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STUDIES ON VO (IV) COMPLEX OF SCHIFF BASE LIGAND DERIVED FROM NINHYDRIN AND SEMICARBAZIDE

By
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Dedication

This work is dedicated to my darling wife Fantaye Gurmessa and daughter Ayantu Gudeta

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List of Abbreviations and symbols

A	Absorbance
B.M	Bohr Magneto
c	Concentration
DMSO	Dimethyl sulfoxide
DMF	N, N- Dimethyl formamide
DNA	Deoxyribonucleic acid
DSCI	1, 2- desemicarbazone-indan-3-one
ε	Molar extinction coefficient
EPR	Electron paramagnetic resonance
l	Path length
L	Liter
mg	Milligram
mL	Milliliter
π	Pi
PLTSC	Pyridoxalthiosemicarbazone
PLITSC	Pyridoxalisothiosemicarbazone
PLSC	Pyridoxalsemicarbazone
RNA	Ribonucleic acid
Rp	Ruhemann’s purple
TLC	Thin Layer Chromatography
Uv-Vis	Ultraviolet-Visible
VO(IV)DSCI	Oxonanadium(IV)-1,2-disemicarbazone-indan-3-one

Abstract

The catalytic and material properties of vanadium compounds and their effects in biological systems have long provided the impetus and fuel to studies of vanadium science. The expanding knowledge of the role of vanadium in biological systems and of the potential of vanadium compounds as therapeutic agents has led continuously increasing interest in the coordination chemistry and solution chemistry of this element. Vanadium complexes with mixed ligands containing oxygen and nitrogen atoms are known to have high redox stability. In this context, the ninhydrin-semicarbazone Schiff base ligand with nitrogen and oxygen coordinating atoms was chosen for this study.

The oxovanadium (IV) complex of the type [VO(DSCI] has been prepared using template method of synthesis with Schiff base ligand derived by condensation of ninhydrin and semicarbazide wherein the VO^{2+} cation acts as a template. Tentative structure of the complex has been proposed on the basis of characterization by electrical conductance, magnetic moment and electronic spectra. The oxovanadium (IV) complex is a five coordinated square-pyramidal wherein the Schiff base ligand acts as a tetradentate ONNO donor coordinating via the azomethine nitrogen atoms and enolized oxygen atoms of the amide group. The assignment of the geometry is corroborated by magnetic moment and electrical conductance measurements.

Key Words: Oxovanadium (IV) complex, Schiff base, Ninhydrin, Semicarbazide, 1, 2-disemicarbazone-indan-3-one.

1. INTRODUCTION

1.1 Background

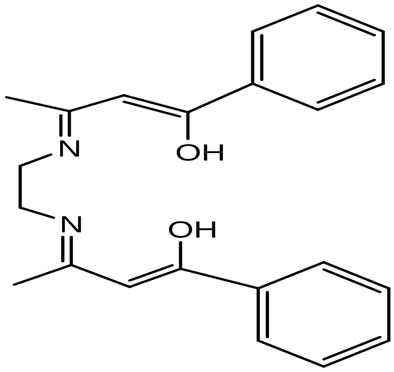
Metal complexes play an essential role in agriculture, pharmaceutical and industrial chemistry. Schiff bases which are condensation products of primary amines and aldehydes or ketones (RCH=NR’, where R & R’ represent alkyl and /or aryl substituents), are potential ligands in coordinating to metal ions to form these metal complexes. The use of Schiff bases and their metal complexes as catalysts, in various biological systems, as polymers and dyes, and as anti-fertility and enzymatic agents have been reviewed recently by Kumara et al. [1].

Some transition metals are essential for the normal functioning of living organisms. Metallo-drugs are becoming an interesting research area after the discovery of cisplatin. Since then, many complexes have been synthesized and tested on various biological systems. Copper complexes are known to have a broad spectrum of biological action, but its concentration as free metal ion inside cells should be lower than 10^{-15} M (calculated)/10^{-12} M (observed). The chemistry of vanadium with multidentate ligands has achieved a special status in the last decade because of its catalytic and medicinal importance. Mishara et al. [2] recently studied coordination complexes of VO(II), Co(II), Ni(II) and Cu(II) with two new tridentate and bidentate Schiff base ligands *i.e.*, 2-hydroxy acetophenone-2- amino-4-chlorophenol and 2-chlorobenzylidene-2-amino-4-chlorophenol , that coordinate through N and O donor atoms. According to their result, chelation might be helpful in tailoring the structure and monitoring the antimicrobial activity and therapeutic potential of a drug; thus giving a new thrust area in the field of metallo-drugs (bio-inorganic chemistry) through molecular biology [2].

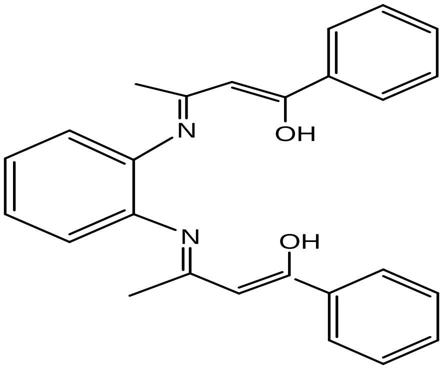
Coordination complexes are gaining increasing importance in recent years particularly in design of repository; slow release or long acting drugs in nutrition and in the study of metabolism. The metal ions are also known to accelerate drug action. The interaction of metal ions with nucleic acids and nucleic acid constituents has been actively studied in the recent years [3]. Among the metal complexes so far investigated, it is well known that transition metal complexes inhibit

DNA or RNA polymerase activities and induce strand scission of DNA in presence of H_2O_2. Therefore, it is not surprising that transition metal coordination compounds are of great interest as potential drugs. A general study of the structural and bonding features of the various Schiff base complexes can help better understanding of the complex life processes. These findings of structural studies are interesting in that the Schiff base ligands can control the stereochemistry of the complex and provide us with numerous examples of unusual geometries about the central metal ion. Therefore, they can serve to illustrate the coordination flexibility of these ions [3]. In this context, the Cu(II), Ni(II), Co(II) and Zn(II) complexes were synthesized using the Schiff bases formed by the condensation of semicarbazide hydrochloride and 2,4-pentanedione/methylacetoacetate/acetoacetanilide by N. Raman et al. The complexes were found to be active against microorganisms. The antimicrobial activity of the ligand is enhanced by the chelation with metal(II) ions. The DNA cleavage experiments showed all the complexes afford a pronounced discernible DNA [3].

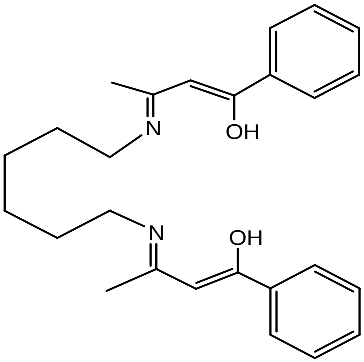
Schiff bases offer a versatile and flexible series of ligands capable to bind with various metal ions to give complexes with suitable properties for theoretical and/or practical applications. Of the various classes of Schiff base which can be prepared by condensation of different types of amines and carbonyl compounds salicylaldimines, potential O, N-donors derived from salicyldehyde and primary amines, are very popular due to diverse chelating ability. A. A. Ahmed et al.[4] synthesized and characterized the following Schiff base ligands formed by condensation reaction of benzoylacetone with ethylenediamine, o-phenylenediamine and 1,6-hexanediamine to obtain H_2L_1 = [$C_{22}H_{24}N_2O_2$], H_2L_2 = [$C_{26}H_{24}N_2O_2$] and H_2L_3 = [$C_{26}H_{32}N_2O_2$] respectively. The fourth Schiff base ligand H_2L_4 = [$C_{34}H_{28}N_2O_2$] is formed by the condensation of o-phenylenediamine with benzoin. The structure of these Schiff base ligands are shown below[4].



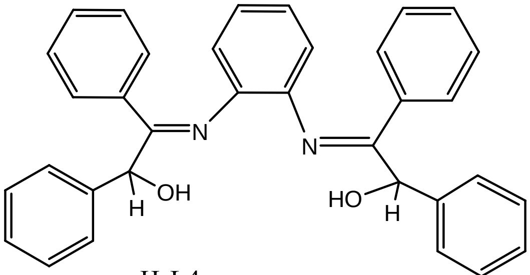
H_2L1



H_2L2



H_2L3



H_2L4

Figure-1: Structures of Some Schiff Bases

Schiff bases have also been widely used as ligands because of high stability of the coordination compounds and their good solubility in common solvents. The π-system in a Schiff base often imposes a geometrical constriction and affects the electronic structure as well. Thermo-chemical properties of Schiff bases have attracted many researchers' attention in view of their ability to coordinate metal ions, acting as bidentate or tetradentate ligands in metal chelates involving a NO or ONNO-Schiff-base donor atom sets. These Schiff base metal derivatives have considerable interest due to their role as model complexes to biological systems, contributing to the knowledge of their structure and behavior [4].

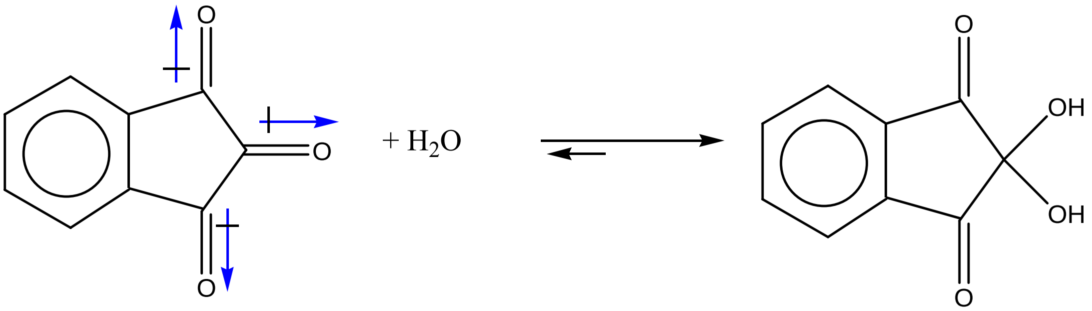
In general, metal complexes of Schiff bases are extensively studied due to synthetic flexibility, selectivity and sensitivity towards a variety of metal atoms. They are found useful in catalysis, in medicine as antibiotics and anti-inflammatory agents and in the industry as anticorrosive agents.

Moreover, Tetradentate Schiff bases with an ONNO donor atom set are well known to coordinate with various metal ions, and this has attracted many researchers. Complexes of Schiff base ligands have been studied for their dioxygen up-take and oxidative catalysis. Also complexes of transition metals (II), which involve derivatives of salicyldehyde and diamine, have gained considerable attention and prominence. This is because of their potential as catalysts for the insertion of oxygen into an organic substrate. These and other useful applications of metal complexes derived from Schiff base ligands initiated many researchers to actively and continuously undertake extensive research work in this area.

1.2 Reactions of Ninhydrin

Ninhydrin (triketohydrindene hydrate) is a white to brownish white crystalline powder, soluble in water and alcohol. It turns red when heated above 100 ^{O}C and its decomposition range is 240–245 ^{O}C. Ninhydrin is extensively used in the analytical determination of amino acids and related structures, and potentially can react with a variety of primary and secondary amines producing Ruhemann purple color [5]. Since its discovery, extensive efforts have been made to apply manual and automated ninhydrin reactions as well as ninhydrin spray reagents to the detection, isolation and analysis of numerous compounds of interest across a broad spectrum of disciplines. These include agricultural, biochemical, clinical, environmental, food, forensic, histochemical, microbiological, medical, nutritional, plant, and protein sciences [5].

Like all hydrates, ninhydrin is in equilibrium with the related carbonyl compound. It is a stable hydrate form of its parent carbonyl compound (1, 2, 3-indantrione) as depicted in scheme-1. The strong electron withdrawing groups on α-C (alpha carbon) destabilizes an adjacent carbonyl group because of repulsion of adjacent positive charges. Hydrate formation overcomes the forces of repulsion. Therefore, the hydrate of the middle carbonyl group of ninhydrin removes both pairs of repulsions [5].



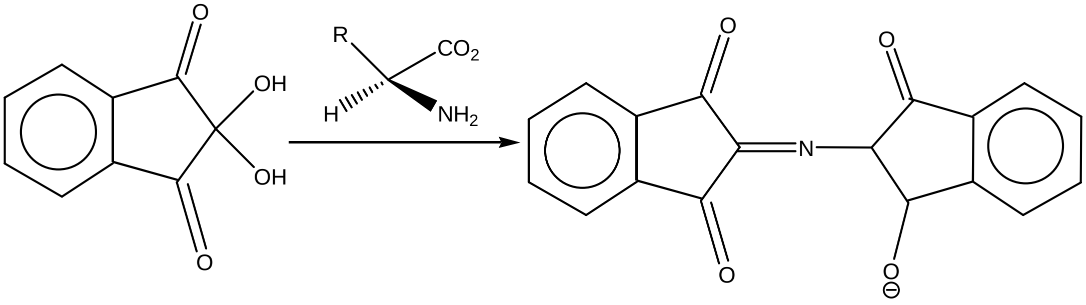
1,2,3-Indan-trione

Ninhydrin

Scheme-1: Hydrate formation reaction of 1,2,3-Indan-trion

1.2.1 Reactions of Ninhydrin with Amino acids

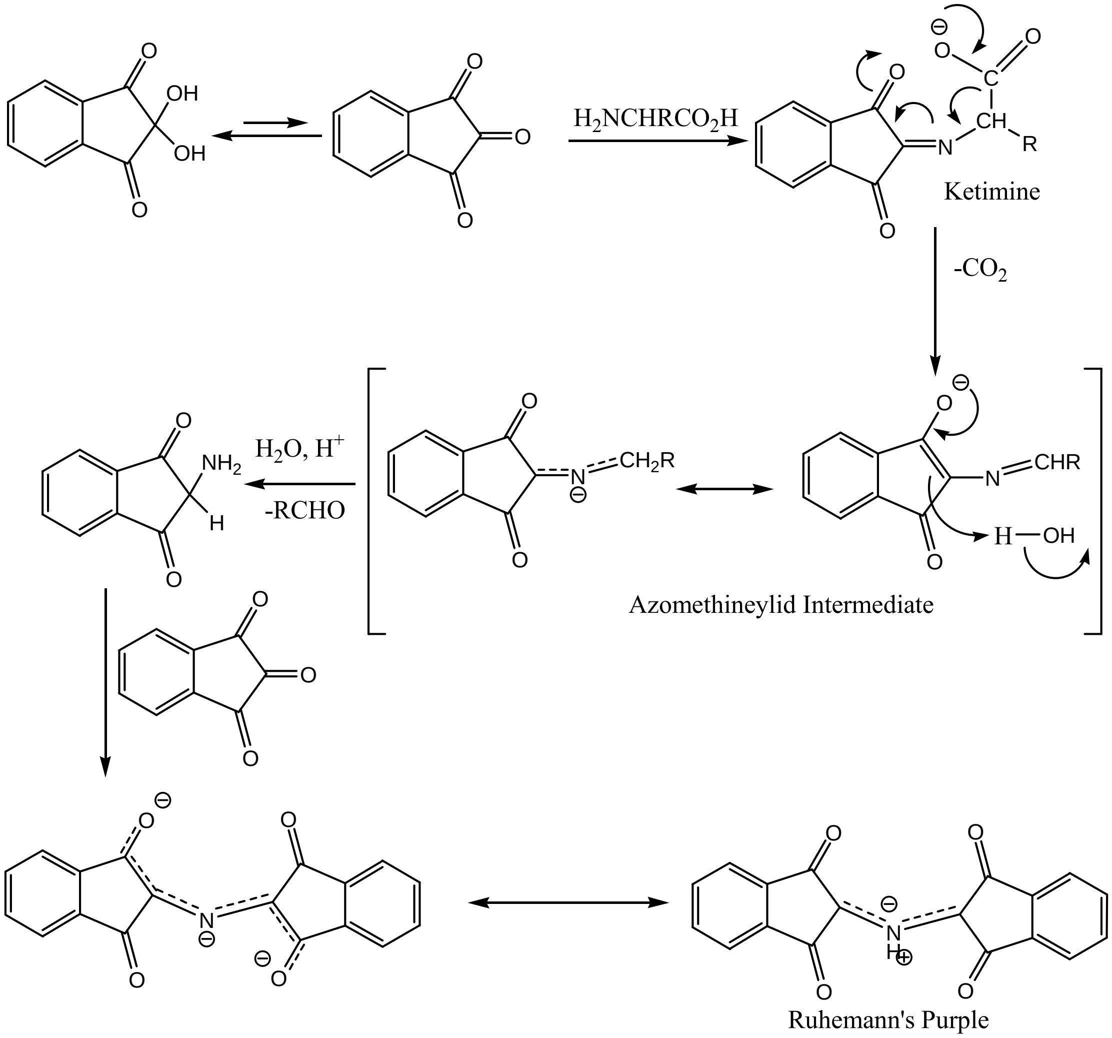
Ninhydrin is the hydrate of indan-1,2,3-trione, a molecule that reacts with amino acids to give the purple dye used in quantitative analysis of amino acids. The reaction of ninhydrin with primary amino groups to form the purple dye now called Ruhemann's purple (RP) was discovered by Siegfried Ruhemann in 1910 [5, 6] (scheme-2).



Scheme-2: Rp formation reaction

One of the most important discovery concerning ninhydrin reaction is the observation that complexation of Ruhemann's purple (RP) with certain metal ions enhances the sensitivity of the analyses by allowing estimation of the resulting chromophore by fluorescent, luminescent, phosphorescent, and laser techniques [6]. This modification, now widely used in forensic sciences to determine faint fingerprints, applies to agricultural and biomedical sciences also. The development of fluorogenic ninhydrin reagents and their use in forensic science, as well as the application of ninhydrin reagents in environmental chemistry, food chemistry, clinical chemistry, microbiology, pharmacology, and toxicology, are active areas of current research [6].

Three general steps were identified in the reaction of ninhydrin with amino acids. The first step involved the attack of the amine functionality of an amino acid on the 2-carbonyl of ninhydrin to form a Schiff base. Decarboxylation and hydrolysis led to an amine containing intermediate, which then formed the Ruhemann's Purple product by condensation with a second molecule of ninhydrin [7]. The products of the reaction of α-amino acids with ninhydrin are CO_2, an aldehyde (RCHO), and RP, (Scheme-3).



Scheme-3: The reaction of Ninhydrin with α -Amino Acids

The Ketimine (Schiff base) is a potential ligand, that can act as a tridentate forming two stable five membered rings on complexation as shown in fig.2 [5].

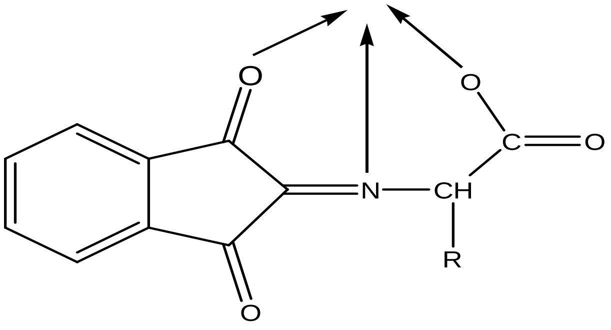
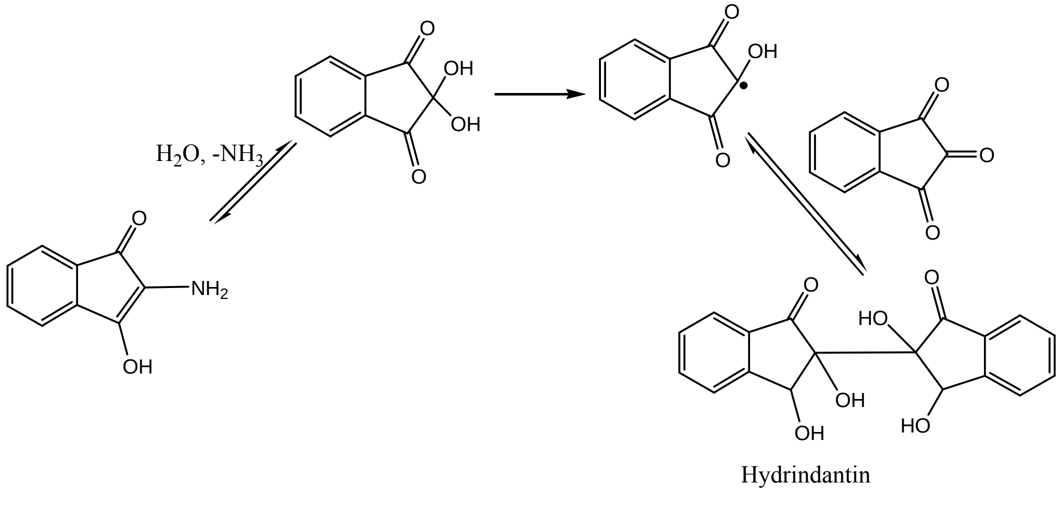


Figure-2: Possible metal binding centers of a Schiff base derived from Ninhydrin and α-Amino Acid.

There are a number of factors that affect the yield of the Ruhemann's Purple product including the concentration, the pH, and the type of amine group reacting (amino acids react faster than amines) [7]. At low concentrations of ninhydrin, the 2-amino-1,3-indanedione product decomposes into ammonia and 2-hydroxy-1,3-indanedione which then gets trapped by a second molecule of ninhydrin to give hydrindantin [7]. Hydrindantin can also be formed via the ninhydrin ketyl radical, formed from the photo-cleavage of the C-OH bond which then couple to form hydrindantin (scheme-4) [7].



Scheme-4: Formation of the side product hydrindantin, in the ninhydrin reaction

At high pH, the unprotonated amino group of the amino acids or the intermediate product can act as a good nucleophile, while at low pH these amino groups are protonated making them less nucleophilic, so that the reaction does not form the Ruhemann's Purple product in acidic conditions. The optimum pH for the reaction of ninhydrin with amino acids is around pH 5; however this varies with the amino acid [6, 7].

Different amino acids react with ninhydrin at different rates. Friedman [6] reviewed that the ninhydrin reaction was second order and proposed that the rate determining step involved the nucleophilic displacement of a hydroxy group on ninhydrin by a non-protonated amino group. Because the zwitterionic form of the amino acid carried a positive charge on the nitrogen atom, the anionic form was the active nucleophile. The azomethine ylide intermediate was seen to form readily when amino acids reacted, via decarboxylation of the carboxylic acid group, in contrast to the relatively slower reaction rate for amines, which require proton abstraction *alpha* to the amino group. The different reaction rates explain why amino acids are said to react more readily than amines with ninhydrin [7].

Mehabaw Getahun et al [8] also synthesized complexes of Mn(II), Fe(III), Co(II), Ni(ii) and Zn(II) with an intermediate Schiff base IDIP (Indane-1,3-dione-2-imine-N-2-propionate) derived from Ninhydrin and α,L-alanine. On the basis of elemental analysis, molar conductance, magnetic susceptibility, infrared and electronic spectral studies, they characterized the complexes. According to the result, the ligand (Schiff base) was shown to behave as a monobasic tridentate ONO donor. The Mn(II), and Fe(III) complexes were found to contain only one ligand molecule plus water and chlorine(s) per metal ion, while all the others contain two ligand molecules per metal ion. An octahedral geometry has been proposed for the metal complexes [8] (Fig. 3,4,5).

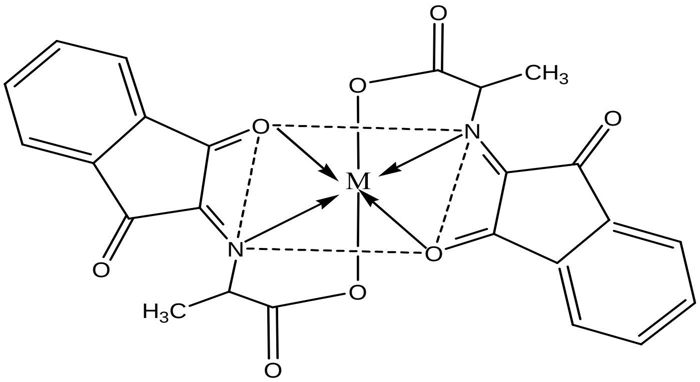


Figure-3: Structure of Metal complexes of IDIP {[ML2], M= Co(II), and Zn(II)}

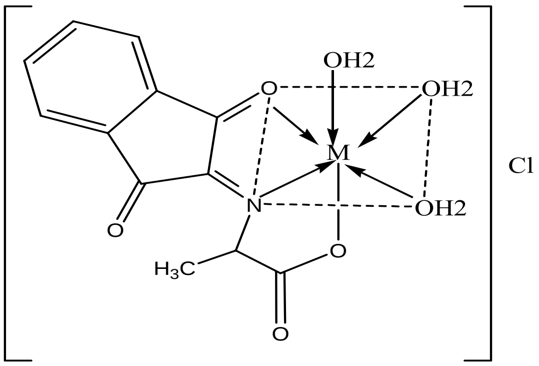


Figure-4: Structure of Mn(II) of IDIP {[ML(H_2O)$_3$]Cl, M= Mn(II)}

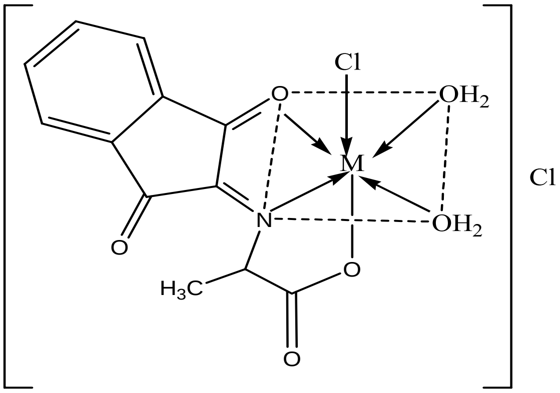
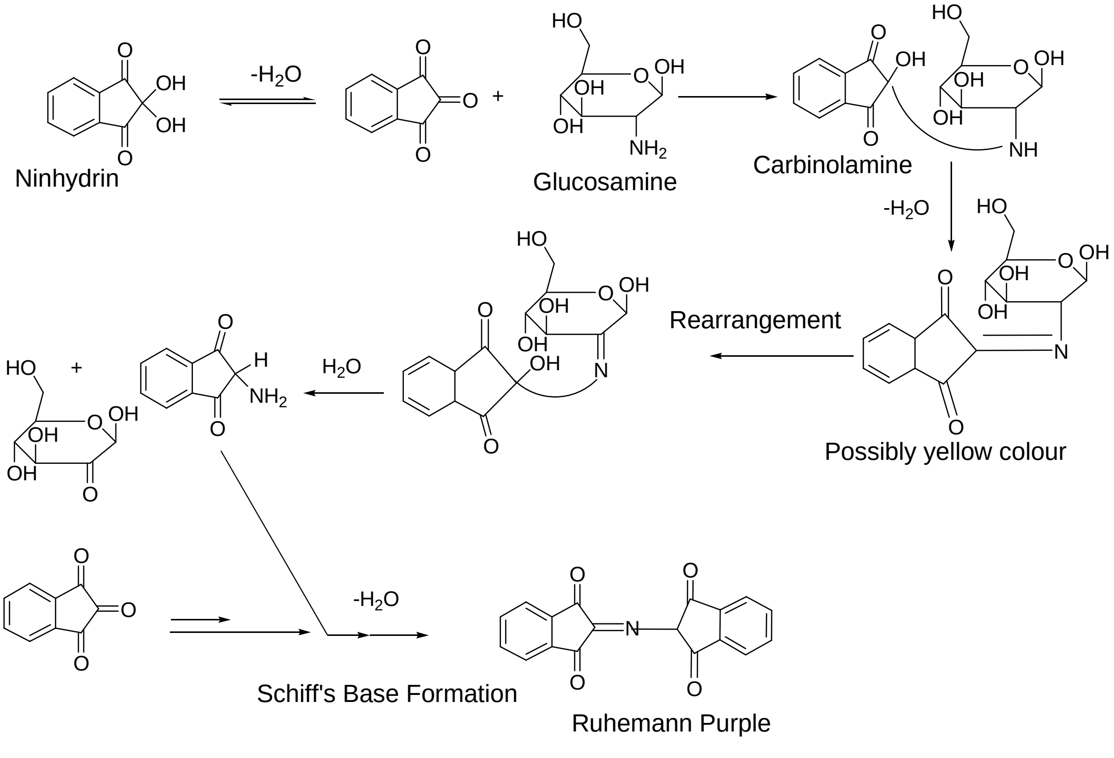


Figure-5: Structure of Fe(III) complex of IDIP {[ML(H_2O)$_2$Cl]Cl, M= Fe(III)}

1.2.2 Reaction of Ninhydrin with Amines

It is interesting to note that under acidic condition, ninhydrin can react with a variety of primary and secondary amines resulting in a so-called Ruhemann purple color (diketohydrindamine diketohydrindylidene). Comparing this with amino acid reaction, it is significantly slower. The published works indicate that for accuracy purposes, the most important factors involved in the quantitative production of Ruhemann purple include a high concentration of aqueous ninhydrin solution, a high reaction temperature, and optimum acidic condition [5-7]. Recently, a new method has been developed by Y. Wu et al. [9] based on ninhydrin–glucosamine reaction. In their study, they pointed out that ninhydrin–glucosamine reaction was affected by the following factors: (1) reagent (ninhydrin) and glucosamine concentrations and ratios; (2) reaction temperature; (3)

reaction time; (4) reaction solution pH; and (5) assay time of the reacted solution for maximum stability. According to their report, ninhydrin solution with the concentration of 0.8% was selected for further studies. With the increase of reaction temperature, the time for the color formation was significantly reduced. Therefore, in order to assure completion of the reaction process, 100 ^{O}C for 5 min was selected in their work. The pH of the mixture of ninhydrin and glucosamine is greater than 4.0. Hence, pH 5.0–6.0 was selected as experimental range. The quantities and ratios of glucosamine to ninhydrin had been optimized to higher ratio to obtain significant product. The study has also revealed a mechanism for the reaction of ninhydrin and glucosamine. This mechanism is based on the Schiff's base formation, as a result of diketohydrindamine–diketohydrindylidene, reaction product which is similar to the ninhydrin–amino acids reaction exhibiting Ruhemann purple that can be quantitatively determined at 570 nm (Scheme-5) [9].



Scheme-5: Proposed mechanism of *Ruhemann* purple from ninhydrin–glucosamine reaction (*Schiff*'s base formation).

1.3 Formation and Application of Semicarbazones

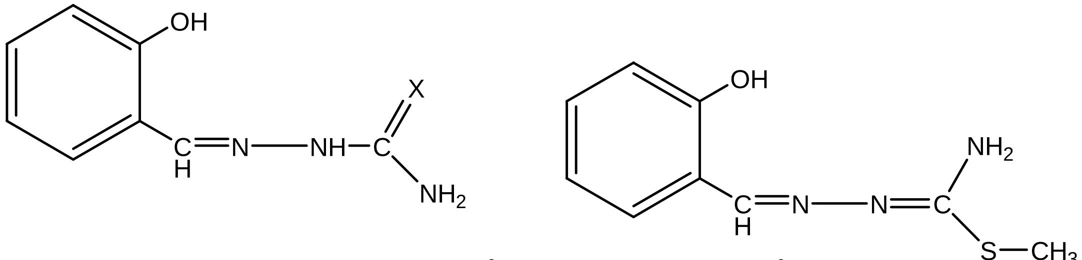
A semicarbazone is a derivative of an aldehyde or ketone formed by a condensation reaction between a ketone or aldehyde and semicarbazide.

For ketones: $H_2NNHCONH_2 + R_2COR \xrightarrow{\qquad} R_2C{=}NNHCONH_2$

For aldehyde: $H_2NNHCONH_2 + RCHO \xrightarrow{\qquad} RCH{=}NNHCONH_2$

The rates and equilibrium constants of reactions of carbonyl compounds with nucleophiles such as semicarbazide are affected significantly by variations in the pH of the reaction medium [10]. For reactions of carbonyl compounds with reagents such as semicarbazide, the desired pH is produced and maintained by buffer solutions. The maximum rates for the reactions of most aldehydes and ketones with semicarbazide occur in the pH range of 4.5-5.0, and the rates decrease at pH either above or below this value [10]. For the purpose of making derivatives of carbonyl compounds, semicarbazide is best used in an acetate buffer ($CH_3CO_2H/CH_3CO_2^-$) solution which maintains a pH in the maximum rate range, 4.5-5.0.

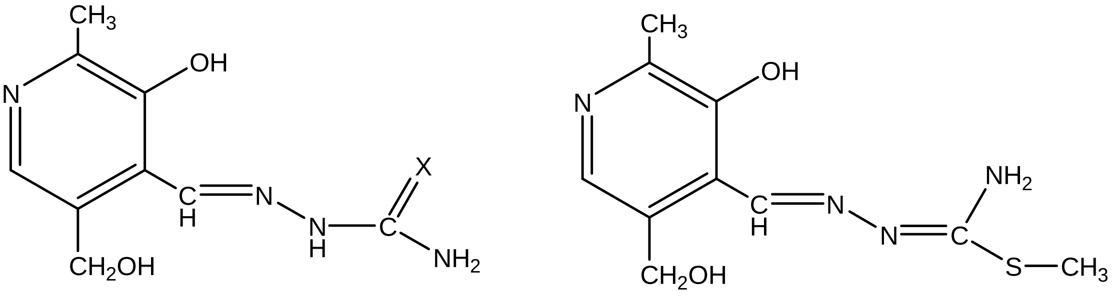
Due to their good complexing properties, biological activity and analytical application, semi-/thiosemi-/isothiosemicarbazides and their Schiff bases of different denticity, as well as their metal complexes, have been subject of many studies [11, 12]. Apparently, the most numerous among them are the complexes with tridentate salicylaldehyde semi-/thiosemi-/isothiosemicarbazones. In contrast to salicylaldehyde semi-/thiosemicarbazones, whose donor atoms are O, N, X (X=O or S), the third donor atom with isothiosemicarbazone derivatives is the nitrogen of the isothioamide group.



($X = O \longrightarrow H_2L^1$: $X{=}S \longrightarrow H_2L^2$) H_2L^3

Figure-6: Structural formulas of salicylaldehyde semi- (H_2L_1), thiosemi- (H_2L_2) and *S*-methylisothiosemicarbazone (H_2L_3).

The investigation of metal complexes with Schiff bases derived from pyridoxal (PL), *e.g.*, 3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carboxaldehyde (one of the forms of vitamin B6), and amines, and/or amino acids, have also been the subject of great interest of many researchers. Pyridoxal semi-, thiosemi- and isothiosemicarbazones (PLSC, PLTSC and PLITSC, respectively) (Fig. 7) form a special group of these ligands [12].

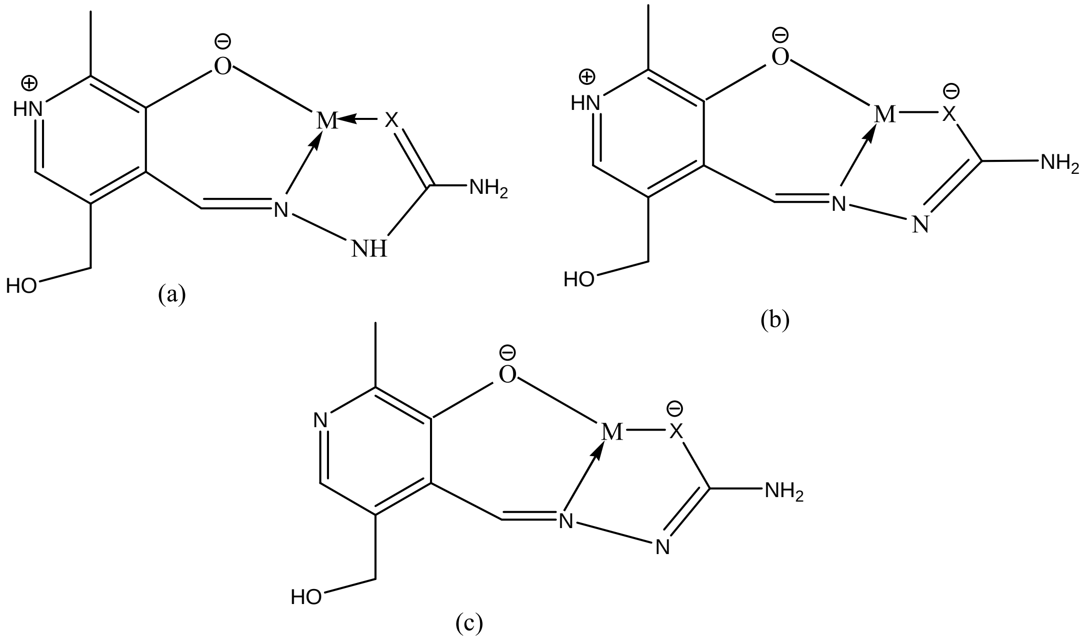


X=O → PLSC, X= S → PLTSC

PLITSC

Figure-7: Structural formulas of pyridoxal semi- (PLSC), thiosemi-(PLTSC) and isothiosemicarbazone (PLITSC).

The common coordination mode of these ligands is presented in fig.8. As it can be seen, of seven potential ligator atoms of all three ligands, three are engaged in coordination, two of them being identical for all three ligands. Namely, the identical ligators are the phenolic oxygen and hydrazine N1 nitrogen. In the case of PLSC and PLTSC, the third ligator atom is the oxygen or sulfur atom of the amide, i.e. thioamide group (fig. 8 a, b,c) [12].



(a)

(b)

(c)

Figure-8: Coordination modes and ligand forms of PLSC, PLTSC (a, b, c)

There are a large number of works on the coordination chemistry, analytical applications and biological activity of thiosemicarbazones and semicarbazones. A considerable amount of work has been done on the biological activity of semicarbazones and their metal complexes. Recently, it has been shown that SCs of aromatic and unsaturated carbonyl compounds have anticonvulsant properties and their great advantage over TSC analogues is their lower neurotoxicity [13].

With regard to biological importance of metal complexes with semicarbazones, nickel (II) complexes with semicarbazone ligand show antibacterial activity and copper (II) complexes containing semicarbazone have also displayed biological properties. Some nickel (II) complexes with octadiensemicarbazones exhibit strong inhibitory activity against *Staphylococcus aureus and Escherichia Coli*. In vitro anticancer studies of several nickel (II) complexes with naphthaquinone semicarbazone and thiosemicarbazone on MCF-7 human breast cancer cells reveal that semicarbazone derivative with its nickel (II) complexes is more active in the inhibition of cell proliferation than the thiosemicarbazone analogues [13].

1.4 Chemistry of Vanadium (V)

Vanadium, a group V trace element that belongs to the first transition series of elements, is ubiquitously distributed and represents the 21st most abundant element in the earth's crust. Nils Sefstrom, a Swedish chemist, has been credited for its discovery in 1831 [14]. It was named after Vanadis, the Norse goddess of beauty, youth and luster, because its salts possess beautiful colors. The element can exist in a wide range of oxidation states ranging from -1 to +5, and, thus, its chemistry is complex [14].

The oxidation states and stereochemistry for vanadium are summarized in Table-1 [15]. The +4 oxidation state, which is generally the most stable one for vanadium, is best represented by the vanadyl ion, VO^{2+}, which is stable in aqueous solution and under complexation with a wide range of ligands.

Table-1: Oxidation states and stereochemistry of Vanadium

Oxidation State	Coordination No.	Geometry	Examples
V^{-1}, d^6	6	Octahedral	$VO(CO)_6^-$, $Li[V(bipy)_3].4C_4H_8O$
V^0, d^5	6	Octahedral	$V(CO)_6$, $V(bipy)_3$
V^1, d^4	6	Octahedral	$[V(bipy)_3]^+$
	7	Tetragonal pyramidal	η^5-$C_5H_5V(CO)_4$,
		Monocaped octahedral	$V(CO)_2(dmpe)_2Cl$
V^{II}, d^3	5	sp	$(2,6\text{-}Ph_2C_6H_3O)_2V(py)_3$
	6	Octahedral	$[V(H_2O)_6]_2^+$
V^{III}, d^2	4	Tetrahedral	$[VCl_4]^-$
	5	tbp	$VCl_3(NMe_3)_2$
	6	Octahedral	$[V(NH_3)_6]^{3+}$
V^{IV}, d^1	4	Tetrahedral	VCl_4, $V(NEt_2)_4$
	5	Tetragonal Pyramidal	$VO(acac)_2$
	6	octahedral	VO_2(Rutile), $V(acac)_2Cl_2$
V^V, d^0	4	Tetrahedral (C3v)	$VOCl_3$
	5	tbp	VF_5 (g)
	6	octahedral	VF_6^-, V_2S_5
	7	pentagonal bipyramidal	VO $(Et_2NCS_2)_3$

1.4.1 Oxovanadium Ions and Complexes

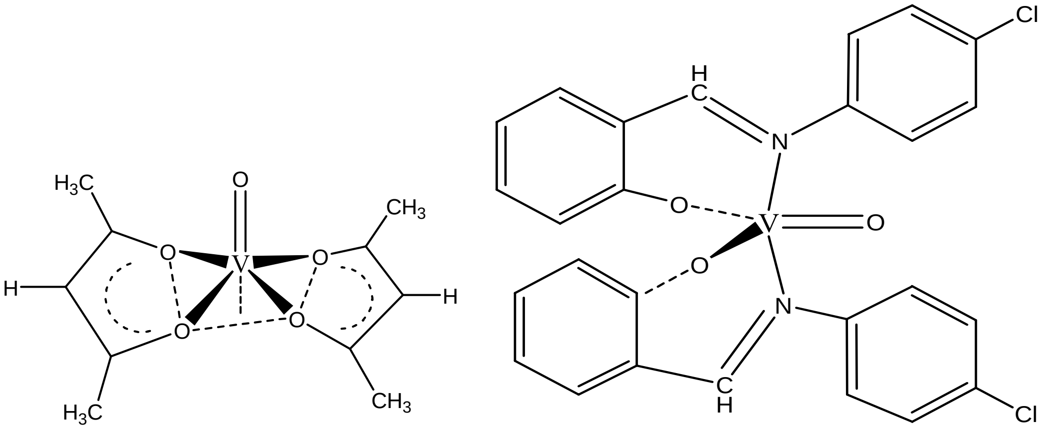
The two oxo ions, VO_2^+ and $VO^{2+,}$ have an extensive chemistry and form numerous complex compounds. All of the compounds show IR and Raman bands that are characteristic for M=O groups. The VO_2^+ group is angular. Examples of complexes are cis-$[VO_2Cl_4]^{3-}$, cis-$[VO_2EDTA]^{3-}$, and cis-$[VO_2(ox)_2]^{3-}$. The cis arrangement for dioxo compounds of metals with no d electrons is preferred over the trans arrangement, because the strongly π-donating O ligands then have exclusive use of one dπ orbital each (d_{xz}, d_{yz}) and share a third one (d_{xy}), whereas in the trans configuration they would have to share two dπ orbitals and leave one unused[15].

Oxovanadium (IV) or vanadyl cation, VO^{2+}, dominates vanadium (IV) chemistry. It is among the most stable and important of vanadium species. The VO unit persists through a variety of chemical reactions. It is obtained by mild reduction of the VO_2^+ ion or by oxidation by air of V^{3+} solution [16,].

$$VO^{2+} + 2H^+ + e^- \longrightarrow V^{3+} + H_2O \qquad E^o = +0.34\ V$$

$$VO_2^+ + 2H + + e^- \longrightarrow VO^{2+} + H_2O \qquad E^o = +1.0\ V$$

Although most oxovanadium(IV) complexes are blue green, certain Schiff base complexes may vary from yellow to maroon (reddish purple), and display two other physical properties (1) an EPR spectrum with characteristic g values and ^{51}V hyperfine coupling (8- lines) and (2) a strong V=O stretching band in the IR in the range 950 to 1000 cm^{-1} [15,16]. There is an extremely wide range of complexes that, depending on the nature of the ligands, are cationic, neutral, or anionic and either five-coordinate, where the stereochemistry is that of the square pyramid, or six-coordinate, containing a distorted octahedron. Examples are $[VObipy_2Cl]^+$, $VOacac_2$, and $[VO(NCS)_4]^{2-}$. Oxovanadium (IV) complexes range from distorted trigonal bipyramidal as in the Schiff base complex (fig.9b) to square pyramidal as in fig.9a. The V=O bond is very strong, possibly having partial triple bond character and the V=O distances are thus very short (1.55-1.68 Å) with a dependence on the nature of the ligand set, especially the strength of coordination in the position trans to the V=O bond. Donors that increase electron densities on the metal reduce acceptor properties toward O thereby lower the V-O multiple bond character and the stretching frequency. In some solids the V=O units are arranged in linear chains to give V=O …. V=O chains with long O…V distances of about 2.5 Å.



(a) (b)

Figure-9: Square pyramidal and trigonal bipyramidal structure of vanadyl complexes.

In vanadium chemistry, the VO^{2+} and VO^{3+} motifs have received considerable attention probably due to their involvement in many vanadium-dependent enzymes, viz., nitrogenases, haloperoxidases, phosphomutases etc [17]. Catalytic activity of some vanadium(V) complexes in olefin polymerization has recently been discovered. Moreover, the discoveries of several medicinal properties of vanadium complexes viz., insulin-mimetic, anticancer, antitumor and antifungal/antibacterial activities have stimulated further research in this area. In most cases the active site contains either of these two motifs coordinated by oxygen–nitrogen atoms. The strong affinity of these two motifs towards O, N-donor ligand is probably due to their hard acidic nature and selective stabilization of these two motifs depends upon the basicity of donor atoms. These ligands have a tendency to stabilize the vanadium in its highest oxidation state [17].

Many different VO (IV) complexes with tridentate ligands with ONO sites, tetradentates of the type N_2O_2, and recently, N_2N_2 sites have been prepared and characterized. Saied M**.** E. Khdil and Hoda F. O. El-Shafiy [18] synthesized and characterized VO (IV) complex derived from asymmetric Schiff base ligands (N_2O_3) on the bases of IR, magnetic susceptibility, molar conductance and electronic spectra. Based on their analysis, they proposed that the geometry around the vanadium is octahedral as shown below in Fig.10. In addition, the V=O stretching frequencies for the complexes appeared in the region 955-980 cm^{-1} which is consistent with a six coordination geometry [18].

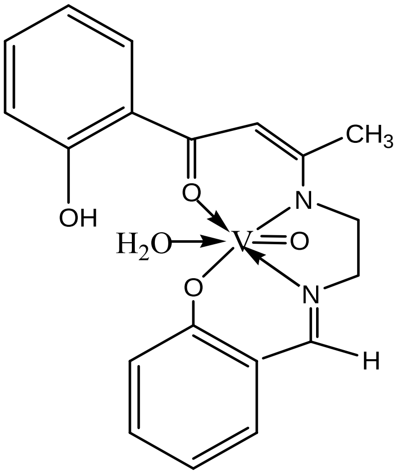


Figure-10: Structure of the VO (IV) Complex of pentadentate Schiff base ligands with N_20_3 donor sites

H. Temel et al [19] have also reported the synthesis and characterization of a new oxovanadium complex of a Schiff base derived from the condensation of 1,2-bis(p-aminophenoxy)ethane with salicylaldehyde (Fig. 11) and its oxovandium(IV) complex (fig.12).

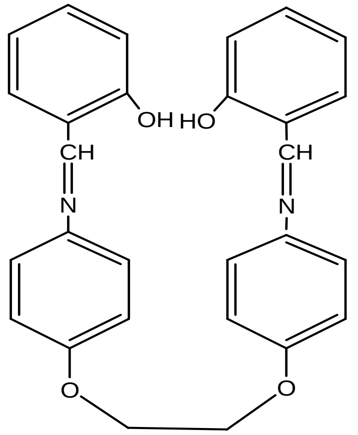


Figure-11: N,N-bis(Salicylidene)-1,2-bis-(p-aminophenoxy)ethane

Based on their analysis, they suggested square-pyramidal structure for the VO(IV) complex of the ligand N,N-bis(Salicylidene)-1,2-bis-(p-aminophenoxy)ethane [19].

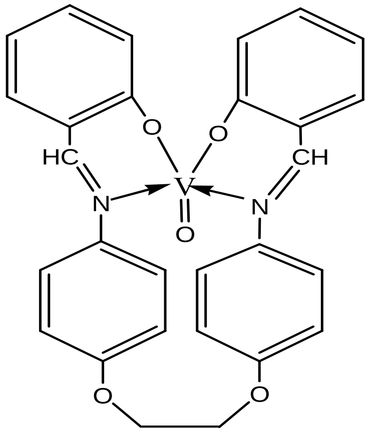
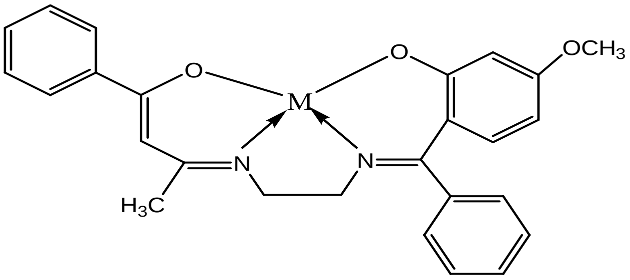


Figure-12: Suggested structure of the square-pyramidal VO(IV)L complex of the ligand N,N- bis(Salicylidene)-1,2-bis-(p-aminophenoxy)ethane.

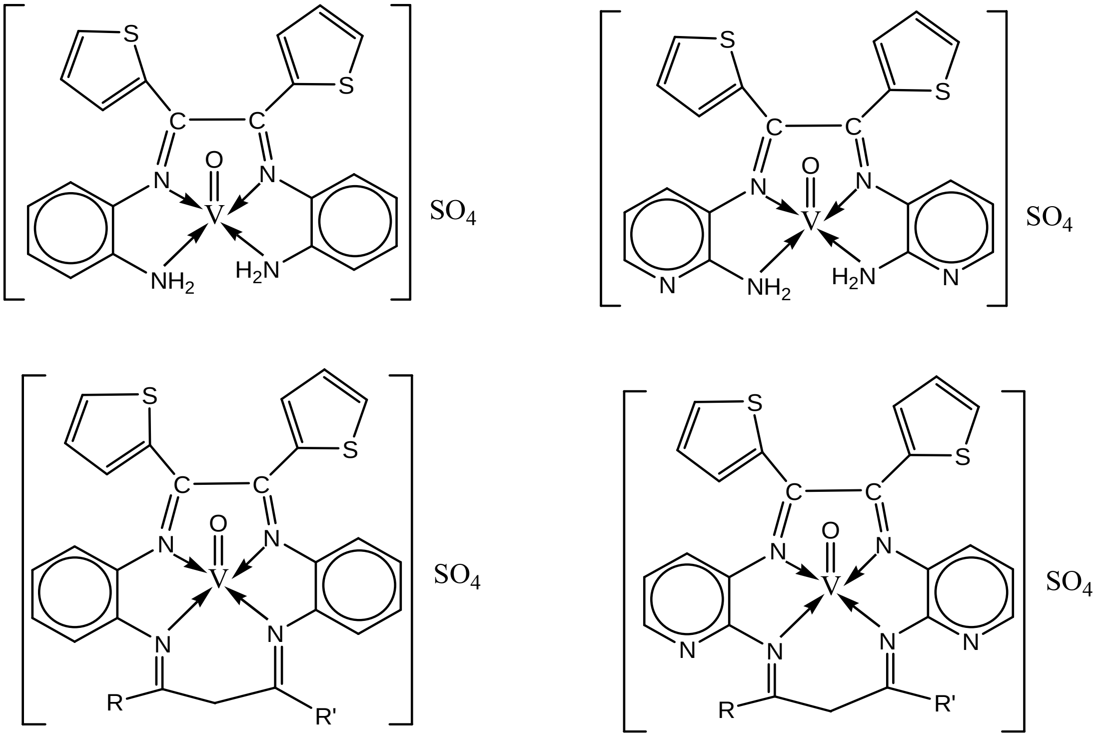
A. A. Osowole [20] has also synthesized and characterized VO (IV), Ni (II) and Cu (II) complexes of the asymmetric Schiff base (derived from condensation of 1-phenyl-1,3-butanedione, ethylenediamine and 2-hydroxy- 4-methoxy benzophenone), by elemental analyses, conductance, magnetic, infrared and electronic spectral measurements. The ligand is tetradentate coordinating *via* the imine N and enolic O atoms. The Ni(II) and Cu(II) complexes adopt a four coordinate square planar geometry, the VO(IV) complex is five coordinate square-pyramidal [20]. The assignment of geometry is collaborated by magnetic moments and electronic spectra measurements. He investigated that the oxovanadium(IV) complex electronic spectrum showed three absorption bands at 15.45, 17.55 and 26.50 kK respectively, consistent with a five coordinate, square-pyramidal geometry and is assigned to $b_2 \rightarrow e^*$, (band I), $b_2 \rightarrow b_1$ (band II) and $b_2 \rightarrow a_1$ (band III) transitions.



M = VO(IV), Ni(II), Cu(II)

Figure-13: Square planar geometry for Ni(II) and Cu(II) Complexes and Square pyramidal geometry of VO(IV) complex.

S.N. Thakur et al. [21] have also reported the template synthesis and characterization of oxovanadium (IV) complexes with ligands derived from di-2-thienylethanedione and 1,2-diaminobenzene or 2,3-diaminopyridine and their cyclization reactions with β-diketones, including acetyl-acetone, benzoylacetone, thenoyltrifluoroactone and dibenzoylmethane. According to the result of their analysis, the electronic spectra showed bands in the regions of 835-906 nm, 628-665 nm and 447- 474 nm, similar to other five coordinate oxovanadium (IV) complexes involving nitrogen donor atoms. The observed bands have been assigned to $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$ transitions, respectively [21].



R	R’	β- Diketone
CH_3	CH_3	Acetylacetone
C_6H5	CH_3	Benzoylacetone
C_4H_3S	CF_3	Thenoyltrifluoroacetone
C_6H5	C_6H5	Dibenxoylmethane

Figure-14: The Proposed Structure of the VO (IV) Complexes with ligands derived from di-2-thienylethanedione and 1,2-diaminobenzene.

1.4.2 Applications of Vanadium

As it has been reviewed under the chemistry of vanadium, research interest in V/O chemistry derives from its utility in several biological and industrial processes [22]. The coordination chemistry of vanadium has acquired renewed interest since the discovery of vanadium in organisms such as certain ascidians and Amanita mushrooms and as a constituent of the cofactors in vanadate-dependent haloperoxidases and vanadium nitrogenase [17, 22]. Recent advances in catalytic and medicinal properties of vanadium complexes have stimulated their design and synthesis. The biochemical aspects of vanadium complexes have further promoted the coordination chemistry of vanadium. Its biological significance is further exemplified by its incorporation in natural products and enzymes as potent inhibitors of phosphoryl transfer. Vanadium-containing compounds have their utility as insulin mimetic and anti-amoebic agent. The potential of vanadium complexes as anti-amoebic agents has thus far only been marginally explored. It is also suggested that vanadium could be considered as a representative of a new class of non-platinum metal antitumor agents [22-24].

1.5 Aim and Scope of the Study

The hard acidic nature of the two commonly occurring motifs of vanadium, viz. VO^{2+} and VO^{3+} is probably the main reason for their rich chemistry with O, N donor ligands [25]. The coordination chemistry of oxovanadium (IV) (i.e. VO^{2+} or vanadyl ion) is more interesting and rather more important because of two main reasons [26]. Firstly, the vanadyl complexes are finding more and more importance in biological systems. Secondly, the coordination number and geometry of this metal is highly ligand dependent. Moreover, vanadyl ion is less toxic than vanadate ion. Since 1990, many vanadyl complexes with different coordination modes have been proposed to have in vitro insulin-mimetic activity and in vivo antidiabetic blood glucose lowering activity [21, 25, 26]. Majority of enzyme inhibition studies of vanadium complexes contain oxygen coordinating atoms which are known to exhibit high hydrolytic but low redox stability. However, vanadium complexes with mixed oxygen and nitrogen atoms are known to have high redox stability [26]. In this context, the ninhydrin-semicarbazone Schiff base ligand with nitrogen and oxygen coordinating atoms was chosen for investigation in our laboratory. The synthesis and characterization of ninhydrin-disemicarbazone-NDSC (1,2-disemicarbazone-indan-3-one) and its coordination with nickel metal center was reported recently in this laboratory[27]. The synthesized Ni(II) complex has an octahedral geometry with the ligand behaving as a neutral tetradentate ONNO donor. The direct synthesis of this Schiff base from Ninhydrin and semicarbazide was found to be very slow, and the amount of the expected Schiff base ligand was not significant. The VO^{2+} ions, however, enable an accelerated template synthesis with sufficient yield [28]. Therefore, the template method was chosen to synthesis the complex in this study. Semi-, thiosemi-, and isothiosemicarbazones, (SC, TSC, and ITSC, respectively) as well as their metal complexes have been the subject of great interest of many researchers for a number of years. The significance of these compounds, apart from their diverse chemical and structural characteristics, stems not only from their potential but also from their proved application as biologically active molecules of a wide spectrum of activity [11, 12]. Furthermore, bearing in mind that many semi- and thiosemicarazones form stable colored metal complexes, some of them have been proposed as analytical reagents. The coordination chemistry of semi-, thiosemi- and isothiosemicarbazones appeared to be very interesting from the point of view of both the number of metals forming complexes with them and the diversity of the ligand systems themselves. With such important applications of the semicarbazone, oxovanadium (IV) complex of Ninhydrin-semicarbazone ligand may prove to have interesting potential medical applications considering the insulin mimicking properties of some vanadium compounds. This project is then aimed at the synthesis and characterization of oxovanadium (IV) complex of Schiff base ligand 1,2-disemicarbazone-indan-3-one (DSCI) derived from ninhydrin and semicarbazide by template method. However, the application of this complex is not studied and reported under this project work due to time constraint.

2. EXPERIMENTAL SECTION

2.1 Materials and Measurements

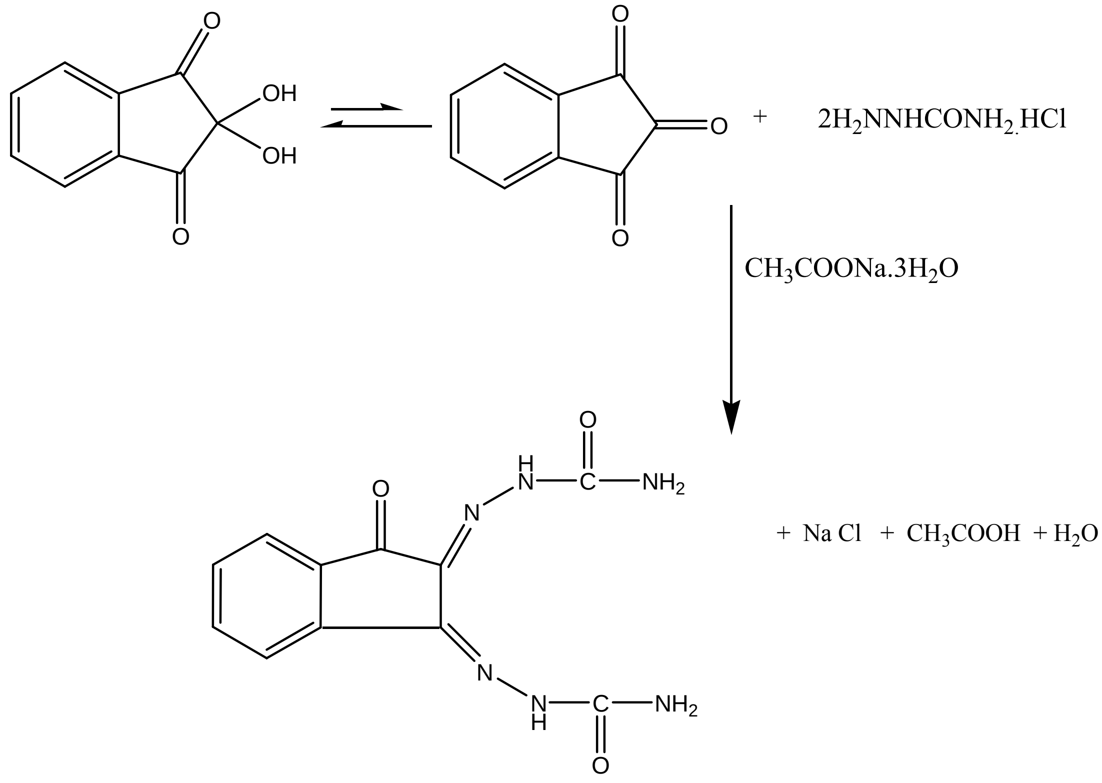
Most chemicals used in the investigation were of A.R grade. Vanadyl sulfate hydrate, $VOSO_4.H_2O$ (BDH), Ninhydrin (Pharmacos), Semicarbazide hydrogen chloride (BDH) and sodium acetate trihydrate ($CH_3COONa.3H_2O$) were used. Other reagents used in this investigation were barium chloride, sodium sulfite, nitric acid, concentrated hydrochloric acid, sulfuric acid, ammonium metavanadate and hydrogen peroxide solution (3%). Absolute ethanol and methanol and/or aqueous ethanol and methanol were used as the solvents for the synthetic methods. Ethanol and methanol were distilled before use. DMSO and DMF were also used for spectroscopic measurements.

UV-Vis spectrophotometric measurements were made in the range 200-800 nm using Spectronic Genesys 2PC spectrophotometer. The melting point or decomposition temperatures of the products were determined with Stuart SMP3 Digital Melting Point apparatus. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using Sherwood Scientific magnetic susceptibility balance. Conductivity measurements of the metal complexes in DMF were carried out using EC 214 Bench type conductivity meter (Hanna Instrument).

2.2 Synthesis of the Ligand and Metal Complex

2.2.1 Formation of the Ligand 1, 2-Disemicarbazone-Indan-3-one (DSCI) [27]

The synthesis and characterization of the ligand DSCI has been already reported in our lab. The reported reaction was found to be very slow and the yield obtained was not significant [27]. As such, in this study the Schiff base ligand was prepared in the presence of a metal ion. The vanadyl cation, VO^2+, is supposed to enable an accelerated synthesis with significant product, in the reaction mixtures of the precursors (template synthesis).

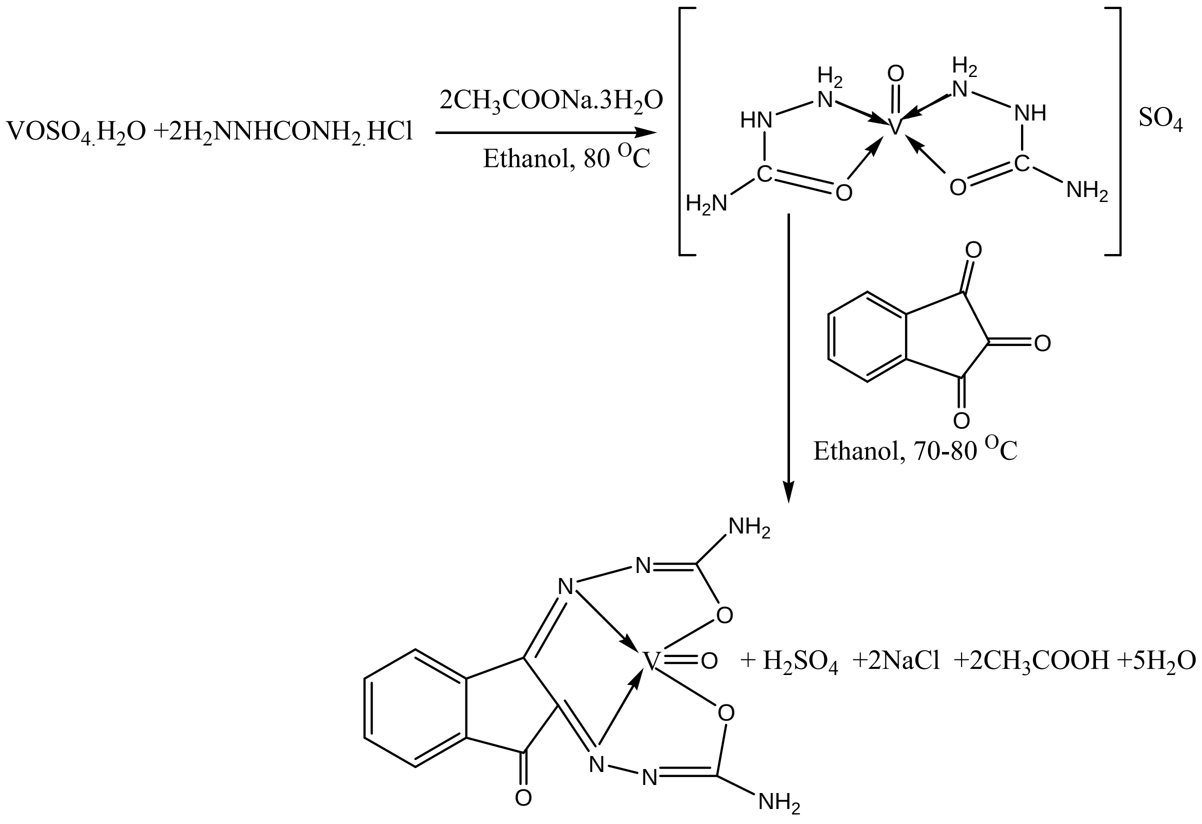


Scheme-6: Structure of the ligand DSCI [27]

2.2.2 Synthesis of Oxovanadium (IV) Complex

Preparation of oxovanadium (IV) complex with ligand derived by condensation of semicarbazide hydrogen chloride with ninhydrin:

A solution of vanadyl sulfate hydrate, $VOSO_4.H_2O$ (3.0mmol, 0.52 g) was prepared in ethanol (30 ml). It was added to a mixture of semicarbazide hydrogen chloride (6mmol, 0.67g) and sodium acetate trihydrate (6mmol, 0.82g) prepared in aqueous ethanol (15 mL in 1:2 volume ratios) in round bottom flask. The mixture was refluxed for about thirty minute. A blue solution was obtained. To the refluxing solution, ninhydrin (3mmol, 0.53g) dissolved in ethanol (30 mL) was added (in 1:2:1 molar ratios). A yellowish colored suspension was observed after 20-minute reflux. The reflux was continued for about ten hours until a light green precipitate was formed. The precipitate was filtered by suction filtration in hot condition. Then, it was washed thoroughly with ethanol and aqueous ethanol, dried and stored in dessicator. Yield: 70%; and melting point: 288 ^{O}C.



Scheme-7: Reaction Path for the Formation of [VO(IV) DSCI] Complex

2.2.3 Spectrophotometric Determination of Vanadium

A standard solution (1x10^{-2}M) was prepared by dissolving 0.29g of ammonium metavanadate, NH_4VO_3, in 250mL of distilled water. 1mL ≡ 0.5 mg of vanadium. Five series of standard solutions of volumes 0.2 mL, 0.4 mL, 0.6 mL, 0.8 mL and 1.0 mL were added to five separate 50mL volumetric flasks. To each of these solutions, 5mL of 1M H_2SO_4 acid and 1.25mL of 3% H_2O_2 were added and red brown solutions were obtained. Each mixture was diluted to up to the mark with distilled water. The absorbance of the solutions was finally measured at 450nm against blank solvent. The calibration graph was constructed between the absorbance and concentrations of the standards to evaluate the concentration and/or mass of vanadium in the complex by applying Beer-Lambert law.

The sample solution containing unknown concentration of vanadium was prepared by digesting 20mg of V(IV) complex in 10mL concentrated HNO_3 acid twice to remove the organic part.

Distilled water and 4mL of HNO_3 were used to dissolve the residue left after digestion. The contents were transferred to a 50mL volumetric flask to which a distilled water was added to up to the mark to dilute the solution. Then, 25mL of the solution was delivered to another 50mL volumetric flask to which a few drops (8-10 drops) of diluted solution of $KMnO_4$ were added to oxidize V(IV) to V(V). To this mixture, 5mL of 1M H_2SO_4 acid and 1.25mL of 3% H_2O_2 were added and the mixture was shaken gently until the slightly violet colored permanganates decolorized. A red-brown colored mixture was obtained. It was then diluted up to the mark with distilled water. The absorbance of the sample was measured by a visible-detection at 450nm like the standard solutions. The concentration and/or mass of vanadium were evaluated from the slope of the calibration graph plotted between absorbance and concentrations of the standard solutions.

2.3 Methods

In this study, the method used to synthesis the complex is template method. The ligand is formed in the presence of the VO^{2+} cation that enhances the reaction rate by a particular geometrical orientation imposed by metal coordination.

2.3.1 Qualitative Tests

1. Purity test: The purity of the synthesized complex was checked by thin layer chromatographic (TLC) methods. A mixture of solvents in appropriate ratios (1:5 v/v of DMSO: $CHCl_3$) has been used as a mobile phase due to the insolubility of the complex in most solvents.

2. Sulphate test: The presence of sulphate ion in the complex was tested by adding 2N barium chloride solution to a solution of VO(IV) complex digested by concentrated nitric acid. This has been done to see whether a white precipitate of barium sulphate formed.

3. Vanadyl cation, VO^{2+}, test: The presence of the Vanadyl ion has been tested by the addition of 2N NaOH solution to the solution of the complex prepared to check whether a brown suspension of oxovanadium (IV) hydroxide forms.

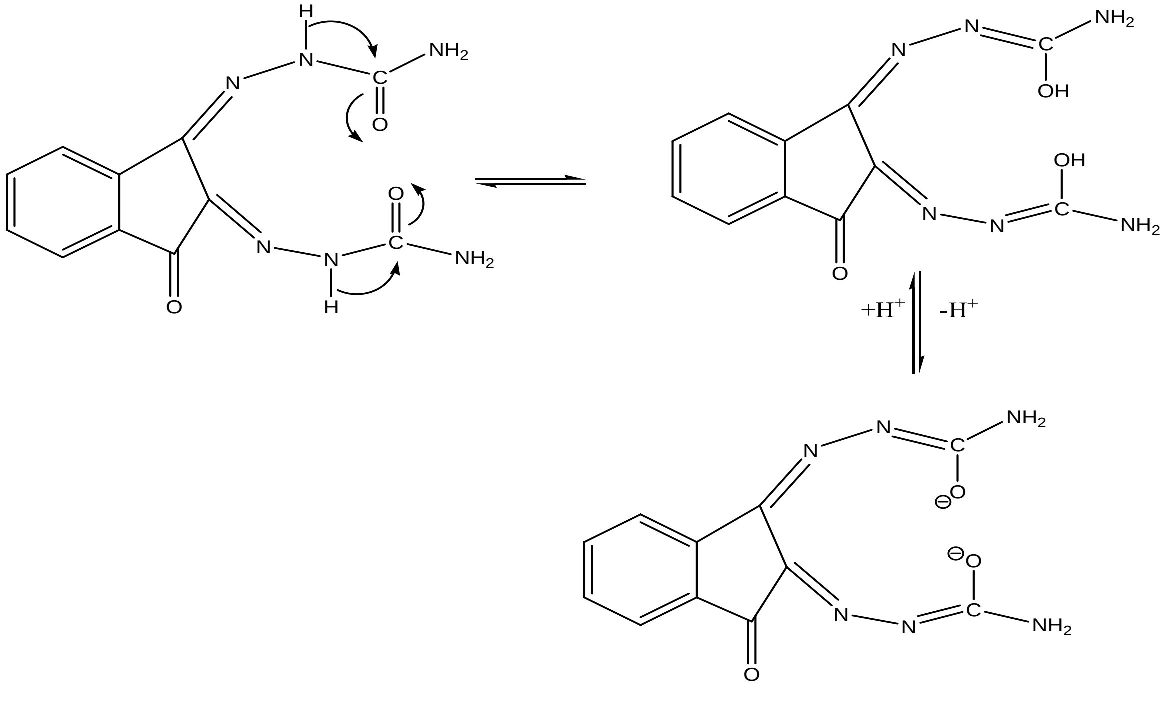
2.3.2 Quantitative Test

The amount of vanadium in the complex was estimated by spectrophotometric analysis. This has been done by adding H_2O_2 to a solution containing H_2SO_4 solution and comparing colorimetrically against a standard having the same acidity and containing the same volume of H_2O_2 solution. The mass and/or concentration of vanadium in the complex were then evaluated from the slope of the linear curve obtained from the calibration graph constructed between the absorbance and concentrations of the standards. Full procedure is explained in detail in section 2.2.3.

3. RESULT AND DISCUSSION

3.1 Enolization of the Ligand 1,2-disemicarbazone-indan-3-one (DSCI)

In this study, the ligand was formed in the presence of the metal ion (VO^{2+} ion) by the template method. The free ligand and its Ni(II) complex have been synthesized and characterized previously in our laboratory [27]. The ligand is behaving as a neutral tetradentate ONNO donor ligand coordinating via the two-azomethine nitrogen atoms and the two oxygen atoms of the amide carbonyl groups to Ni(II). When semicarbazide hydrogen chloride and ninhydrin are reacted in the presence of vanadyl sulfate, immediate condensation to the Schiff base, deprotonation of the enolised amide group and coordination to the vanadyl cation occurs [28]. Hence, coordination has been occurred via the two azomethine nitrogen atoms and the two oxygen atoms obtained by the deprotonation of the enolised amide oxygen in the current work. The deprotonation was occurred in situ during the synthesis process. The deprotonation is expected as the synthesized complex was found to contain no sulfate ion. The complex is non-electrolyte.



Scheme-8: Deprotonation of the enolised amide group

3.2 Characterization of the Complex [VO(IV)DSCI]

The template reaction of vanadyl sulfate hydrate with semicarbazide and ninhydrin precursors resulted in the formation of a characteristic complex VO(IV)-1,2-disemicarbazone-indan-3-one. The synthesis of the complex by the template method was accompanied by characteristic color changes during the course of the reaction - blue to yellow and then to light green was observed.

3.2.1 General Characteristics of VO (IV) complex

The synthesized VO (IV) complex of 1, 2-disemicarbazone-indan-3-one is colored. It is solid, stable in air and moisture. The complex is soluble in DMF and DMSO, insoluble in water and other common solvents. The complex has specific melting ranges. The general physical characteristic of the complex is given in Table-2 below.

Table-2: General Physical Characteristics of the Complex and the precursors

Compound	Mol. Wt.	Color	Melting/decomp. Temp.	Yield in %
Ninhydrin	178.3	Pale yellow	240-245 °C	-
Semicarbazide	111.5	white	175 °C	-
[VO(IV)DSCI]	339	Light green	287-290°C	70

3.2.2 Analytical Studies

3.2.2.1 Qualitative Test

1. Purity Analysis

The purity of the complex was checked by using the thin layer chromatographic (TLC) method [29]. This has been done by using silica coated aluminum plates as stationary phase and a 1:5 volume ratios of DMSO /chloroform as a mobile phase. A single spot was detected. This indicates that the complex is some what pure.

2. Sulfate Analysis

The presence of sulfate ion in the synthesized complex was tested by using a solution of barium chloride. The complex was first digested in concentrated nitric acid. To the saturated solution of the complex, dilute solution of barium chloride was added and the mixture was allowed to stand overnight to give enough time for precipitation to form. No precipitate was observed. The absence of a white precipitate indicated the absence of sulfate ions in the complex.

3. Vanadyl Cation, VO^{2+}, Analysis

V (IV) exists as vanadyl cation, VO^{2+}, in acidic solution [30]. In this work, the presence of this cation was tested by using 2N sodium hydroxide solution. The formation of a brown suspension vanadium hydroxide when 2N NaOH was added to the solution of oxovanadium (IV) complex confirmed the presence of VO^{2+} cation in the complex [30].

3.2.2.2 Quantitative Determination of Vanadium by Spectrophotometric Analysis

When H_2O_2 is added to a solution containing small quantities of vanadium (V) (up to 0.1mg of vanadium per mL) in sulfuric acid solution, a reddish-brown coloration is produced. This is thought to be due to the formation of a compound of the type $(VO)_2(SO_4)_3$ [31]. A large excess of H_2O_2 tends to reduce the color intensity and to change the color from red-brown to yellow. In this study, the vanadyl sulphate method was used for the determination of vanadium in the synthesized VO(IV) complex. Addition of 5mL of 1M H_2SO_4 acid solution and 1.25mL of 3% H_2O_2 to both the prepared standard solutions of known concentration and volume, and to the sample solution of unknown concentration and known volume resulted in the formation of red-brown colored solutions. The absorbance of both the standard and the sample solution were recorded at specific wavelength of 450nm according to the procedure from a literature [31]. The recorded absorbance values for the standards corresponding to the concentrations 7.84×10^{-5}M, 1.18×10^{-4}M, 1.57×10^{-4} M and 1.96×10^{-4} M were 0.054, 0.064, 0.073, and 0.082 respectively.

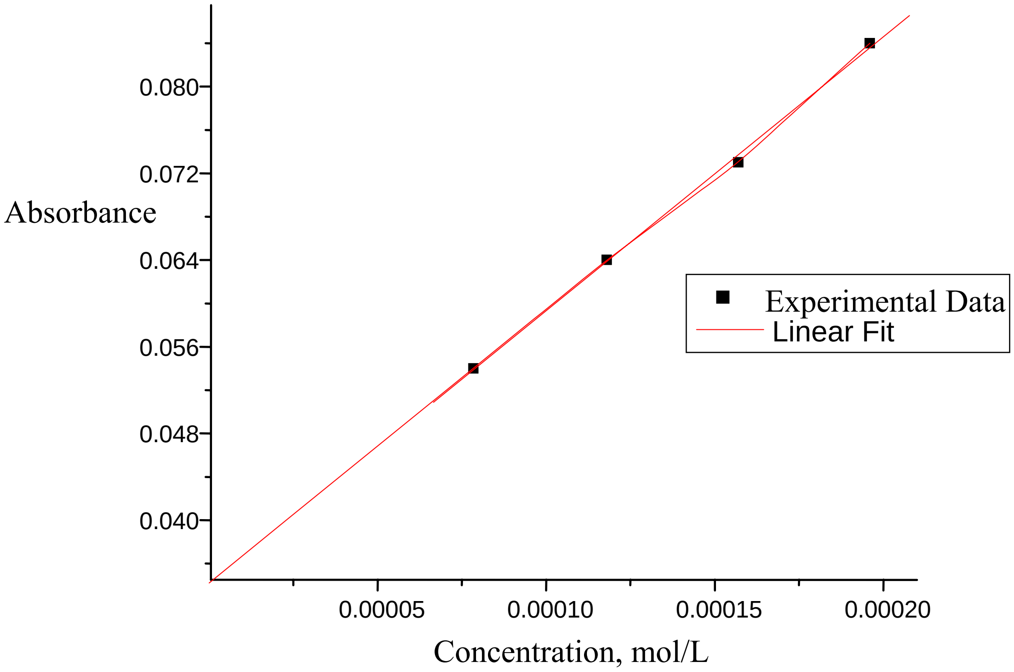


Figure- 15: Beer-Lambert's law: Calibration graph of Absorbance Vs Concentration

From the graph plotted between these absorbance values of the standards and their concentrations, it was observed that Beer's law was obeyed by the linear plot passing through the origin. The concentration and/or mass of vanadium in the complex were evaluated from the slope of the linear graph. That is, $\mathbf{A = \varepsilon lc}$, from which $\boldsymbol{\varepsilon} \mathbf{l} = A/c$ where $\boldsymbol{\varepsilon} \mathbf{l}$ represents a slope. The concentration of the unknown can then be determined by using the formula:

$$c = A/\boldsymbol{\varepsilon}\mathbf{l}$$

or the mass can be directly obtained by the formula:

$$m = AM/\boldsymbol{\varepsilon}\mathbf{l}$$

if m is the quantity per litre and M molar mass of the compound expressed in gram, **A** is absorbance, **c** is molar concentration , l is path length in cm and **ε** molar absorption coefficient in $Lmol^{-1}cm^{-1}$. The details are given in Table-3 below.

Table-3: Amount of vanadium in VO (IV) Complex from Spectrophotometric Analysis

Slope from the linear regression in L/mol	Absorbance of the sample at 450 nm	Mass of vanadium found (g)	Mass of vanadium found (%)	Mass of vanadium calculated (%)
252.67	0.088	0.002963	14.80	15.04

The above data indicated that the amount of vanadium in the complex synthesized is in close agreement with the theoretically calculated value from the estimated structure of the complex. This in turn confirms the metal to ligand ratio is 1:1.

3.2.3 Molar Conductance

The molar conductance of the complex is given in Table-4. The conductivity value of 10^{-3} M DMF solution of the complex was found to be almost zero which indicates the non-electrolytic nature of the complex. This property of the complex enabled us to predict the structure of the complex.

Table-4: Molar Conductance Values of the Complex

Compound	Molar conductance in Scm^2mol^{-1}
[VO(IV) DSCI]	Non-electrolyte

3.2.4 Magnetic Properties

The magnetic susceptibility was measured as gram susceptibility, χ_g, at 21 °C and was obtained to be 3.130×10^{-6} for oxovanadium (IV) complex. The following calculations were made to arrive at the magnetic moments:

Molar magnetic susceptibility (χ_M) = χ_g x Molecular weight of the compound.

χ_M is subjected to diamagnetic correction to obtain corrected molar magnetic susceptibility (χ_M^{corr}.), from which the magnetic moment is finally calculated.

Magnetic moment (μeff) = 2.828(χ_M^{corr} x T)$^{1/2}$ (in B.M.)

All substances, even paramagnetic substances, contain some closed shells of electrons as diamagnetism is attributed to the interaction of closed-shell electrons with applied magnetic field. Consequently, paramagnetic substances have a negative (diamagnetic) contribution to their net susceptibility. We use the relation:

$$\chi_M^{corr} = \chi_M - \chi_{dia}$$

Because the diamagnetic contribution, χ_{dia}, is always negative, the corrected molar susceptibility, χ_M^{corr}, is always greater than the uncorrected value [32]. The magnetic moment at the given temperature for VO(IV) complex is given in Table-5 below. The experimental room temperature magnetic moment (B.M.) represents paramagnetism due to VO(IV)-d^1 electron configuration in the complex. Oxovanadium(IV) complexes are expected to have a magnetic moment of 1.73BM, regardless of the geometry, when the orbital contribution is completely quenched by low symmetry fields. In the compound studied, VO(IV)-DSCI complex has a magnetic moment of 1.67BM, which is in the range of the moments of most oxovanadium(IV) complexes [33]. This value for oxovanadium (IV) complex is consistent with five coordinate square pyramidal geometry of the complex.

Table-5: Magnetic Moments of VO (IV) Complex

Complex	μeff, BM (Theoretical)	μeff, BM (Experimental)
VO(IV)L	1.73	1.67

3.2.5 Electronic Spectra

Oxovanadium (IV) complexes have extremely short V=O bond compared to the other equatorial vanadium-ligand (V-L) bonds. Such complexes are therefore under tetragonal compression such that of the five 3d orbitals the dz^2 orbital is the most destabilized. The relative ordering of the d orbitals is then: $d_{xy} < d_{yz} < d_{x2-y2} < d_{z2}$. Such complexes should exhibit three d-d transitions:
$d_{xy} \rightarrow d_{xz}, d_{yz}$; $d_{xy} \rightarrow d_{x2-y2}$; $d_{xy} \rightarrow d_{z2}$ [33]. The assignments of electronic spectral bands of VO^{2+} complexes have been a matter of controversy [34]. Ballhausen and Gray (BG) have provided a convenient energy level scheme for these complexes. In general, oxovanadium (IV) complexes

display 3 low intensity bands in the 10,000-30,000 cm^{-1} range. According to the BG scheme, the first and subsequent charge transfer transitions are predicted to occur at higher energies (beyond 30,000 cm^{-1}) and often band III is not observed, but is thought to be buried beneath the low energy tail of the much more intense charge transfer band. Following the ordering of energy levels (BG scheme), the first band, which is centered at ca 13,000 cm^{-1}, is assigned to an unresolved band resulting from the $d_{xy} \rightarrow d_{xz}$, d_{yz} ($^2B_2 \rightarrow {}^2E$) transition. The second band (in region 15,000-16,000 cm^{-1}) is attributed to $d_{xy} \rightarrow d_{x2-y2}$ ($^2B_2 \rightarrow {}^2B_1$) transitions. The band at about 23,000 cm^{-1} may either be assigned to the $d_{xy} \rightarrow d_{z2}$ ($^2B_2 \rightarrow {}^2A_1$) transition or thought to be a low energy charge transfer band [34].

The electronic spectra of oxovanadium(IV) complex recorded in DMF as a solvent exhibited two bands at 283 nm and 325 nm characteristics of the $\pi \rightarrow \pi^*$ transition and LMCT transition overlapped with the lower energy intra-ligand band respectively (Appendix-1). The expected d-d transitions for the five coordinate square pyramidal VO(IV) complex which consist of three bands as explained above was not well resolved in this work. This is probably due to the very limited solubility of the complex in various solvents. Nevertheless, it is possible to propose the geometry of the complex to be a five coordinated square pyramidal with a formula of [VO(IV)DSCI] based on the analytical, conductance, and magnetic susceptibility data.

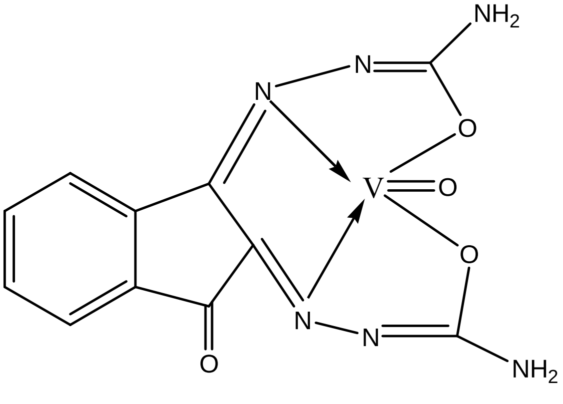


Figure- 16: Proposed structure for [VO(IV)DSCI]

4. CONCLUSION

Ninhydrin and semicarbazide undergo a condensation reaction to give a Schiff base ligand 1, 2-disemicarbazone-indan-3-one, DSCI, in the presence of the VO^{2+}cation. This ligand undergoes immediate deprotonation of the enolized amide group and coordination to the metal ion via the azomethine nitrogen and enolic oxygen atoms forming a distinctly colored complex. DSCI was shown to behave as a tetradentate ONNO donor. Based on the procured data interpretation, a square-pyramid is proposed for the complex.

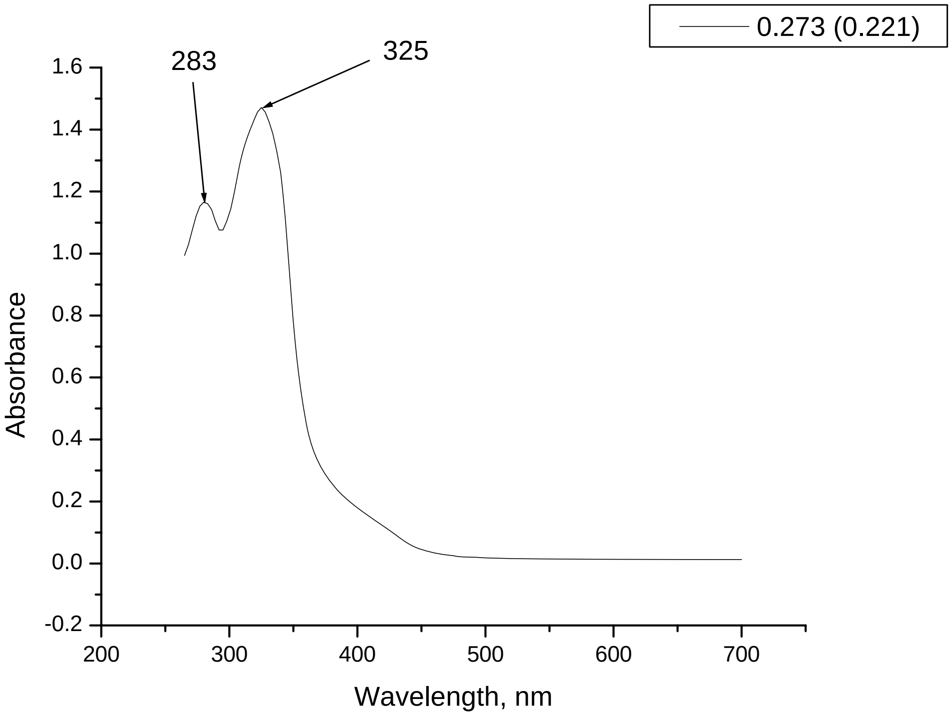
5. REFERENCES

1. Kumar S., Dhar, D. N., and Saxena, P. N. (2009). Application of metal complexes of Schiff bases-A review. *J. SCI. IND. RES. 68*
2. Mishra, A. P., Mishra R. K., and Shrivastava, S. P. (2009). Structural and antimicrobial studies of coordination compounds of VO(II), Co(II), Ni(II) and Cu(II) with some Schiff bases involving 2-amino-4-chlorophenol. *J. Serb. Chem. Soc. 74 (5) 523–535*
3. Raman N., Raja, S.J., Joseph, J., Sakthivel A., and Raja, J.D. (2008). Designing, synthesis, spectral characterization of antimicrobial and dna activetridentate schiff base ligands and their complexes. *J. Chil. Chem. Soc., 53 (3)*
4. Hakim, A., Ahmed, A. and BenGuzzi, S. A. (2008). Synthesis And Characterization of Some Transition Metals Complexes of Schiff Base Derived from Benzidine and Acetyl acetone**.** *Journal of Science and Its Applications 2(1), 83-90*
5. Taye Tilahun. (2007). Synthesis and characterization of metal complex with Ninhydrin and O-Phenylenediamine Derivatives. M.Sc Thesis, AAU, Chemistry Department
6. Friedman, M. (2004). Applications of the Ninhydrin Reaction for Analysis of Amino Acids, Peptides, and Proteins to Agricultural and Biomedical Sciences. *J. Agric. Food Chem. 52, 385-406*
7. Ramachandran S. (2007). Synthesis DFO Derivatives and their Application to Fingermark detection. Ph.D Thesis Submitted to the University of Auckland, New Zealand.
8. Mehabaw Getahun, Raju, V.J.T. and Negussie Reta. (2002). Synthesis and characterization of some metal complexes of Schiff base derived from ninhydrin and alpha,L-alanine. *Bull.chem.soc.ethiop. 16(1), 53-64*
9. Wu, Y., Hussain, M. and Fassihi, R. (2005). Development of a simple analytical methodology for determination of glucosamine release from modified release matrix tablets. *Journal of Pharmaceutical and Biomedical Analysis 38, 263–269*
10. Robert, R. M, Gilbert, G. C. and Martin, S. F. (1994). Experimental Organic Chemistry: A Mini-scale Approach. Saunders College Publishing, Fort Worth, 394-397
11. Leovac, V. (2003). Transition Metal Complexes with Thiosemicarbazied- based Ligands; *J.Serb.Chem.Soc. 68(12)919–927*

12. Leovac, V. M., Jevtovi, V. S., Jovanovi, L. S. and Bogdanovi, G. A. (2005). Metal complexes with Schiff-base ligands: pyridoxal and semicarbazide-based derivatives. *J. Serb. Chem. Soc. 70 (3) 393–422*
13. Leovac, V. M., Markovi, S., Divjakovi, V., Szecsenyi, K. M., Joksovi, M. D. and Leban, I. (2008). Structural and DFT Studies on Molecular Structure of Nickel(II) Chloride Complex with Pyridoxal Semicarbazone (PLSC) : Unusual Coordination Mode of PLSC . *Acta Chim. Slov. 55, 850–860*
14. Srivastava, A. K. and Mehdi M. Z. (2004). Vanadium and diabetes mellitus, Diabetic Medicine, **22**, 2–13
15. Cotton, F.A., Wilkinson, G. and Gaus, P. L. (1970). Basic Inorganic chemistry. 2nd ed, John Wiley & Sons, New York, 483-484.
16. Cotton, F.A, Wilkinson, G., Murillo, C. A. and Bochmann M. (1999). Advanced Inorganic Chemistry, 6th ed, John Wiley & Sons, New York, 714-727
17. Paresh, K. M. (2009). Synthesis and Characterization of Oxovanadium Complexes Featuring O- and N- Environment. M.Sc Thesis submitted to Deemed University, India
18. Khalil, Saied M. E. and El-Shafiy, Hoda F. O. (2000). VO(IV), Fe(III), Co(II) and Cd(II) Complexes of Asymmetric Schiff Base Ligands (N_2O_3): Synthesis and Spectroscopic Studies; Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 30(9), 1817 — 1833
19. Temel, H., Canker, U. and Ugras, H.I. (2004). Synthesis and Characterization of a Novel Oxovanadium(IV) Complex and Conductometric Studies with N,N,O bis(Salicylidene)-1,2-bis- (p-aminophenoxy)ethane. Synthesis and reactivity in inorganic and metal-organic chemistry 34 (4), 819–831
20. Osowole, A. A. (2008). Syntheses and Characterization of Some Tetradentate Schiff-Base Complexes and Their Heteroleptic Analogues. *E-Journal of Chemistry, 5 (1), 130-135*
21. Thakur, S. N., Yadav, K. S., Singh, N. P. and Yadav, H. S. (2008). Template Synthesis and Characterization of Oxovanadium (IV) Complexes with Tetraaza Macrocyclic Ligands and Their Activity on Potato Virus X. *J. Iran. Chem. Soc., 5 (2), 328-335*
22. Koo, B. K., Jang, Y. J. and Lee, U. (2003). Vanadium (IV) Complexes with N, N, S-Donor Systems. *Bull. Korean Chem. Soc. 24 (7).*

23. Mishra, A. P. and Soni, M., (2008). Synthesis, Structural, and Biological Studies of Some Schiff Bases and Their Metal Complexes. Metal-Based Drugs
24. Manivannan, V., Hoffman, J. T., Dimayuga, V. L., Dwight, T., and Carrano, C. J. (2007). A comparison of vanadyl acetylacetonate complexes of N_2O heteroscorpionate ligands that vary systematically in donor set. *Inorganica Chimica Acta 360(9), 529–534*
25. Ghosh, T. and Mondal B. (2008). Mixed-ligand Hydrazonato-Oxovanadium(V) Complexes incorporating Salicylaldehyde as Co-ligand. *INDIAN J CHEM, SEC A*
26. Jamal, R. A. (2007). A Detailed Spectroscopic Study of Quadravalent Oxovanadium Complexes of Aroylhydrazine, Ph. D Thesis submitted to University of Karachi
27. Gizaw G/Silassie (2007). Studies on Ni(II) Complex derived from Ninhydrin disemicarbazone, M.sc Thesis submitted to Addis Ababa University.
28. Rehder D., Vergopoulos, V., Priebsch, W., and Fritzsche, M. (1993). Binding of L-Histidine to vanadium. In Hawthorne, M.F. (ed) *Inorg. Chem. , 32, 1844-1849*
29. Vogel, A. I. (1961). A Textbook of Quantitative Inorganic Analysis, 3rd edition, Lowe and Brydone, London
30. Vasilyeva, Z., Granovskaya, A., and Taperova A. (1986). Laboratory Manual for General and Inorganic Chemistry, Mir Publishers, Moscow, 249-250.
31. Basset, J., Denny, R. C., Jeffery, G. H. and Mendham, J. (1978). Vogel's Textbook of Quantitative Inorganic Analysis; 4th ed., Longman Group Limited; Longman, 752-753
32. Jolly, W. L. (1970). The Synthesis and Characterization of Inorganic Compounds. Prentice-Hall, Inc.
33. Dutta, R. L. (1989). Inorganic Chemistry, 3rd ed. The New Book Stall, Calcutta, 275-276.
34. Agarwal, R. K., Singh, L., Sharma, D. K., and Singh, R. (2005). Synthesis, Spectral and Thermal Investigations of Some Oxovanadium (IV) Complexes of Hydrazones of Isonicotinic Acid Hydrazide. *Turk J Chem 29, 309 – 316.*

Appendix- 1: Electronic spectra of [VO(IV)DSCI] complex



Declaration

I the undersigned confirm that this project work 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 have been duly acknowledged.

Name: _____________________ Signature: ________________

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

Advisor: ______________________
Signature: _____________________

Place and date of submission: School of Graduate Studies
Addis Ababa University
June, 2010