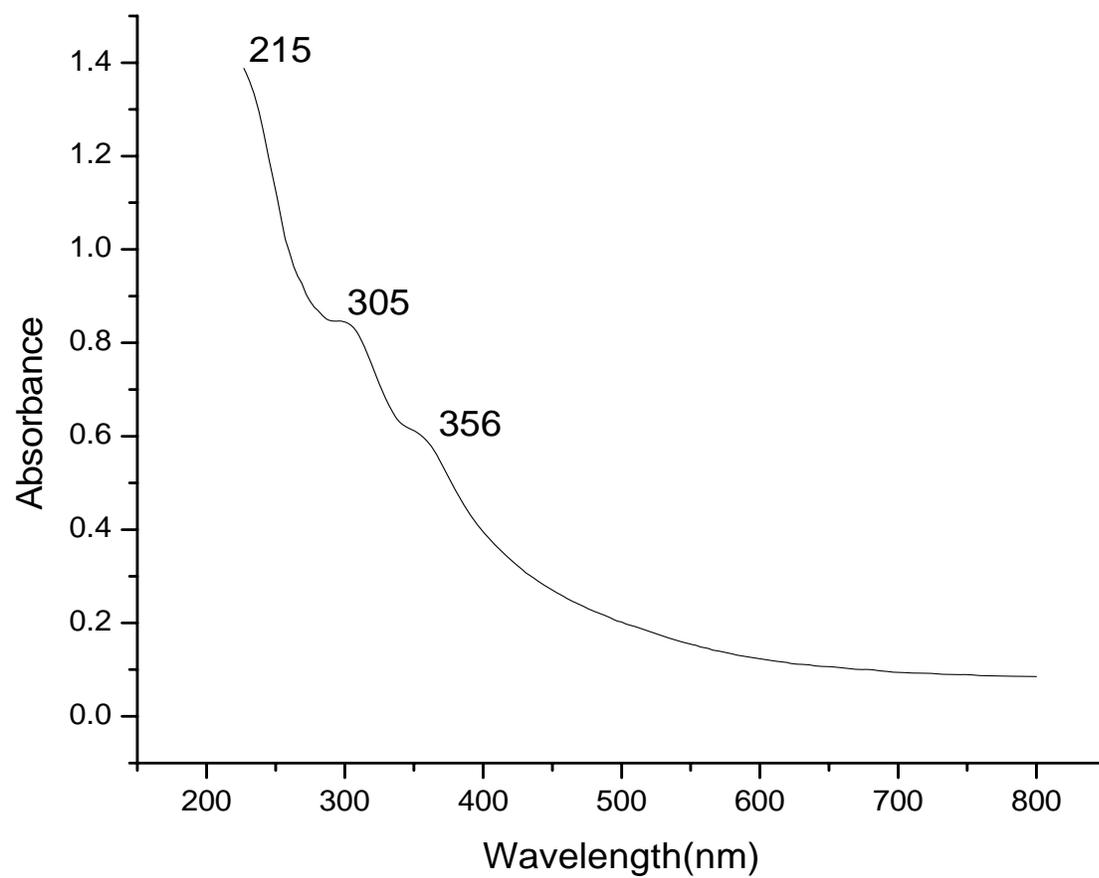
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Appendix 2 Electronic spectrum of Fe-L^D complex



Appendix 3 Electronic spectrum of Fe-L^T complex

