ADDIS ABABA UNIVERSITY

OFFICE OF RESEARCH AND GRADUATE PROGRAM

GRADUATE PROJECT
CHEM 774

Synthesis and Characterization of Oxovanadium (IV) Complexes of Multidentate Ligands Derived from Symmetric Triazines

BY

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July 2006

Synthesis and Characterization of Oxovanadium (IV) Complexes of Multidentate Ligands Derived from Symmetric Triazines

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M. Sc. PROJECT SUBMITTED

TO

DEPARTMENT OF CHEMISTRY

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July 2006

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Acknowledgment

I would like to express my deepest and truthful gratitude and respect to my advisors Prof. V.J.T. Raju and Dr. Yonas Chebude for their significant observations and direction, invaluable advice and guidance, continuous supervision and encouragement, assistance and support that greatly encouraged me to accomplish this project work.

I am also thankful to Prof. Negussie Retta for his invaluable suggestions and comments. I would acknowledge Dr. Peter Licence and Mr. Butler, University of Nottingham for the Elemental Analysis data. I would express my thank to Dr. Teketel Y. for providing the supporting electrolyte to run the CV. I also acknowledge the cooperation of Assefa, Ashenafi and Muluken in conducting the experiment.

I would like to express my pleasure and hearty gratitude to my wife, Desta Mengistie, my father, Mamo Mengistu, my mother, Sinke Deneke and my sisters, Misrak Mamo, Meskerem Mamo, Mulu Mamo and Addisalem Mamo for their moral and material help. I truly want to extend my appreciation to Yeshewawork Asmamaw and Aynalem Tsige for their consistent advice and material help in all of my personal and social troubles.

I would also like to acknowledge my colleagues (classmates). I am thankful to Belina Terfasa for his support to run UV-Vis spectroscopy and his advice.

Finally I am very grateful to the department of chemistry, Dila university college (DUC) for giving me the opportunity to undertake this postgraduate study.

List of abbreviation

tbp	trigonal by pyramidal
tpt	2,4,6 tri (4-pyridyl) 1,3,5-triazine
acac	acetyl acetone
DMF	dimethylformamide
DMSO	dimethylsulfoxide
TMS	tetramethylsilane
$CDCl_3$	duterated chloroform
$DMSOd_6$	hexaduetrated dimethylsulfoxide
TLC	Thin layer Chromatography
LMCT	ligand to metal charge transfer
UV-	ultraviolet
BMOV	Bis (maltolato) oxovanadium (IV)
DCPTZ	Synthesis of 4-Phenoxy-2,6-Dichloro s-Triazine
HBHTZ	4-hydroxy-2,6-Bis (Hydrazino)-s-Triazine
HBHATZ	4-hydroxy-2,6-Bis (Hydroxyamino)-s-Triazine
VO(II)-HBHT	4-hydroxy-2,6-bis(hydrazino) s-triazine vanadyl(II)
$VO(II)-(HBHAT)SO_4$	4-hydroxy-2,6-bis(hydroxyamino)-s-triazine-μ-sulphatovanadyl(II)

Synthesis and Characterization of Oxovanadium (IV) Complexes of Multidentate Ligands Derived from Symmetric Triazines

Abstract

Two new vanadyl(IV) complexes with s-triazine based ligands, 4-hydroxy,2,6,bis (hydrazino)-s-triazine and 4-hydroxy-2,6-bis(hydroxyamino)-s-triazine were synthesized and characterized by elemental analysis, electronic, FTIR, ^{1}H NMR, ^{13}C NMR spectroscopy. In addition magnetic susceptibility, cyclic voltammetry, conductivity measurement, melting point determination and vanadium and sulphate estimation were also undertaken. Elemental analysis and IR data revealed bi-dentate nature of the ligand and participation of SO_4^{2-} in coordination of the VO(II)-HBHATZ complex. The non-electrolytic nature of complexes was ascertained from conductivity measurements UV-Vis and magnetic susceptibility measurements indicate a square pyramidal geometry of the complex.

1. Introduction

The relationship between the structure of benzene and that of pyridine extends to other six membered conjugated ring systems with more than one nitrogen atom in the ring. There are altogether eight heterocyclic systems known, (including pyridine) which have one or more sp^2-hybridized nitrogen atoms in the ring [1]. They are shown in figure 1.

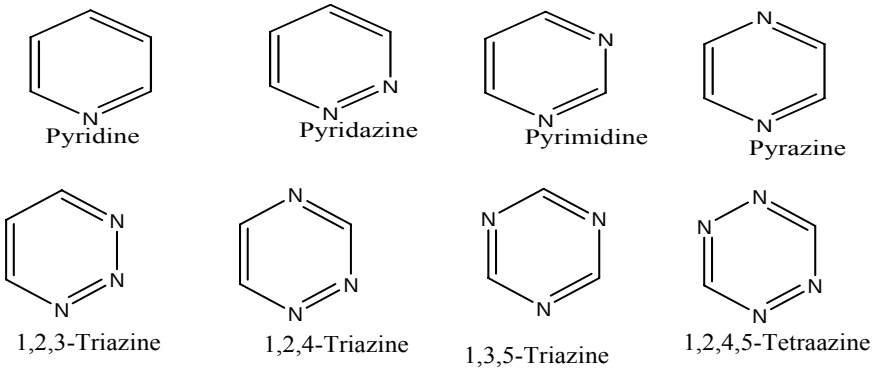


Figure 1. Aza derivatives of benzene.

The reduced π electron density at the carbon atoms compared with those of benzene, particularly at the 2 and 4 positions is illustrated for pyridine by the calculated values shown in figure 2 [2].

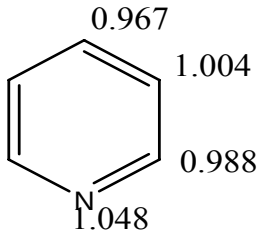


Figure 2. Distribution of π-electron density in pyridine (calculated by an abinitio method)

As the number of nitrogen atoms in the ring increases, the reduction of electron density at carbon becomes more marked, the energies of the π-molecular orbitals are lowered, particularly those orbitals with large coefficient on nitrogen. For this reason the aromatic heterocycles of this type are often referred to as π-deficient heterocyclic compounds. As a result, electrophilic attack on the ring carbon atoms becomes increasingly difficult and nucleophilic attack becomes easier [3].

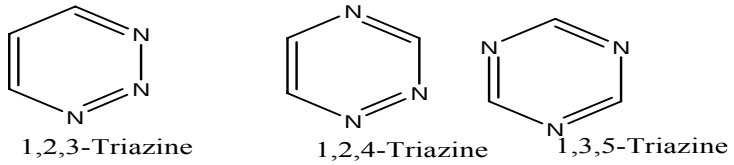
These heterocycles, diazine, triazines and tetrazines can all be regarded as quite stable and aromatic in character, although their resonance energies are lower than those of benzene and are rapidly decomposed by water [4]. They have non- bonding lone pairs of electrons on nitrogen, which allow hydrogen bonding. This, with the dipole moment accounts for the water solubility of these compounds. They are also weaker bases [5].

With the sole exception of C-5 of pyrimidine all the ring carbon atoms in these heterocycles lie ortho or para to at least one ring nitrogen atom. These provide selective activation of specific positions in the ring systems [6].

1.1. Chemistry of s-Triazine and its Derivatives

The six membered heterocycle consisting of three nitrogen atoms and three carbon atoms alternately located in the ring is known as the symmetrical triazine ring system [7]. This heterocycle is originally abbreviated as s-triazine (or symmetrical Triazine), although the designation 1, 3, 5-triazine is also common; numbers refers to ring nitrogen atoms. The s-triazine (III) system was also known as kyandine (cyanidine), γ- triazine, hydrogen cyanide trimer or vedita [4]. Ring nitrogen positions 1, 3 and 5 are equivalent, as are ring carbon positions, 2, 4 and 6.

The other two isomeric six member hetrocycles containing three nitrogen and three carbon atoms in the ring are asymmetrical triazine (II) designate as-triazine (asym–triazine), 1,2,4-triazine, α–triazine or iso–triazine and vicinal triazine (I) designated v-triazine (Vic-triazine), 1,2,3-triazine, or β - triazine.



I II III

Figure 3. The isomers of triazine.

X–ray studies on triazine have shown that the carbon nitrogen distances are all 1.317Å, and that the ring is planar but not a regular hexagon. The angles at whose apices lie nitrogen and carbon atoms are 113.2^{o} and 126.8^{o}, respectively [8].

S–triazines are common reagents and readily form derivatives, which are used as pharmaceuticals and herbicides. They are important precursors in formulating bactericides and fungicides and preservation in oil field applications. Triazines are also used as disinfectant, industrial deodorant, biocide in water treatment and as a bleaching agents [9]. Large amounts of triazines are used in the manufacture of resin modifiers such as melamine (2,4,6-triamino-1,3,5-triazine) and benzoguanamine (2,4-diamino-6-phenyl 1,3,5-triazine) [10]. They are also useful as chromophore groups in colorants [11]. A number of triazine containing molecules have been used in crystal engineering and have allowed outstanding new developments in the area of tailored functional materials [12]. They have proven their great potential in the rising area of material chemistry, both for their π–interaction abilities and for their aptitude to be involved in intricate hydrogen – bonded network [13].

S–triazine is highly reactive and unstable, and hence does not normally serve as a starting material for the synthesis of triazine derivatives. The majority of substitution reactions of s–triazines are nucleophilic substitutions of chloro triazines in particular 2,4,6-trichloro s-triazine (cyanuric chloride) and with the exception of triazine prepared by ring forming reaction. Most derivations originate from cyanuric chloride.

Cyanuric chloride exists in the form of white crystals with a pungent odor. The compound is soluble in many non- polar and semi polar organic solvent including acetone, ether, benzene and chloroform. It reacts slowly with water.

Although reactions may occur at the ring nitrogen atoms, most of the reactions of cyanuric chloride involve the chlorine atoms, which can be made to react selectively one or more at a time, with nucleophilic reagents. The reactivity of cyanuric chloride may be compared to that of acid chlorides and in fact, cyanuric chloride may be considered as a nitrogen analogue of an acid chloride.

Cyanuric chloride is an excellent synthon for the straightforward preparation of highly structured multi topic molecules. Indeed each chloride atom of 2,4,6-trichloro-1,3,5-triazine can be substituted by any nucleophile (figure 4). The first substitution is exothermic and so the reaction mixture must be cooled down to 0 ^{o}C. The second chloride substitution can be performed at room temperature finally the third position is functionalized under solvent reflux.

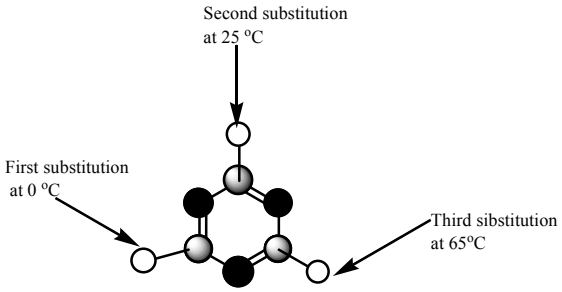


Figure 4. Differential reactivity of 2,4,6-trichloro-1, 3,5-triazine[6]

Therefore, by carefully controlling the reaction conditions, 2,4,6 trisubstituted triazines can be synthesized by selective addition of nucleophiles such as, amines, alcohols, thiols or Grignard reagents. The yield of each substitution often exceeds 95% and the symmetric trisubstituted derivatives can be obtained in a one-pot synthesis. Various solvents can be used such as tetrahydrofuran (thf), acetonitrile, diethyl ether, and 1,2 dimethoxy ethane.

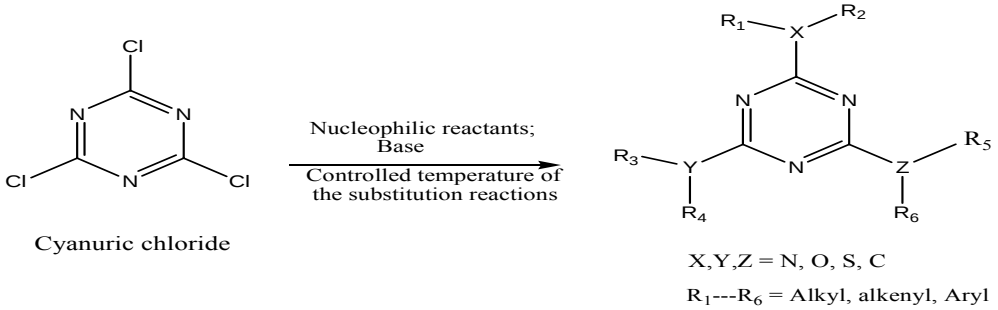
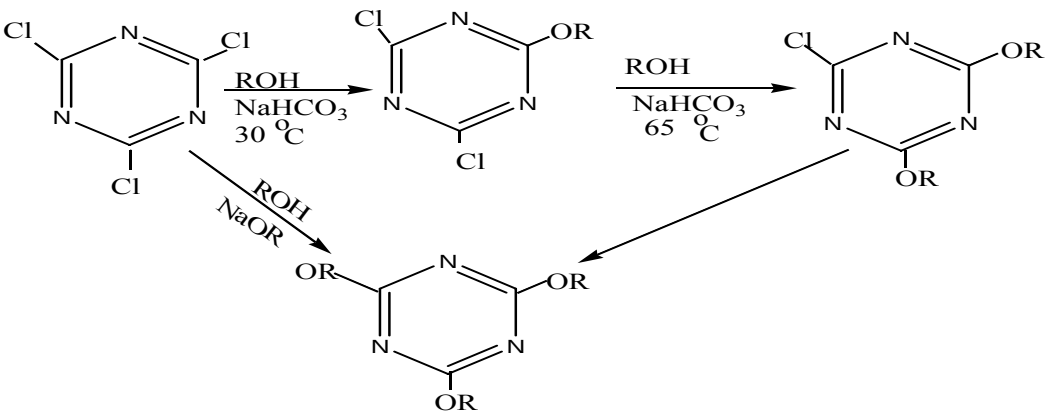


Figure 5. Preparation of polyfunctional triazine derivatives.



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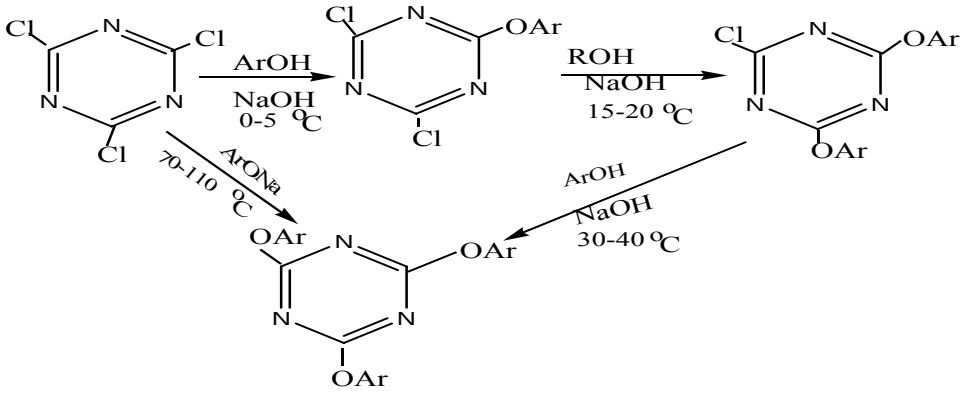

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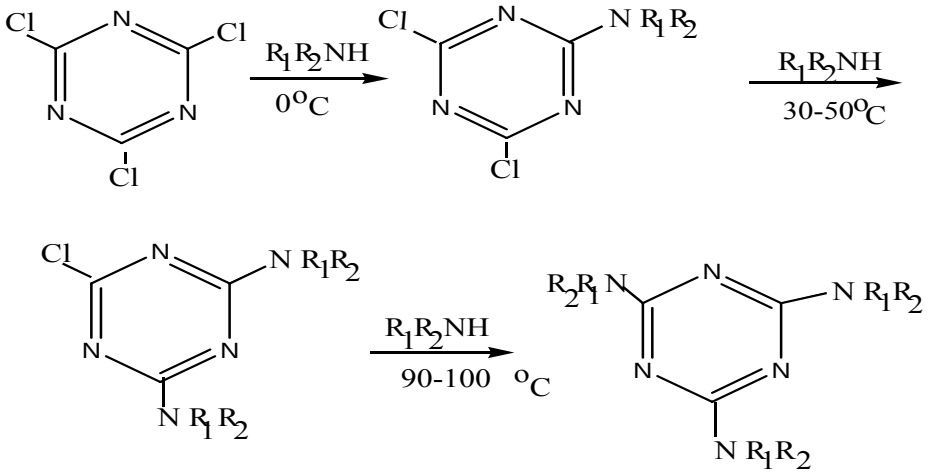

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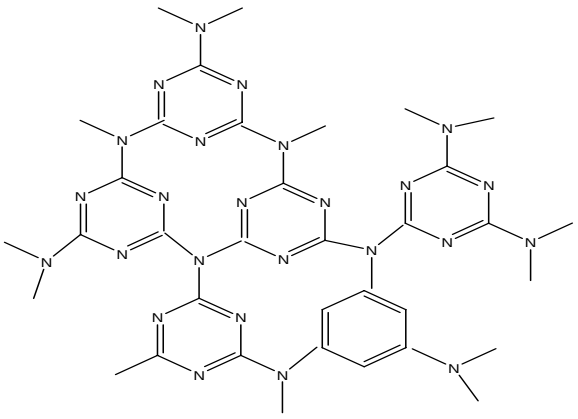
Figure 6. Reactions of cyanuric chloride a) With 10 % NaOH
b) With alcohols and phenols c) With amines

Reaction of cyanuric chloride or its partially aminated derivatives with ammonia or with primary or secondary amines affords a convenient route to substituted melamine (2,4,6 triamino s–triazines).

The reactions of cyanuric chloride have been summarized by Fierz David and Matter but besides its reaction with ammonia and a few amines most of which were aromatic, the formation of amino chloro s-triazines has not been generally studied until recently [14].
If the basic character of an aromatic amine is sufficiently reduced by negative groups, the last halogen of cyanuric chloride cannot be replaced.

Cyanuric chloride is considered as a suitable molecular precursor for the synthesis of graphitic forms of carbon nitride (g-C_3N_4). In most of the postulated structures of g-C_3N_4, s–triazine ring systems are linked through N–atoms forming extended 2D sheets (figure 7a).

Recently another possible building block for g-C_3N_4 was taken into account (figure 7b) tri s-triazine rings C_6N_7, which are cross-linked by trigonal N atoms. The possible condensation of three s- triazine rings and the existence of a "cyambeluric nucleus" C_6N_7 (b) was first postulated by Pauling and Sturdyvant [15].



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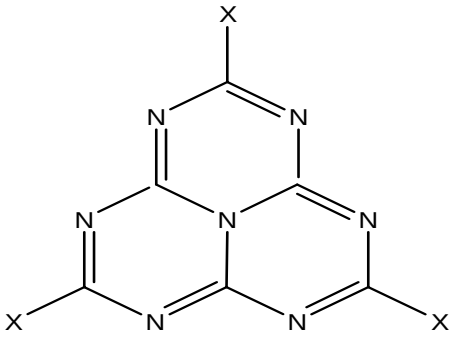

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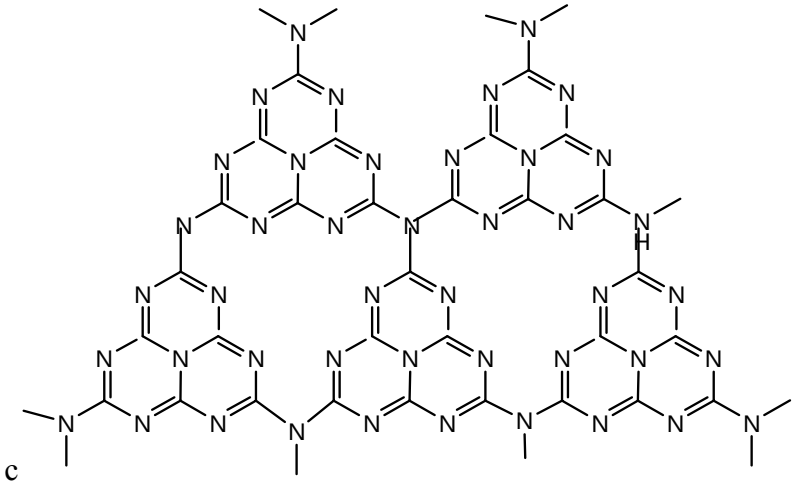


c

Figure 7. a) s-triazines b) cyambeluric nucleus c) tri-s-triazines

1.2. Metal Complexes of s-Triazine Ligand

Metal complexes of biologically active organic compounds have promising applications in view of enhanced lipo solubility and reorganized electron density distributions. Modified antimicrobial, insecticidal, insect growth regulating, herbicidal and plant growth regulating activities of metal complexes derived from active organic ligands have been documented in the literature. Enhancing and diminishing effects on the derivative have been explained on the basis of the coordinating centers and structure of the metal complexes [16].

Symmetrical triazines with Cl, OCH_3, SCH_3,-NR_2 (R = H or allyl) substituents such as simazine, prometons, prometryn, aziprotry etc. have gained world wide recognition for their outstanding herbicidal properties. However, the wide utilization of these herbicides in the crop management has created a challenging problem in terms of residual herbicides. These are remnant herbicides in agricultural production, which are causing serious symptoms in animal and human consumer. Two approaches are currently validating the detoxification of remnant herbicides. One of them is derviatization of the herbicides into less harmful compounds after crop development while the other is metal ion associated degradation or deactivation of the herbicides [17]. Studies have shown that metal ions can show remarkable effect in catalyzing the decomposition of herbicides [16].

Due to the electronegativity difference between nitrogen and carbon, the π-electrons in the ring of s-triazines are located in the vicinity of nitrogen centers. A polar mesomeric form II (figure 8) that bears additional unshared pair of electrons on nitrogen is likely to result in potential metal binding characteristics [18].

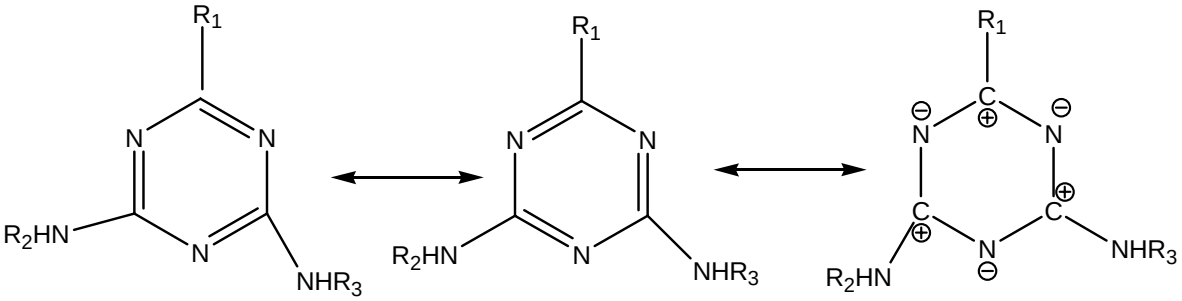


Figure 8. Resonance structure of s-triazines

Coordination compounds from 1,3,5-triazine based ligands are increasingly reported in the literature [19]. This is undoubtedly due to the ease of preparing intricate polydentate star shaped ligands using simple and high yielding reactions especially one ligand, namely 2,4,6-tri-(4-pyridyl)-1,3,5-triazine (figure 9) has been extensively used in the field of crystal engineering during the past ten years.

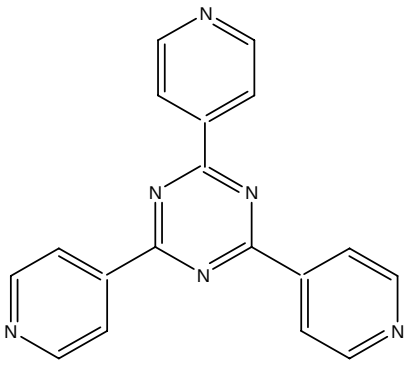


Figure 9. 2,4,6 tri (4-pyridyl) 1,3,5-triazine (tpt)

In 1996, Robson and coworkers described a unique system of two inter penetrating coordination networks based on tpt and copper (I) building blocks (figure 10) [20]. Almost at the same time, Fujita and coworker reported a similar octahedral cage assembled from tpt and palladium (II) nodes.

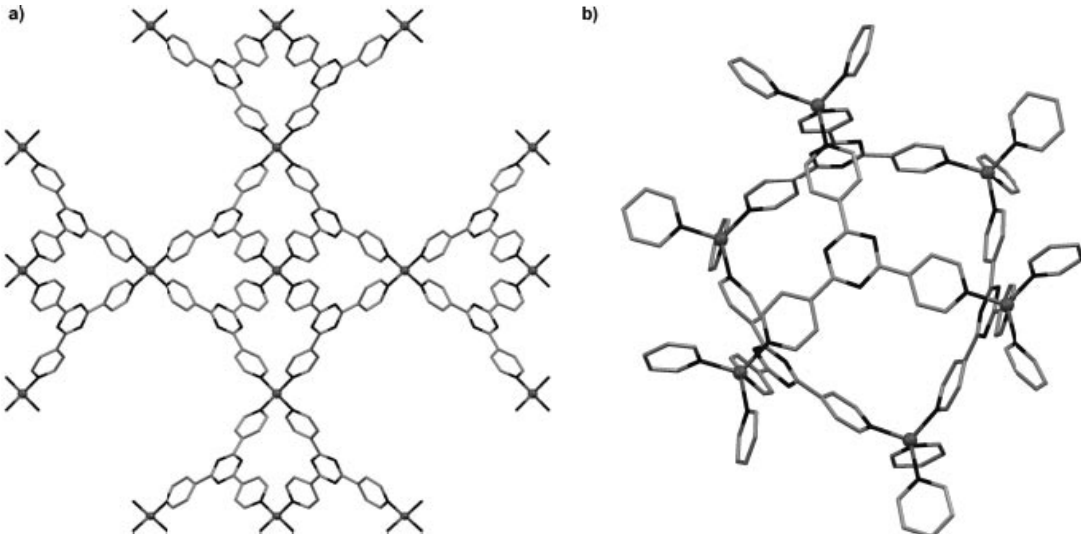
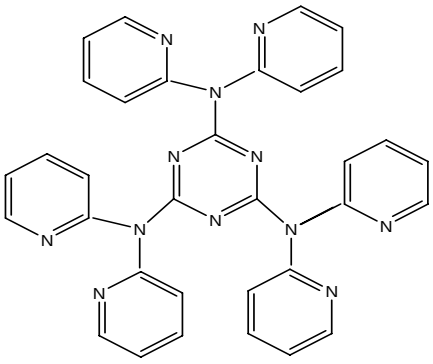


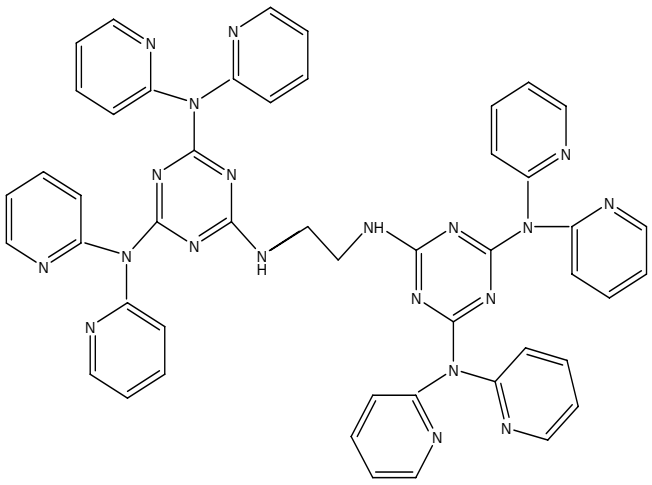
Figure 10. tpt and copper (I) building blocks a) Cubic (3,4)-connected net.
b) Octahedral host chamber

More recently a series of polydentate ligands have been prepared according to the synthetic pathway depicted in figure 4 and some of them are reported in figure 11. The simple dpyatriz ligand arises from the substitution of the three chlorides of cyanuric chloride by 2,2-dipyridyl amine. Reaction of Cu (II) nitrate with dpyatriz in acetonitrile at room

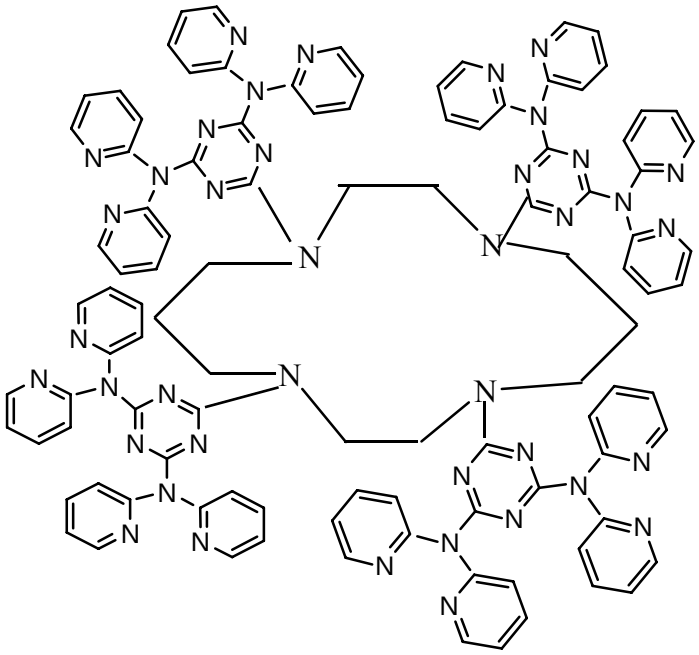
temperature produces a 1D ladder coordination polymer whose crystal structure is depicted in figure 12.



Dpyatriz



Optrizediam



Azadendtriz

Figure 11. s-Triazine based ligands used to prepare supra molecular coordination compounds

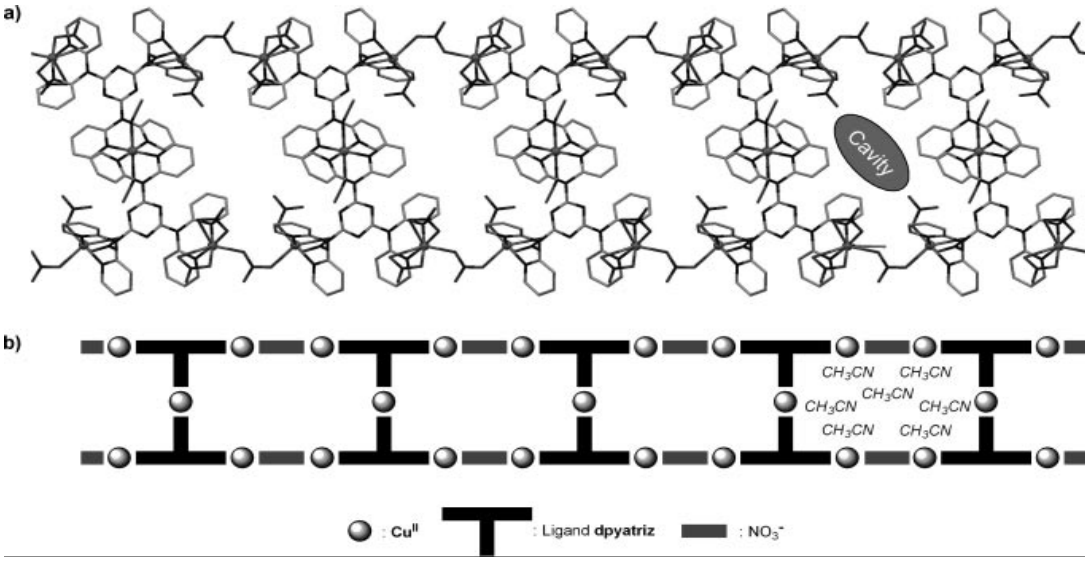


Figure 12. a) 1D ladder coordination polymer obtained from the ligand dpyatriz and $Cu(NO_3)_2$ and b) its schematic representation.

Another attractive coordination compound has been obtained by the extended ligand opytrizediam (figure13). Indeed, the reaction of copper (II) chloride with this ligand in methanol leads to the formation of 1 D zigzag coordination polymer (figure 14). Reaction of copper (II) chloride with the ligand azadendtriz in dichloromethane /water yields the tetra copper complex depicted in figure 12, where the triazinyl groups are stacked two by two in a parallels mode.

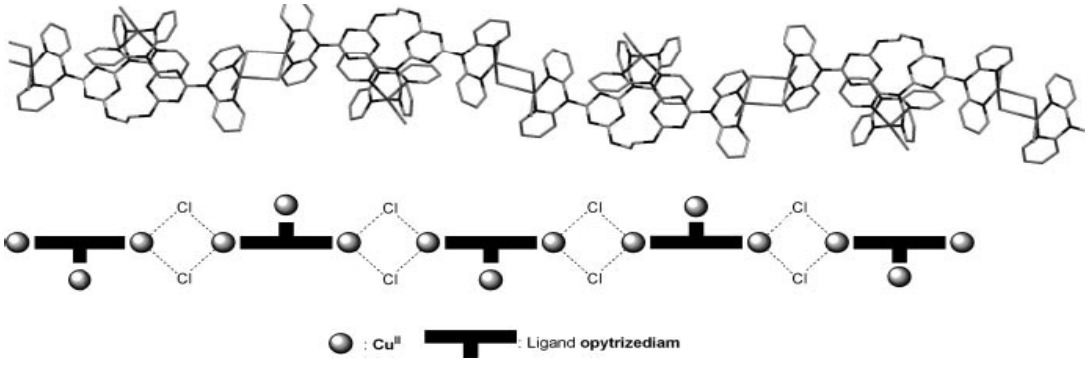


Figure 13. a) 1D zigzag coordination polymer obtained from the ligand opytrizediam and $CuCl_2$ and b) its schematic representation

Interests in synthesis, structure and application of transition and non-transition metal complexes of substituted s-triazine have been shown. Complexes of Ca^{2+}, Sr^{2+}, and Ba^{2+} with tri mercapto triazine, those of Pb^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+} with 2,4,6-tris-(2-pyrdyl) 1,3,5-triazine have been reported [21].

A one dimensional chain [Fe(1,3,5-triazine2,4,6-tricarboxylate)[H_2O]n^{n-} with heptacoordinate Fe(II) centers was prepared by reacting 1,3,5-s-triazine 2,4,6-tri carboxylate with ferric ions in water and investigated for its magnetic properties [22].

The stereochemical aspects and electro chemical properties of Rh (III), Os (III), RU (III), and Re (III) metal complexes with tris-(pyridy)-1,3,5-triazine were reported [23]. Metals, Co (II), Ni (II) Cu(I) Zn(II) complexes with 2,4,6-tris (hydrazino)s-triazine were reported [24].

1.3. Chemistry of Hydrazine and Hydroxylamine

The chemistry of hydrazine (the nitrogen analog of ethane, one of the homologous series of hydronitrogens) has been studies extensively for almost three quarters of a century [25]. Hydrazine, N_2H_4 (figure 14a), in which the oxidation number of nitrogen is -2, and hydroxylamine, NH_2OH (figure 14b), in which it is -1 are isolobal molecules that are formally related to NH_3 by the replacement of an H atom by an NH_2 group or an OH group, respectively. Both compounds are liquids at room temperature. In each case, the electronegative substitute makes the nitrogen lone pair less readily available and results in weaker Bronsted base (and hence stronger acidity for conjugate acids) than NH_3 [26].

Table I pKa values of the ions

Ions	NH_4^+	$N_2H_5^+$	NH_3OH^+
pKa	9.26	7.93	5.82

The Lewis base strength is reduced in the same way. Hydrazine may be looked upon as the nitrogen analog of hydrogen peroxide (see table I). The intermediate aquo ammono compound is hydroxylamine.

Figure 14. Structure of a) N_2H_4 b) NH_2OH

Table II Hydrazine as an Ammono Analog of Hydrogen peroxide

HOH water HOOH	$HONH_2$	HNH_2, ammonia $H_2N\ NH_2$
H_2O – O Hydrogen peroxide	H_3N – O Hydroxylamine (amine oxide)	H_3N – NH Hydrazine (amine imide)
Basicity (electron pair donor) → ← Oxidizing power Reducing power →		

Hydrazine is prepared by the oxidation NH_3 by hypochlorite ion (ClO^-) (Raschig synthesis) [25].

$$2NH_3(aq) + ClO^-(aq) \longrightarrow N_2H_4(aq) + Cl^-(aq) + H_2O(l)$$

Hydrazine (melting point 2 ^oC, boiling point 113 ^oC) is strongly associated through hydrogen bonding, with large dipole moment (1.83 to 1.90 Debye) It is an endoergic compound (ΔG_f^{Θ} = +149 kJ/mol), kinetically fairly inert, and widely used as a reducing agent, for example, it is used to reduce dissolved oxygen in boiler water to suppress corrosion.

$$N_2H_4(aq) + O_2(g) \longrightarrow N_2(g) + 2H_2O(l)$$

Hydrazine is a much stronger reducing agent in basic solution than in acidic solution

$$N_2(g) + 5H^+(aq) + 4e \longrightarrow N_2H_5^+(aq) \qquad E = -0.23\ V \text{ at pH} = 0$$

$$N_2(g) + 4H_2O(aq) + 4e \longrightarrow N_2H_4(aq) + 4OH^-(aq) \qquad E = 1.16\ V \text{ at pH} = 14$$

Solutions of hydrazine in water are available commercially in several concentrations containing 40, 85 and 100 % hydrazine hydrate, (N_2H_4-H_2O). It is useful directly for a variety of chemical reactions such as those involved in the synthesis of azides by reaction with nitrous acid and nitriles, and for solvolytic reactions in which the ester group or an active halogen in an organic compound is replaced by the hydrazide radical.

$$HONO + N_2H_4 + KOH \longrightarrow KN_3 + 3H_2O$$

$$RCOOR' + N_2H_4 \longrightarrow RCON_2H_3 + R'OH$$

Hydrazine has tendency to coordinate the hydrogen ion to form the corresponding onium ion, $N_2H_4{\cdot}H^+$ and has ability to act as an electron pair donor in the formation of metallic ion complexes. In forming such hydrazinates it behaves very largely as a bidentate molecule.

Hydrazine derivatives are nowadays at considerable technical and commercial importance [27], in the synthesis of heterocycles (pyrazoles), as reagents in organic chemistry in pharmacological activity, and in particular, a cytotoxic effect [28] as fuel and explosives, as preservative, photographic developers and chemiluminescent material in metal processing industry. In production of plasticizer and softeners manufacture of resins coatings, and adhesives, suggested for use as insecticides,

The ability of hydrazine to serve as an electron pair donor has been noted in its tendency to form the hydrazonium ion and possibly the $N_2H_6^{++}$ ion. The assumption may be made that both nitrogen atoms of hydrazine act as electron pair donors [25].

The condensation reaction of hydrazine with carbonyl functional group is very well known and results in the formation of imines (Schiff bases) known as hydrazones [29].

$$y + H_2N\text{-}NH_2 \longrightarrow [-\underset{\displaystyle OH}{\overset{\displaystyle L}{\overset{|}{\underset{|}{C}}}}\text{-}NH\text{-}NH_2] \longrightarrow C{=}N\text{-}NH_2 + H_2O$$

Scheme I. Condensation reaction of hydrazine.

Hydrazine substituted s-triazine is expected to undergo similar reaction because of its nucleophilicity and aromatic character. The electron rich hydrazine group will have a better stabilizing effect on the electron deficient s-triazine ring, while providing significant chelating centers. The synthesis of 2,4,6-tris(hydrazino)-1,3,5-triazine has been reported [24].

Hydroxylamine, NH_2OH, is an unstable endoergic compound (ΔG_f^{Θ} = + 23 kJ/mol), which is prepared by the reduction of NO_2^- ions by HSO_3^- ions in neutral solution, followed by acidification and heating. In the first stage SO_3^{2-} attacks NO_2^- and forms an N-S bond in the second stage this N-S bond is hydrolyzed.

$$NO_2^-(aq) + 2HSO_3^-(aq) \xrightarrow{0\ ^oC} N(OH)(SO_3)_2^{2-}(aq) \xrightarrow{H^+\ 50\ ^oC} H_3NOH^+ + 2SO_4^{2-}(aq)$$

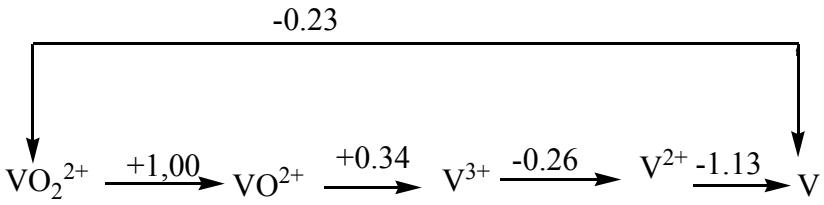
Although the standard potential indicates that hydroxylamine can serve as either an oxidizing agent or a reducing agent the latter reactions generally occur more readily, as in.

$$4Fe^{3+}(aq) + 2NH_3OH^+ \longrightarrow 4Fe^{2+}(aq) + N_2O(g) + 6H^+(aq) + H_2O(l)$$

Hydroxylamine hydrochloride has been used in several chromogenic reactions for the determination of total vanadium. This reagent can act as either an oxidizing or a reducing agent, and can also be involved in complex formation with various vanadium species. In acidic solution (below pH 3) and at concentrations commensurate with those of the vanadium, the hydroxylamine behaves as a reducing agent, resulting in the formation of the vanadyl VO^{2+} cation. As the pH and the hydroxylamine concentrations are increased, the hydroxylamine acts as an oxidizing agent, producing $VO_2(NH_2OH)_2^+$, a colorless vanadium-hydroxylamine complex that predominates at pH 4-9 and at hydroxylamine concentrations greater than 0.5 $moldm^{-3}$. A further increase in the hydroxylamine concentration to >3 mol dm^{-3} results in the reduction of vanadium to the tetravalent state, with the formation of a violet $VO(NH_2OH)_4^{2+}$ complex and the evolution of nitrogen gas from the solution [30].

1.4. CHEMISTRY OF VANADIUM

Vanadium, group 5B element atomic number 23, atomic weight 50.94 is normally present of very low concentration ($<10^{-8}$ M) in virtually all cells of plants and animals [31]. It has a wide range of oxidation state with extensive redox chemistry. Oxidation states are found as low as -3 and as high as +5 [32].



The oxidation states and stereochemistries for vanadium are summarized in Table III [33].

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 III: Oxidation states and stereochemistry of Vanadium

Oxidation state	Coordination number	Geometry	Examples
V^{I-}, d^6	6	Octahedral	$V(CO)_6^-$, $Li[V(bipy)_3].4C_3H_8O$
V^0, d^5	6	Octahedral	$V(CO)_6$, $V(bipy)_3$
	7	Monocapped octahedral	$[V(CO)_3[(PMe_3)_4][V(CO)_6]$
V^I, d^4	6	Octahedral	$[V(bipy)_3]^+$
	5	Tetragonal pyramidal	$\eta 5\text{-}C_5H_5V(CO)_4$
V^{II}, d^3	7		
	6	Octahedral	$V(CO)_2(dmpe)_2Cl$
			$[V(H_2O)_6]^{2+}$,$[V(CN)_6]^{4-}$
V^{III}, d^2	3	Planar	
	4	Tetrahedral	$V[N(SiMe_3)_2]_3$, $V[CH(SiMe_3)_2]_3$
	5	tbp	$[VCl_4]^-$
	6	Octahedral	$[trans\text{-}VCl_3(SMe_2)_2$,$VCl_3(NMe_3)_2$
	7	Pentagonal bipyramidal	$[V(NH_3)_6]^{3+}$
			$K_4[V(CN)_7].2H_2O$
V^{IV}, d^1	4	Tetrahedral	
	5	Tetragonal pyramidal	VCl_4 ,$V(NEt_2)_4$
		tbp	$VO(acac)_2$, $PCl_4^+VCl_5^-$
	6	Octahedral	$VOCl_2$ $trans\text{-}(NMe)_4$
	8	Dodecahedral	VO_2(rutile) ,$VO(acac)_2(py)_2$
			$VCl_4(diars)_2$,$V(S_2CMe)_4$
V^V, d^0	4	Tetrahedral(C_{3v})	
	5	tbp	$VOCl_3$
		Sp	$VF_5(g)$
	6	Octahedral	$CsVOF_4$
	7	Pentagonal bipyramidal	$VF_5(s)$, V_2O_5 ,$[VO_2(ox)_2]^{3-}$
			$VO(NO_3)_3.CH_3CN$,$VO(Et_2NCS_2)_3$

1.5. The Oxovanadium(IV) Ion (VO^{2+}) and Its Complexes

This ion dominates vanadium (IV) chemistry. It is obtained by mild reduction of the VO_2^+ ion or by oxidation by air of V^{3+} solution

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

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

Almost all compounds containing the VO^{2+} unit are blue 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}. Because, as noted later, VO^{2+} complexes may be five or six coordinate with the additional ligand (trans to the V=O bond) showing various degrees of interaction all of the spectral features reflect the exact nature of the ligand set. 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 again, a dependence on the nature of the ligand set, especially the strength of coordination in the position trans to the V=O bond. In some solid compared the V=O units are stacked to give V=O …. V=O chains.

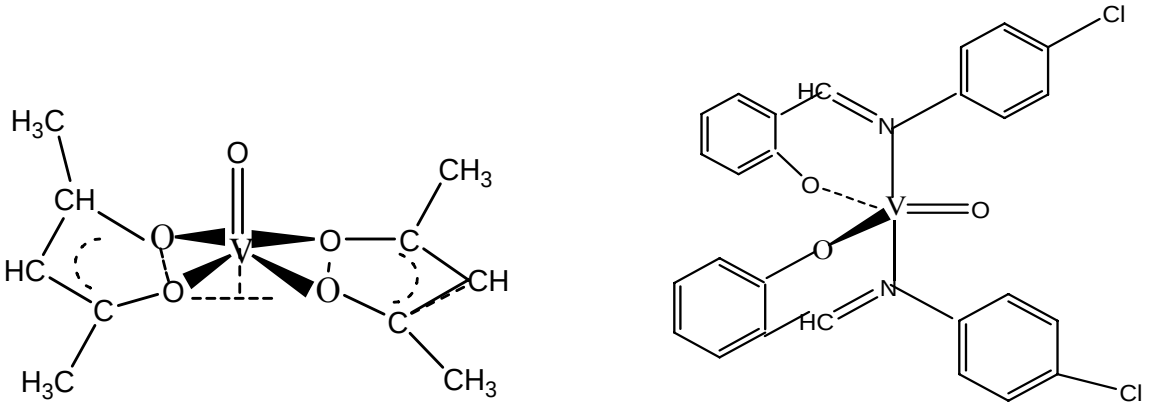


Figure 15. Square pyramidal and trigonal bypyramidal structure of vanadyl complexes

Vanadyl complexes generally contain four additional ligand and are square pyramidal (figure 15) in few cases distorted trigonal bypyramidal. Many of these d^1 complexes are blue (as a result of a d-d transition) and may take on a weakly bound sixth ligand trans to the oxoligands. The vanadyl V-O bond length 1.58 Å in $(VO(acac)_2)$ is short compared with the four V-O bond lengths to the acac ligand (1.47 Å). The short bond distances in vanadyl complexes together with high V=O stretching wave numbers provide strong evidence for V=O multiple bonding where lone pairs on the oxygen ligand are donated to the central vanadium. The d-p π orbital overlap involved in a multiple bond is illustrated in (figure 16). Four p-p overlap may also make a significant contribution. This strong multiple bonding with the oxygen appears to be responsible for the trans influence of the oxo ligand, which disfavors attachment of the ligand trans to oxygen [34].

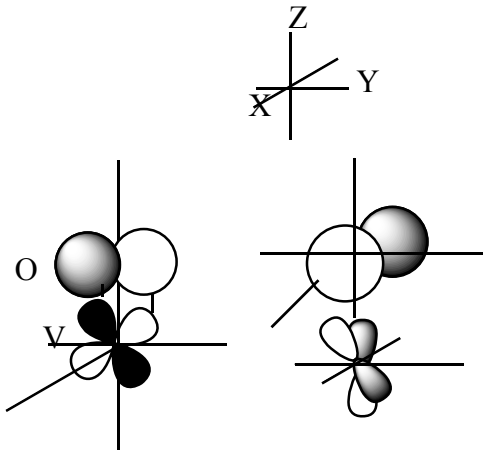


Figure 16. The d-p π-bonding between oxygen and vanadium in the vanadyl moiety, VO^{2+}

Both electron pairs for the two π bonds are donated from the oxide ligand to the metal d_{zx} and d_{yz} orbital.

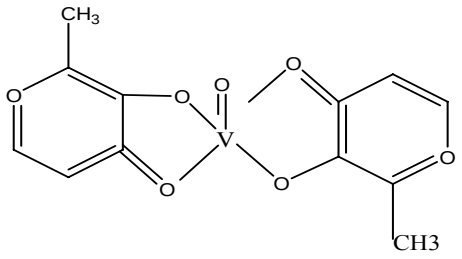
The visible spectra of VO(II) complexes are characterized by three spin allowed d-d transitions $^2B_{2g}—^2E_g$,$^2B_{2g}—^2B_{1g}$ and $^2B_{2g}—^2A_{1g}$ are generally observed in the region 10000 -15,000, 15000-19000 and 19000-26000 cm^{-1} respectively for octahedral geometry. The magnetic moments of VO(II) complexes lie in the range 1.70 to 1.73 BM. This result is expected because the ligand field about the VO(II) ion is strongly axial and hence all the orbital contribution to the moment is quenched.

Although there are nearly 60 oxometal entities known with transition metal of the type MO_x^{n+} only two UO^{2+} and VO^{2+} have been prepared in a large number of varieties of stable complex [35, 36]. The coordination chemistry of oxovanadium (IV), Oxovanadium (V) and di-oxovanadium (V) has acquired new interest as these complexes can serve as good models for vanadium containing biomolecules, as, insulin mimetic [37, 38] potential therapeutic application, studies on the metabolism and detoxification of vanadium compounds under physiological conditions and the stability and speciation of vanadium complexes in bio fluids have further influenced the study of coordination chemistry of vanadium.

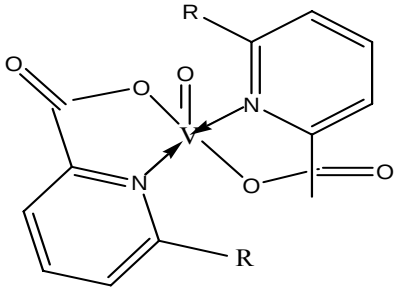
Oxovanadium compounds have great versatility for adjustment of pharmacological characteristics. They have attracted interest due to their effects on activity of several enzymes, and due to their application as catalysts, for example oxovanadium compound $VO(OR)Cl_2$, has been demonstrated to be an efficient Lewis acid with one electron oxidation capability to induce oxidative transformation, such as ring opening oxygenation and dehydrogenation. They are efficient systems for degradation of amino acids by use of high oxidation state of oxovanadium compounds [39].

Vanadium plays a number of roles in biological systems. It is present in vanadium dependent haloperoxidase and nitrogenase enzymes, and many sea squirts accumulate it in very high concentration. The most recent studies concern the insulin mimetic activity of vanadium compounds. All these observations suggest interactions between vanadium ions and proteins [40].

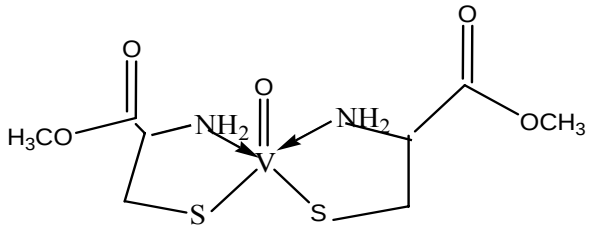
Three general classes of vanadium containing compounds are of interest for their utility on insulin mimetic agents 1) inorganic vanadium salts, both anionic (vanadates $[VO_4^{3-}]$) and cationic (vanadyl VO^{2+}) 2) complexes resulting from combination of vanadium (v) and hydrogen peroxide (mono and diperoxovanadates) $[VO(O_2)\ (H_2O)_2\ (L\text{-}L)]^{n-}$ (n = 0, 1) and $[VO(O_2)_2\ (L\text{-}L)]^{n-}$ (n =1, 2, 3) and 3) chelated vanadium (V) complexes [41].
Bidentate ligands with one ionizable proton can be used to form neutral metal complexes. Oxygen rich ligands (example Maltol) also tend to be water soluble. These properties together (neutral charge and aqueous solubility) contribute to high oral bioavailability. Some examples of penta coordinated oxovanadium complexes are shown below [42, 43].



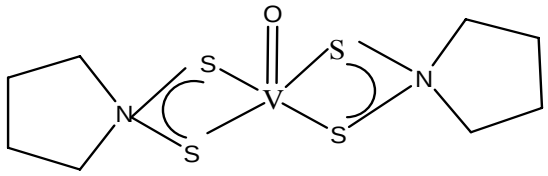
Bis (maltolato) oxovanadium (IV) (BMOV



Oxobis (picolinato) vanadium (IV) – VPA

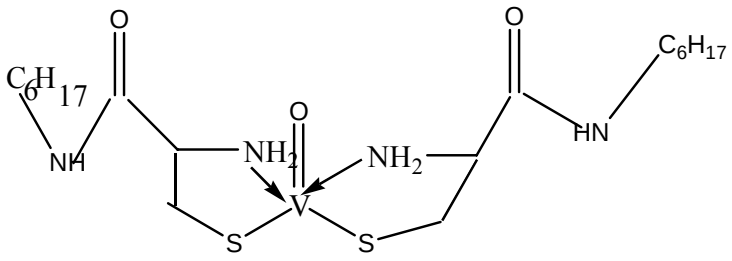


Bis(methyl picolinato)oxovanadium(IV) (VO- MPA).

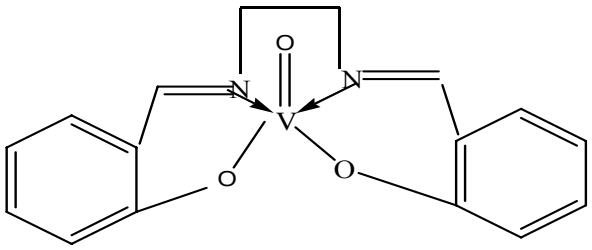


Bis(cysteine methyl ester) vanadium(IV) (VCME)

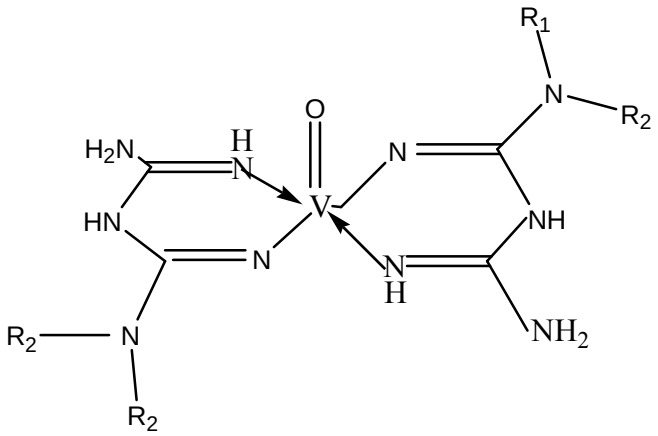
D



Oxobis (pyrrolidine-N-Carbodithioato)vanadium (IV) (V-P).



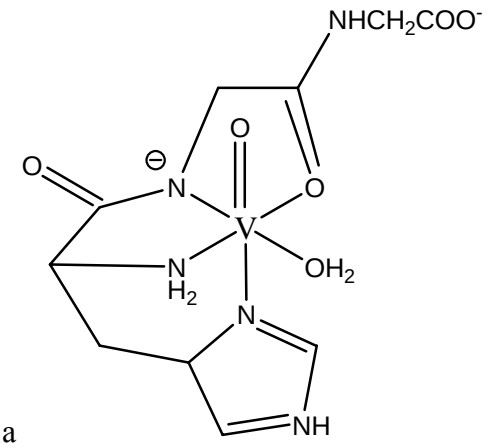
Naglivan [oxobis N-octyl cysteine amido vanadium (IV)]



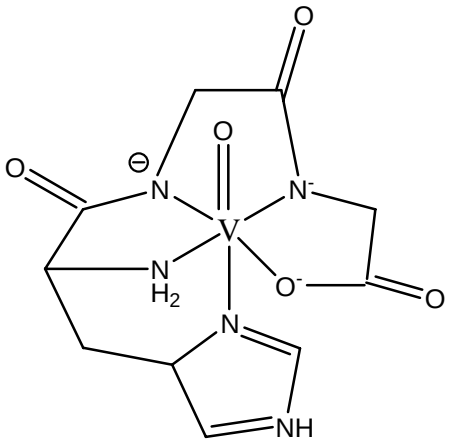
VO-Salen [N.N- Disalicylidineethylenediamine] oxovanadium (IV)

Figure 17. Structure of some oxovanadium complexes

Vanadium(IV) and vanadium(V) coordinate polydentate ligands with N and O donor atoms in most cases, resulting in complexes of different stoichiometries and structures depending on ligand design, pH, metal to ligand ratio and total vanadium concentration [44, 45].



a



b

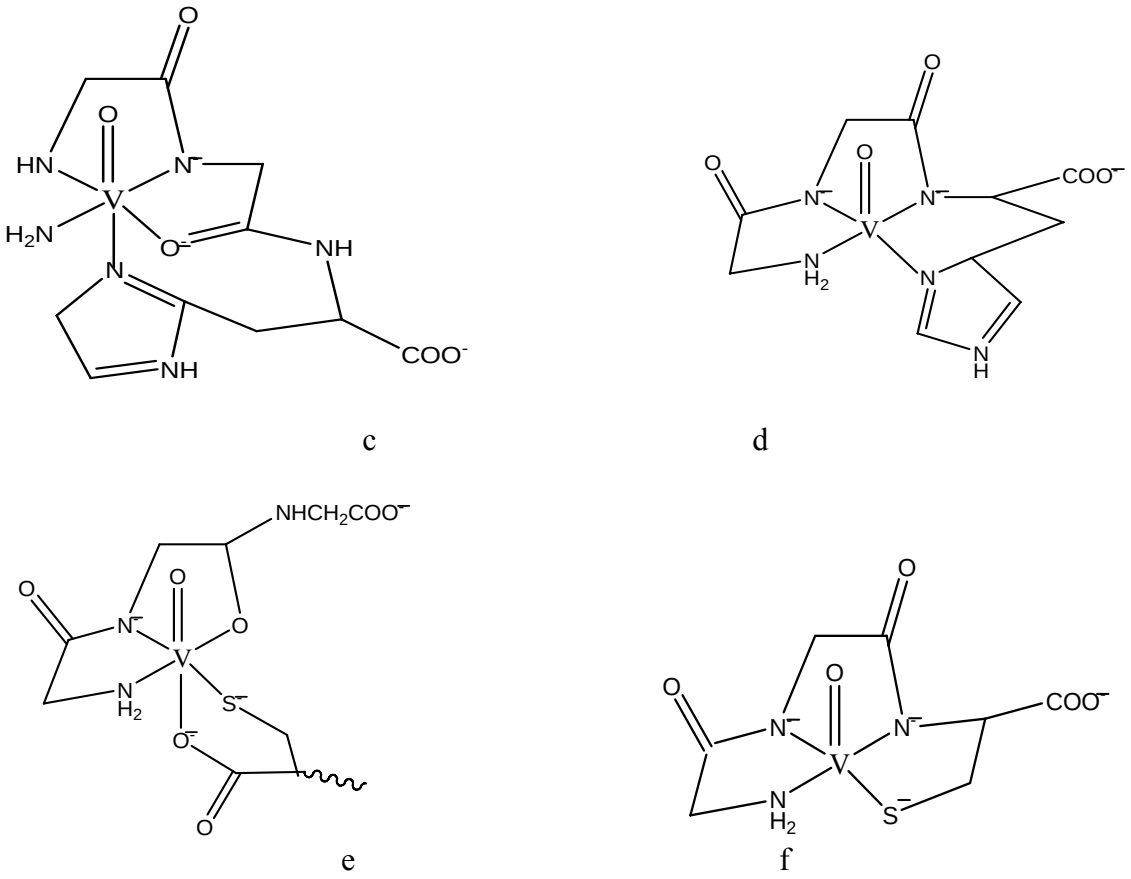


Figure 18. Structures of V^{IV} O complexes formed by His–Gly-Gly (a,b) Gly-Gly-His (c, d) and Gly-Gly-cyst and Gly-Gly-Cyst (e, f) with deprotonated amide groups.

Vanadium(V) has stereochemically flexible coordination geometries ranging from tetrahedral and octahedral to trigonal bipyramidal and pentagonal bipyramidal, which are thermodynamically plausible [46]. It can also form mono and poly nuclear oxovanadium complexes [47].

The biological properties of vanadium complexes are strongly dependent on their solution structures. The examination of the structural and chemical selectivity of complexes with di or poly functional ligands is an important contribution to understanding the modes of action of vanadium in biological systems [48, 49]. Thus the study of their behaviors in an aqueous medium at different pH values is necessary to obtain the structures of the different species, as well as their thermodynamic and kinetic stabilities [50].

2. Materials and Methods

2.1. Objective and Scope of the Present Investigation

S-triazine derivatives and their metal complexes have a wide range of applications in agriculture, pharmaceutical, analytical fields, polymer chemistry and catalysis. The oxo vanadium complexes of s-triazines have many applications in optimizing biochemical function involvement in pathways relevant to the enzymatic activity, as an effective oral substitute of insulin (A potent antidiabetogenic drug) and used also as molecular conductor, molecular machines and electronics.

Literature review reveals that a lot of work has been done on different oxovanadium complexes of ligands having N and O donor sites. In addition s-triazine complexes of different metals were studied and reported. However, the synthesis and characterization of oxovanadium complexes of 4-hydroxy-2,6-bis(hydrazino)-s-triazine (HBHTZ) and 4-hydroxy-2,6-bis-(hydroxy amino) s-triazine (HBHATZ) have not been yet reported.

In view of a wide range of possible applications this work is aimed to synthesize new materials of enhanced complexity and potential functionally using oxovanadium(IV) and multidentate s-triazine, specifically, oxovanadium complex derived from two ligands, i.e. 4-hydroxy-2,6-bishydrazino-1,3,5-triazine and 4-hydroxy-2,6-bis(hydroxyamino)-s-triazine starting from cyanuric chlorides and characterization of the complexes using Spectroscopic techniques, cyclic voltammetry (CV), conductivity and magnetic studies.

2.2. Experimental

Reagents: The reagents used were cyanuric chloride (Aldrich) hydrated hydrazine, phenol, NaOH, HNO_3. Reagent grade of hydrated vanadyl sulphate (BDH, Chem.) was used. The solvents were purified and dried by distillation. The solvents used were dichloromethane (, acetonitrile, dioxane, n-hexane, chloroform, ethanol, dimethylsulfoxide (DMSO), dimethylformamide (DMF) and methanol. Other general-purpose reagents were NH_4VO_3, H_2O_2, $AgNO_3$, $BaCl_2$, HCl, H_2SO_4 and HNO_3. Analytical reagent tetrabutylammoniumtetrafluoroborate was used as a supporting electrolyte for recording cyclic voltammograms of the complexes.

Apparatus: The ^{13}C NMR spectra and the ^{1}H NMR spectra were recorded using Bruker ARX 400 NMR spectrometer at 100 MHz and 400 MHz respectively. Chemical shifts are reported in ppm downfield from TMS using $CDCl_3$ and $DMSOd_6$ as a solvent. The IR spectra were obtained with a Perkin Elmer BTX-FTIR in the range of 400 – 4000 cm^{-1} using KBr disks. Electronic spectra was obtained using GENESYS 2PC spectrometer in λ = 200 - 800 nm. Melting points or decomposition temperatures of ligands and complexes were determined on electrothermal IA 9200, digital melting point apparatus. Conductivity in solution of the complexes was measured by using JENWAY 4330 conductivity and pH meter. The measurement of magnetic susceptibility was carried out using MSB–AUTO-SHERWOOD, scientific instrument. Cyclic voltammetery measurements made on a-BAS CV-50 W voltammetric analyzer, using platinum bead electrodes Quasi Ag/AgCl reference electrode. Elemental analysis of C, H and N was done by using Exter Analytical CE 440 EA analyzer.

2.3. Synthesis of Ligands

2.3.1. Synthesis of 4-Phenoxy-2,6-Dichloro s-Triazine (DCPTZ)

A suspension of cyanuric chloride (3.6 g, 0.02 mol) in 50 cm^3 dichloromethane in a 100 cm^3 round bottom flask equipped with a magnetic stirrer was cooled in an ice bath. A

solution of sodium hydroxide (0.8 g, 0.02 mol) and phenol (1.88 g, 0.02 mol) in 20 cm^3 of H_2O was added drop wise to the suspension over a period of 15 min, keeping the temperature at about 5 ^oC. The reaction mixture was then stirred for 3 hours in the cooled ice bath. The non- dissolved particles were removed by filtration. The filtrate was evaporated using rotary vapor. The lower organic phase was then separated, washed with dilute sodium hydroxide solution and dried over calcium chloride. A white crude product was obtained which upon recrystalization from n-hexane /chloroform (3:1) Yield; 3.7 g (78.3 %) of pure product, melting point 111-113 ^oC.

2.3.2. Synthesis of 4-hydroxy-2,6-Bis (Hydrazino)-s-Triazine (HBHTZ)

4-phenoxy 2,6-dichloro triazine (0.90 g, 3.72 mmol) was dissolved with stirring in ethanol (50 cm^3) in a 250 cm^3 round bottom flask equipped with a condenser and a magnetic stirrer. A solution of hydrated hydrazine (80 %) (0.45 ml, 7.44 mmol) was added drop wise while stirring. The clear solution turned milky and some insoluble white particles appeared, when the reaction mixture was refluxed with continuous stirring at about 80-90 ^oC for 3 hours. The white product was then filtered washed with ethanol and water and allowed to dry over $CaCl_2$. Yield; 0.50 g, 85.6 % and it doesn't decompose until 346 ^oC.

2.3.3. Synthesis of 4-hydroxy-2,6-Bis (Hydroxyamino)-s-Triazine (HBHATZ)

A (0.9 g, 3.72 mmol) of 4-phenoxy 2,6 dichloro s-triazine was dissolved in acetonitrile (50 ml) in a 250 ml round bottom flask. To this a solution of Hydroxylamine Hydrochloride in ethanol (0.517 g, 7.44 mmol) was added drop wise while stirring. The reaction mixture was then refluxed with continuous stirring at about 80-90 ^oC for 3 hours. The white crude product was then filtered, washed with cold ethanol dried over $CaCl_2$. Yield; 0.39 g, 59.9 % and it doesn't decompose until 350 ^oC.

2.4. Synthesis of Metal Complexes

An ethanolic solution of 4-hydroxy, 2,6 bis(hydrazino) s-triazine (0.4 g, 1.74 mmol) was treated with $VOSO_4 \cdot H_2O$ (0.14 g, 0.857 mmol) in ethanol and the mixture was refluxed for about 8 hours. The solution initially green gradually changes to greenish yellow and finally to yellow. The solid product formed was filtered, washed with ethanol and dried over $CaCl_2$. The yield was 0.35 g, 70.5 %.

4-hydroxy 2,6-bis (hydroxyamino-s-triazine (0.4 g, 1.68 mmol) was dissolved in ethanol. To this solution, an aqueous ethanol (1:3) solution of hydrated vanadyl sulfate (0.14 g, 0.857 mmol) was added slowly while stirring. It was refluxed for 8 hours initially it became colorless and then light blue solution was formed finally from which a light blue solid was formed. The solid obtained was filtered, washed and dried in a desiccator over $CaCl_2$. The dried precipitate was weighed 0.26 g, which corresponds with 54.16 % yield.

2.5. Analytical Methods

2.5.1. Qualitative Tests

2.5.1.1. Thin layer Chromatography

Thin layer Chromatography (TLC) was used to check the purity of the ligands and the complexes. For this purpose 2 × 4 cm silica coated aluminum plates were used and suitable solvents or mixtures of solvent (Ethyl acetate, ethanol, n-hexane (3:2:1)) in certain proportion were used as mobile phases.

2.5.1.2. Sulphate Test

Sulphate content was tested by slowly adding dilute solution of barium chloride to a hot solution of the nitric acid digested complex. Two of the complex formed by HBHT has no

sulphate content, while the complex formed by HBHAT has some small sulphate content which was quantitatively estimated, subsequently.

2.5.1.3. Vanadyl Test

V^{IV} exists as the VO^{2+} cation in acidic solution. Addition of base to VO^{2+} solutions results in the formation of a grey, hydrous oxide at pH 4**,** which re-dissolves at pH 8 to give a brown solution containing the $V_{18}O_{42}^{6-}$ ion. This ion is equivalent to the V^{V} species $V_{l0}O_{28}^{6-}$Electrolytic reduction of V^{V} or V^{IV} solutions produces V^{III} or V^{II}, both of which are subject to oxidation in air.

Adding 2N alkali solution to vandyl IV solution tested the presences of VO^{+2}, a brown suspension of vanadium(IV) hydroxide confirms its presence, in the complex [51].

2.5.2. Quantitative Determination of Vanadium Contents of the Complexes

Although vanadium can exist in oxidation states from II to V in aqueous solution, most methods have concentrated on its determination in the pentavalent and tetravalent states, as these are the most common forms encountered in inorganic and biological systems. Spectrophotometry is the most common technique used for vanadium determination, owing to the high sensitivity and selectivity achieved in these reactions.

In this work the vanadium was determined quantitatively using hydrogen peroxide method, comparing colorimetrically against a standard having the same acidity and containing the same volume of hydrogen peroxide solution as described in the literature [52].

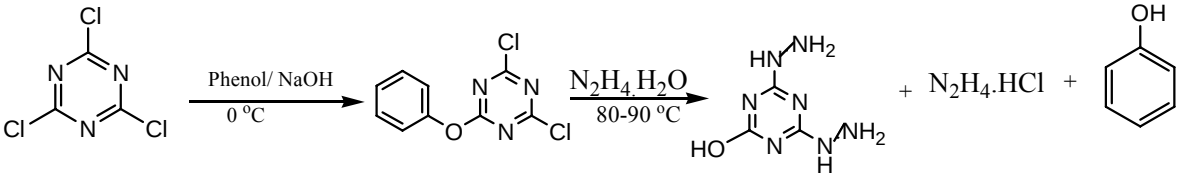
2.5.3. Cyclic Voltammetry

The oxidation states of vanadium in the complexes were determined by using cyclic voltammetry in acetonitrile as a solvent and tetrabutylammoniumtetrafluoroborate as a supporting electrolyte to prepare 0.001 M of the complex.

3. Results and Discussions

3.1. Characterization of HBHTZ

The ligand 4-hydroxy-2,6-bis (hydrazino) s-triazine (HBHTZ) was prepared in a two-step process starting from cyanuric chloride. Initially one of the chlorine on Cyanuric chloride was substituted by a phenoxy function; subsequently the dichlorophenoxy-s-triazine (DCPTZ) was treated with hydrazine hydrate to obtain HBHTZ. The phenoxy group on DCPTZ has been hydrolyzed during the substitution of chloro groups.



Scheme II. Synthesis of HBHTZ

3.1.1. General Properties of HBHTZ

4-hydroxy-2,6-bis (hydrazino) s-triazine (HBHTZ, $C_3H_7N_7O$, Molar mass 157.09 g/mol**)** is a white powder. It doesn't melt and it doesn't decompose until 346 ^oC. This may be due to hydrogen-bonded structure. It is insoluble in most common solvents, but sparingly soluble in DMSO.

3.1.2. Elemental Analysis

The experimentally obtained C, H and N percent elemental analysis shows a good correspondence with the theoretically calculated value. Accordingly the structure of the ligand can be presented as in figure 19.

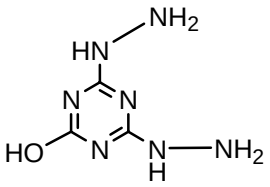


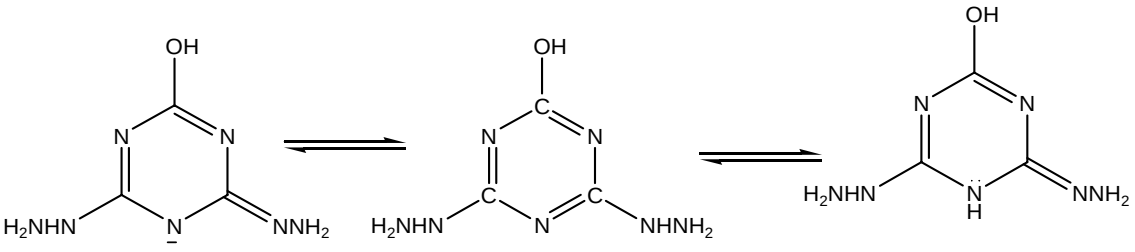
Figure 19. Structure of HBHTZ

Table IV. Elemental analysis results of the ligands and the complexes, experimental (calculated)

Ligand/complex	Molar mass g/ mol	C %	H %	N %	V %
HBHTZ	157.09	(22.93)	4.77 (4.49)	62.40(62.39)	
HBHATZ	177.08	20.91(20.35)	3.63(3.95)	(39.57)	
$VO(HBHT)_2.2H_2O$	396.12	(18.15)	(3.29)	(49.50)	(12.86)
$VO(HBHAT)_2SO_4$	545.96	(13.29)	(1.82)	(25.64)	(18.66)

3.1.3. IR Spectrum of HBHTZ

The IR spectrum (appendix 7.4.1) of the ligand HBHTZ shows a doublet band at 3307-3250 cm^{-1} due to υ-NH_2 asymmetric and symmetric stretching. It appears at lower frequency due to intramolecular hydrogen bonding. An obscured band at 3047 cm^{-1} is due to υ N-H stretching. The broadness of the band (2800-3400) shows the presence of hydrogen bonded OH in the compound. The bands at 1572 and 1511 cm^{-1} are due to C = N, C = O and bending mode of NH_2. The medium intensity bands at 1432, 1212, 1075 and 935 cm^{-1} are because of C=N(ring), C – N, C – O, N-N stretching. The ir spectrum is consistent with the co-existence of tautomeric forms as shown in scheme III.



Scheme III. Tautomeric structure of ligand

Table V: Infrared spectral results of the precursor and **HBHTZ**

Band assignments	**DCPTZ /cm^{-1}**	**HBHTZ /cm^{-1}**
$\upsilon_{(-OH)}$	-	Broad at 2800-3300
υ(-$_{NH2}$ sym)	-	3250
υ (-$_{NH2}$ asym)	-	3307
$\upsilon_{(C=N)}$	1536	1572
$\upsilon_{(C-N)\ (exocyclic)}$	-	1212
$\upsilon_{(C-O)}$	1190	1075
$\upsilon_{(C-Cl)}$	771	-
$\upsilon_{(C=N)}$ ring	1484	1432
$\upsilon_{(N-NH)}$	-	935

3.1.4. ^{1}H NMR Spectrum of HBHTZ

The ^{1}H NMR spectrum of the ligand HBHTZ was measured in DMSO-d_6. The spectrum could be resolved in to three distinct regions a broad singlet at δ 4.0, a triplet at δ 7.2 and broad band at δ 8.05 correspond to NH_2, NH and OH protons respectively. The integration also shows 4:2:1 ratio, which is in agreement with the proposed structure of the ligand.

3.1.5. ^{13}C NMR Spectrum of HBHTZ

The ^{13}C NMR spectrum of the ligand HBHTZ was measured in DMSO-d_6. The spectrum is again not well resolved and integrated due to lack of solubility. However, the peaks can be assigned as follows in the table.

Table VI ^{13}C NMR data of HBHTZ

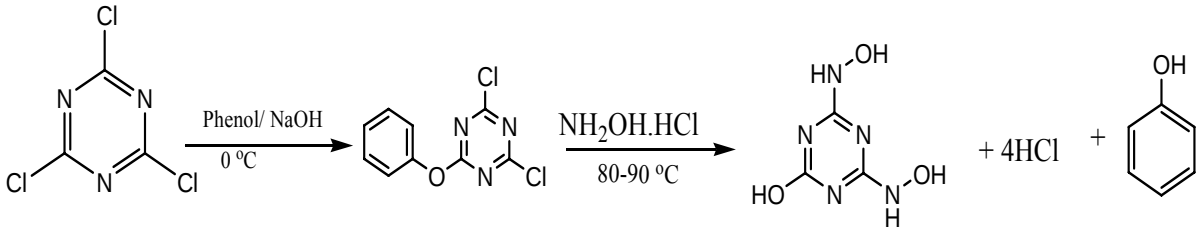
Mode	Shift	Comment (ppm relative to TMS)
C	167.85 167.42	2C 1,3, 5-triazine
C	164	1-O-C. (1,3,5, triazine)

3.1.6. Electronic Spectroscopy of HBHTZ

The electronic spectrum of the ligand HBHTZ is not well resolved due to its low solubility and shows only one absorption band at λ = 283 nm which is probably due to π–π^* transition.

3.2. Characterization of HBHATZ

The ligand HBHATZ was prepared in the same way as the ligand HBHTZ i.e. in a two-step process starting from cyanuric chloride. Initially one of the chlorine on Cyanuric chloride was substituted by a phenoxy function; subsequently the dichlorophenoxy-s-triazine (DCPTZ) was treated with hydroxylamine hydrochloride to obtain HBHATZ. The phenoxy group on DCPTZ has been hydrolyzed during the substitution of chloro groups.



Scheme IV. Synthesis of HBHATZ

3.2.1. General Properties of HBHATZ

4-hydroxy-2,6-bis-(hydroxyamino)-s-triazine (HBHATZ, $C_3H_5N_5O_3$, Molar mass = 177.075**)** is a white powder which does not melt probably due to intramolecular and intermolecular hydrogen bonding. It doesn't decompose until a temperature of 350 ^oC. It is soluble in polar organic solvents such as DMF, DMSO, acetonitrile and dichloromethane.

3.2.2. Elemental Analyses

The experimentally obtained C, H and N percent elemental analysis (table IV) shows a good correspondence with the theoretically calculated value. Accordingly the structure of the ligand can be presented as in figure 20.

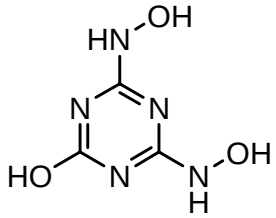
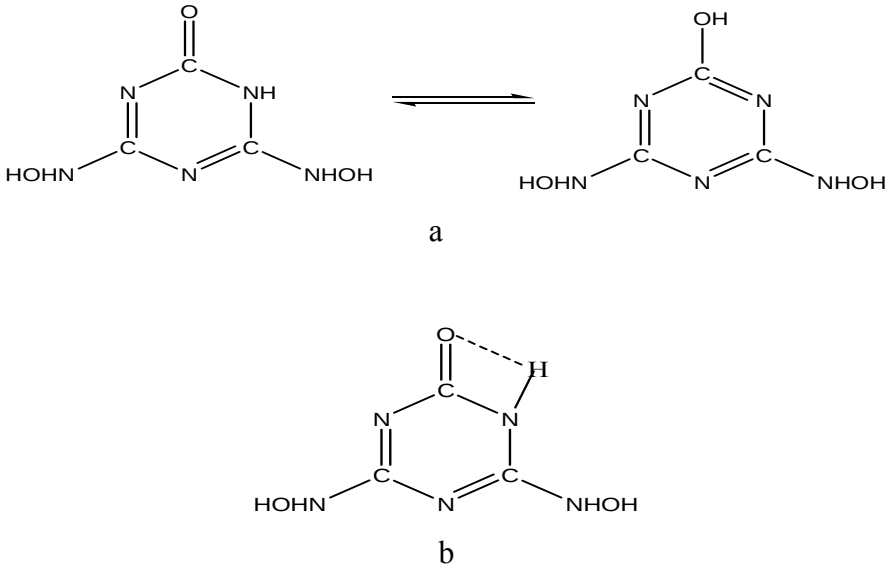


Figure 20. Structure of HBHTAZ

3.2.3. IR Spectrum of HBHTAZ

The IR spectra of ligand HBHATZ shows a band at 3200 cm^{-1} due to chelated OH stretching and the band at 3028 cm^{-1} is due to NH stretching. The band at 2900-2780 cm^{-1} may be assigned to intramolecularly bonded NH to the C=O group (figure 20 a). The bands at 1570 cm^{-1}, 800 cm^{-1} are characteristics of triazine ring which are assigned to stretching and normal triazine ring out of plane vibration band (γ-bending mode) respectively. The HBHATZ ligand shows a specific hydroxyl substituted triazines strong band at 1778, 1752 cm^{-1} due to the C=O stretching vibration of the keto form and a sharp medium intensity bands at 795-750 cm^{-1} is due to the enol form (figure 20 b) [53, 54]. It also shows C–O stretching at 1052 cm^{-1}. These results may be depicted in the scheme below.



Scheme V. Tautomeric structure of HBHATZ ligand

The IR spectra results of the precursor, DCPTZ, and the synthesized ligand, HBHATZ, are summarized in table VII.

Table VII: Infrared spectra results of precursor and ligand **HBHATZ**

IR Band assignments	**DCPTZ(cm^{-1})**	**HBHATZ (cm^{-1})**
$\upsilon_{(-OH)}$	-	3207
$\upsilon(-_{NH}$ sym)	-	3107
υ ($-_{NH}$ asym)	-	3028
$\upsilon_{(NH---O=C)}$	-	2832, 2780
$\upsilon_{(C=N)}$ and $\upsilon_{(C=O)}$	1536	1778,1752
$\upsilon_{(C-N)\ (exocyclic)}$	-	
$\upsilon_{(C-O)}$	1190	1052
$\upsilon_{(C-Cl)}$	771	-
$\upsilon_{(C=N)}$ ring	1484	1461
$\upsilon_{(-N-C)\ bond}$	869	800

3.2.4. ^{1}H NMR- Spectrum of HBHATZ

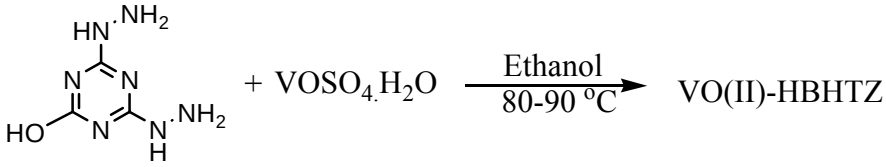
^{1}H NMR of HBHATZ was measured in DMSO-d_6, the spectrum could be resolved in to two distinct regions. A singlet at 11.2 and multiplet at 7.3 corresponding to enolized OH and NH groups respectively. It clearly shows 3:2 ratio of OH to NH when integrated. The NH proton was not observed clearly because of enolization and deprotonation or it may be shielded from exchange probably due to strong hydrogen bonding with the free OH group.

3.2.5. ^{13}C NMR Spectrum of HBHATZ

The ^{13}C NMR spectrum of HBHATZ was resolved; it shows only one-carbon spectra at δ 150because of hydrogen bonding all the three carbons are equivalent.

3.3. Characterization of VO(II)-HBHTZ

The complex was synthesized by simple addition of hot ethanolic solution of one equivalent vanadyl sulphate to an ethanol solution of the ligand and refluxing for 8 hours. Different colors were observed during the synthesis of the complex: green, greenish yellow and finally a pale yellow complex.



Scheme VI. Synthesis of the VO(II)-HBHTZ complex

3.3.1. General Properties of VO(II)-HBHTZ

4-hydroxy-2,6-bis(hydrazino)-s-triazine vanadyl(IV) ($VO(HBHT)_2.2H_2O$, $VOC_6H_9O_2N_{14}$, Molar mass = 396.12 g/mol) is a pale yellow powder soluble in polar solvents such as water, DMSO, DMF and acetonitrile. It doesn't melt but decomposes above 250 ^oC.

3.3.2. Elemental analyses and Molar conductivity

The elemental analysis shows a good correspondence with the theoretical value, which is the metal to ligand ratio, is 1:2 for the complex. The result revealed the presence of two ligands with one as tridentate and the other monodentate.

Many of the methods for the measurement of total vanadium rely on either oxidation or reduction of the vanadium in the sample to a common oxidation state, which then forms a colored complex with various reagents. Quantitative determination of vanadium contents of the complex was carried out by using the colorimetric method and the results obtained are tabulated in table VII.

Table VIII. Vanadium contents of the complex as compared to theoretical value

Concentration of complexes experimental [mg/ml]	Concentration of complexes calculated [mg/ml]	Absorbance	% Transmittance
3.135	2.869	0.335	43

From this result it can be concluded that the ratio of the metal to the ligand in the complex is 1:2 and 1:1.83 theoretically and experimentally respectively.

Molar conductance was determined from conductivity measurement of the complex in DMF as solvent and determination of cell constant was made using the following relation.

$$\Lambda_M = 1000K/C$$

Where: K- specific conductivity and is given by:

$$K\ (\Omega^{-1}\ cm^{-1}) = (1/R_{-1}/R_{DMF})\ b$$

Where: C refers to the concentration in mol L^{-1} and b, the cell constant. The cell constant b is also given by L/A where L and A refer to the length and area of the electrode.
The molar conductance of ca. 10^{-3} M solution of complex in DMF at room temperature was measured to be 10 $\Omega^{-1}cm^2mol^{-1}$.

Table IX: Conductivity data for ligand and complex VO(II)-HBHTZ

Complex	**Molar conductance**
HBHTZ	9 μ s
VO(II)-HBHTZ	10 μ s

This result indicates the non-electrolytic behavior the complex in solution which confirms that the ligand was deprotonated during complex formation.

3.3.3. IR spectrum of VO(II)-HBHTZ Complex

The IR spectrum of VO(II)-HBHTZ taken and is presented in appendix 7.4.1. and the results are summarized in table X.

Table X: Infrared spectra results of ligand and the complex **VO(II)-HBHTZ**

IR band assignments	**HBHT (cm^{-1})**	**VO(II)-HBHTZ (cm^{-1})**
$\upsilon_{(-OH)}$	-	3400
$\upsilon(-_{NH}$ sym)	3307	3315
$\upsilon_{(C=N)}$	1572	1570
$\upsilon_{(C-N)\ (exocyclic)}$	1212	1260
$\upsilon_{(C-O)}$	1075	1113
$\upsilon_{(C=N)}$ ring	1432	1420
$\upsilon_{(N-N)}$	935	960
$\upsilon_{(V=O)}$	-	967
$\upsilon_{(V-N)}$	-	619

The band at 3315 cm $^{-1}$ is sharp and can be assigned to NH stretching and the broad band in the region of 2800-3400cm^{-1} is due to phenolic OH, which may experiences intramolecular hydrogen bonding. The band at 1570 cm^{-1} is due to C=N, C=O stretching and NH_2 bending modes. C–N exocyclic and C–O stretching bands increases from 1212 and 1075 cm^{-1} in the ligand to 1250 and 1113 cm^{-1} respectively. This is because of a double bond character of C–O bond and metal nitrogen bond formation. The N–N band observed at 935 cm^{-1} in the ligand increases to 960 cm^{-1} in the complex, which confirms again the metal nitrogen bond formation. The band at 967 cm^{-1} is the characteristic of V=O bond stretching.

3.3.4. Electronic Spectra of the VO(II)-HBHTZ Complex

The UV-Vis spectrum of VO-HBHTZ taken and is presented in appendix 7.4.5. Oxovanadium (IV) compounds generally display three d-d bands in the regions of 900-625, 690-520 and 470-330 nm, with the extinction coefficients in the 5 -100 M^{-1}cm^{-1} ranges. The tail of strong transitions in the ultraviolet frequently obscures the highest energy band. In the Ballhausen and Gray ligand field scheme these are assigned as B_2-E, B_2-B_1 and B_2–A_1 transitions. However, it should be noted, that there is still no real agreement on the ordering of the levels. The complexes reported here show only two bands in the 330-900nm ranges. It can be assigned as the higher energy band as B_2-B_1 transition with the B_2-A_1 transition obscured by the tails of intense intra ligand transitions in the UV. The low energy B_2-E transition is observed at 860 nm.

Vanadium (V) is a d^0 species and as such no d-d bands are expected and all complexes containing VO_2^+ cation are pale yellow. However, complexes with the VO^{3+} or bare V^V which are bound to phenolic or catecholate groups all display intense absorbance bands in the visible regions from about 550 to 800 nm. These are assigned as ligand to metal charge transfer (LMCT) transitions from the sulphate and hydroxide oxygen to empty d orbital on the vanadium. The lack of visible charge transfer bands when VO^{2+} is coordinated to the ligands is consistent with a rising of the d-orbital energy due to a decreasing net positive

charge at the vanadyl center. This has the effect of raising the LMCT energy in to the UV-region of the spectrum. There also appears to be a correlation between the intensity of the change transfer band and the formal charge on the coordination center, with the highest intensity seen for the highest charge.

3.3.5. Magnetic Susceptibility Measurement of the Complex

The magnetic susceptibility of the complex was measured as gram susceptibility, χ_g, and was obtained to be1.089×10^{-6}. To arrive at the effective magnetic moment of the complex the following calculations were made.

Molar magnetic susceptibility (χ_M) = χ_g × molecular weight of the complex and $\mu_{eff} = 2.828 (\chi_M T)^{1/2}$

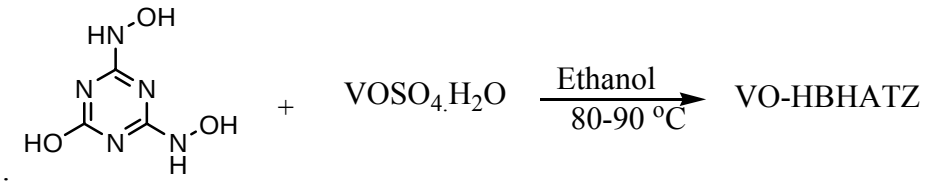
Table XI: Magnetic susceptibility data of complex VO(II)-HBHTZ

Complex	χ_g	χ_M	$\mu_{eff.}$
$V^{IV}O(HBHTZ)_2$	1.089×10^{-6}	4.3137×10^{-4}	1.01

The room temperature magnetic moment of complex shows the paramagnetic nature with a value of 1.01 observed are characteristic of magnetically dilute distorted octahedral and square pyramidal V(IV) complexes (the spin only value for d^1 is 1.73 μB). The abnormality of magnetic moment may be explained by V=O ----- V=O chain formation.

3.4. Characterization of VO(II)-HBHATZ

The complex was synthesized by the same method as the previous complex i.e. by simple addition of hot ethanolic solution of one equivalent vanadyl sulphate to an ethanol solution of the ligand and refluxing for 8 hours. Different colors were observed during the synthesis of the complex; blue, green, light blue and finally light blue complex was formed



Scheme VII synthesis of the complex

3.4.1. General Properties of VO(II)- HBHATZ

4-hydroxy-2,6-bis(hydroxyamino)-s-triazine-μ-sulphatovanadyl(IV) $(VO(HBHAT)_2SO_4$, $(VO)_2C_6H_{10}N_{10}O_{10}S$ Molar mass = 545.961 g/mol) is a light blue powder complex, which decomposes above 320 ^oC. It is insoluble in many solvents; however it is soluble in DMSO and hot DMF.

3.4.2. Elemental Analyses and Molar conductivity

The experimentally obtained C, H and N percent elemental analysis (table IV) shows a good correspondence with the theoretically calculated value. The metal to ligand ratio is 1:2 for the complex. The result revealed the presence of two ligands with one as tridentate and the other monodentate. The colorimetric determination of the metal content also shows the same ratio and is included in the table. The molar conductance of ca. 10^{-3} M solution of complex in DMF at room temperature was 6 $\Omega^{-1}cm^2mol^{-1}$.

Table XII: Conductivity data for ligands and complex VO(II)-HBHATZ

Complex	**Molar conductance**
HBHATZ	54 μ s
V-HBHATZ	6 μ s

This result indicates the non-electrolytic behavior the complex in solution which confirms that the sulphate is coordinated and one of the hydroxyl deprotanated during complex formation.

3.4.3. IR Spectrum of VO(II)-HBHATZ Complex

The IR spectrum of VO(II)-HBHATZ taken and is presented in appendix 7.4.2 and the results are summarized in table XIV.

Table XIII: Infrared spectra results of ligand and the complex **VO(II)-HBHATZ**

Band assignments	**HBHATZ /cm^{-1}**	**VO(II)-HBHATZ /cm^{-1}**
$\upsilon_{(-OH)}$	3207	3422
$\upsilon(-_{NH}$ sym)	3107	3117
υ ($-_{NH}$ asym)	3028	3027
$\upsilon_{(NH---O=C)}$	2832, 2780	2800, 2780
$\upsilon_{(C=N)}$	1778,1752	1778,1752
$\upsilon_{(N-O)}$	1417	1460
$\upsilon_{(C=N)}$ ring	1461	1463
$\upsilon_{(V=O)}$		967, 999
$\upsilon_{(V-N)}$		634
$\upsilon_{(SO4)}$		1000,1137,1200, 712,670 and 447

The IR spectrum of the complex when compared with the free ligand, shows significant vibrations which can be correlated with complex formation. The new and sharp band at 3422 cm^{-1} show the breaking of chelating OH and it is an indication for the presence of non coordinated OH. The band at 3200-3028 cm^{-1} is due to NH stretching. The N- O stretching band at 1417 cm^{-1} in the ligand shifts to the higher frequency indicates the involvement of metal oxygen bond. The broad bands at 1778, 1752, 1724 and 1600 cm^{-1} changed to sharp bands shows the involvement of ring nitrogen of the triazine in the coordination. The new bands at 1200, 1137, 712, 670 and 447 cm^{-1} are due to bridging sulphate group. The band at 601 cm^{-1} shows the metal nitrogen bond formation. The complex exhibit the characteristic V = O stretching band at 969 cm^{-1}. The peak at 1000-

999 cm^{-1} for VO(II)-HBHATZ complex is an indicative of square pyramidal coordination geometry. This highest value shows no weakening of V = O bond by the trans effect.

3.4.4. Electronic Spectroscopy of the VO(II)-HBHATZ Complex

The electronic spectroscopy of the VO^{2+} and HBHATZ complex was not measured due to its low solubility. It is better to use solid reflectance.

3.4.5. Magnetic Susceptibility Measurement of the VO(II)-HBHATZ Complex

The magnetic susceptibility of the complex was measured as gram susceptibility, $\chi_{g,}$ and was obtained to be 1.419×10^{-6} as calculated and tabulated in the table below.

Table XIV: Magnetic susceptibility data of complex VO(II)-HBHATZ

Complex	χ_g	χ_m	$\mu_{eff.}$
$V^{IV}O(HBHATZ)_2$	1.419×10^{-6}	7.7471×10^{-3}	1.360

The complex shows subnormal magnetic moments in comparison with the expected moment corresponding to one unpaired electron. This is explained on the basis of antiferromagnetic interaction due to super exchange phenomenon. The proposed structure presented in figure 21 can reasonably depict appreciable extension of conjugation. However, conclusive evidence will be obtainable from variable temperature magnetic susceptibility measurements.

4. Determination of the Oxidation State of Vanadium in the Complexes using Cyclic Voltammetry

The oxidation states of vanadium in the complexes were determined by using cyclic voltammetry in acetonitrile as a solvent and the results are listed in table XV.

Table XV: Electrochemical data the potential reported Vs quasi Ag/AgCl electrode

Complex	**E^o(V)**	**Solvent**
V-HBHTZ	0.043	Acetonitrile
V-HBHATZ	0.983	Acetonitrile

As can be seen from the results above, the electrochemical properties of both complexes were found to be similar in that they display one reversible redox process each corresponding to oxidation of metal center at positive potentials. In alcohol containing solvents, the vanadium(IV) species were generally spontaneously oxidized by molecular oxygen to yield the mono oxovanadium(V) species. However, in aqueous solvents the complexes were inert to oxygen and could only be oxidized with more vigorous oxidants. The complexes were found to undergo one electron oxidation as evidenced by cyclic voltammetry in acetonitrile solvent. Upon oxidation the yellow color fades and the light blue color changed to intense blue. The voltammograms are presented in appendix 7.5.

Therefore, from the cyclic voltammetric information the oxidation state of vanadium in both complexes is +4.

5. Conclusions

Vanadium(IV) or vanadyl complexes in this project are unstable in air and will spontaneously oxidize to the vanadium(V) states. However, this air oxidizability can be modulated by the nature of the solvent, with the more polar solvents stabilizing the lower tetravalent oxidation state.

The complexes did not contain bare vanadium(IV) and the VO^{3+} ion, since no LMCT bands in their visible spectra-giving rise to intense blue-violet colors, which provide a

means of distinguishing these forms of the metal from the more common VO^{2+} and VO_2^+ ions, which do not have intense LMCT bands. This information used to determine vanadium(IV) must bound to the ligands, as they do not display LMCT bands.

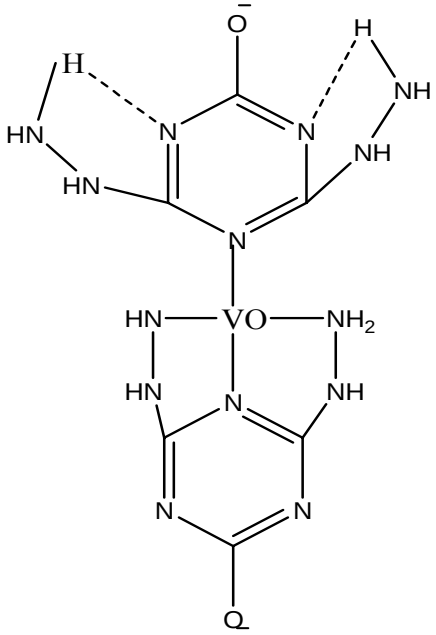
Oxovanadium(IV) compounds, especially BMOV and analogues are clearly effective in improving glucose uptake, decreasing plasma lipids, regulating thyroid hormone production, and ameliorating diabetic cardiomyopathy, retinopathy, and renal hypertrophy. Determining the relative efficacy of new vanadium containing insulin-enhancing agents is an ongoing concern. As my understanding increases of the mechanisms of vanadium `s insulin enhancing effects ability to devise a consistent simple and fast assay will no doubt also increases.

A square pyramidal geometry around the vanadium atom was determined for both complexes. Even though the coordination sphere and the oxidation state of the vanadium atom is the same for the two complexes, the different color and solubility indicates that the bioactivity of these compounds is a complex phenomenon related to different factors such as cellular type and the ligand nature.

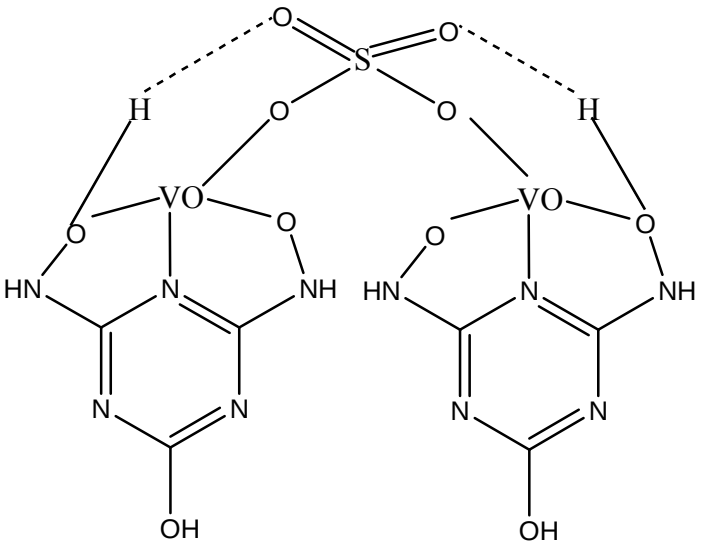
The absence of sulphate in the VO(II)-HBHTZ complex has been confirmed from the sulphate test. Hence for the sake of charge balance the complex is expected to be neutral and the ligands shows a tautomeric form in which deprotonation occurs at OH during complexation.

In VO(II)(HBHATZ)SO_4 complex, the presence of sulphate has been confirmed from sulphate taste. It is bridging the two VO^{2+} ions as observed from IR data.

Therefore, the structures of the new complexes are represented by the following figures.



4-hydroxy-2,6-bis(hydrazino) s-triazine vanadyl(II)



4-hydroxy-2,6-bis(hydroxyamino)-s-triazine-μ-sulphatovanadyl(II)

Figure 21. Proposed structure of the vanadyl complexes with HBHTZ and HBHATZ

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7. Appendices

7.1 List of Tables Pages

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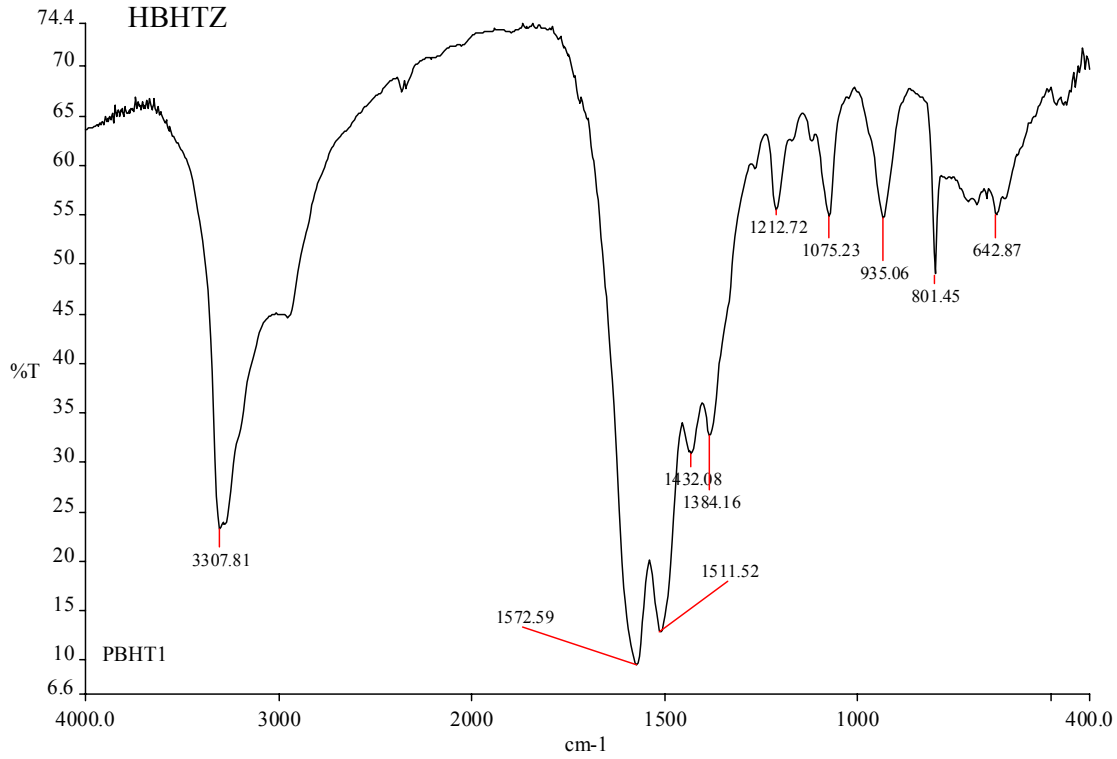
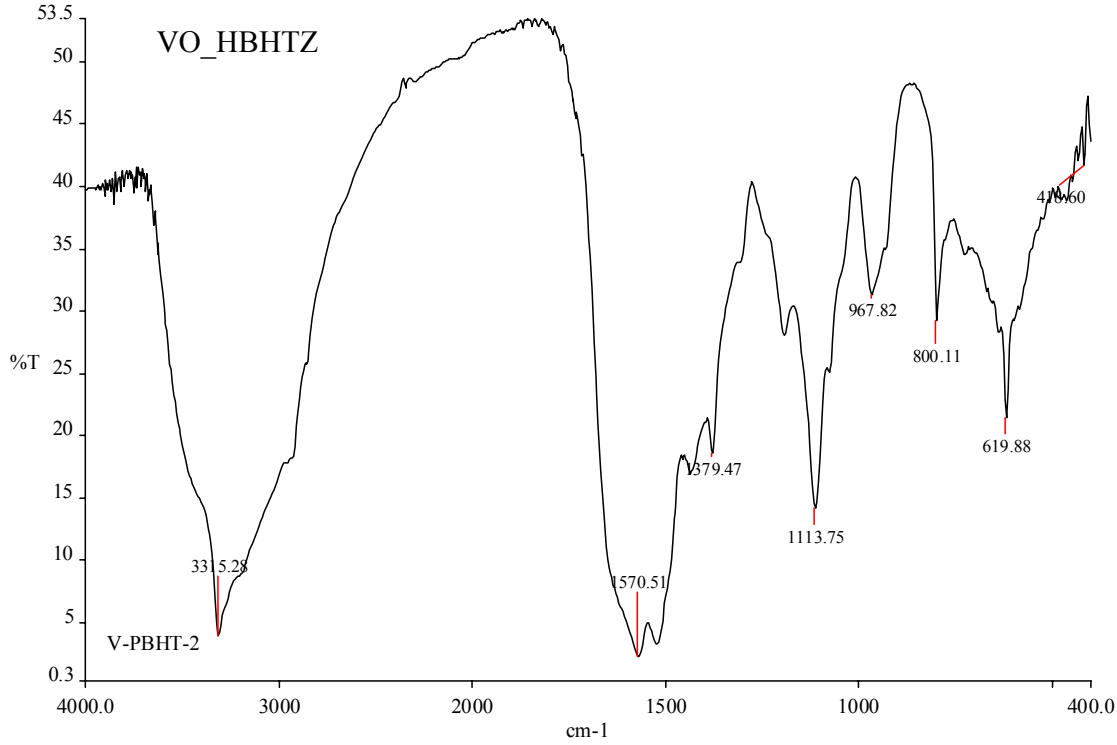
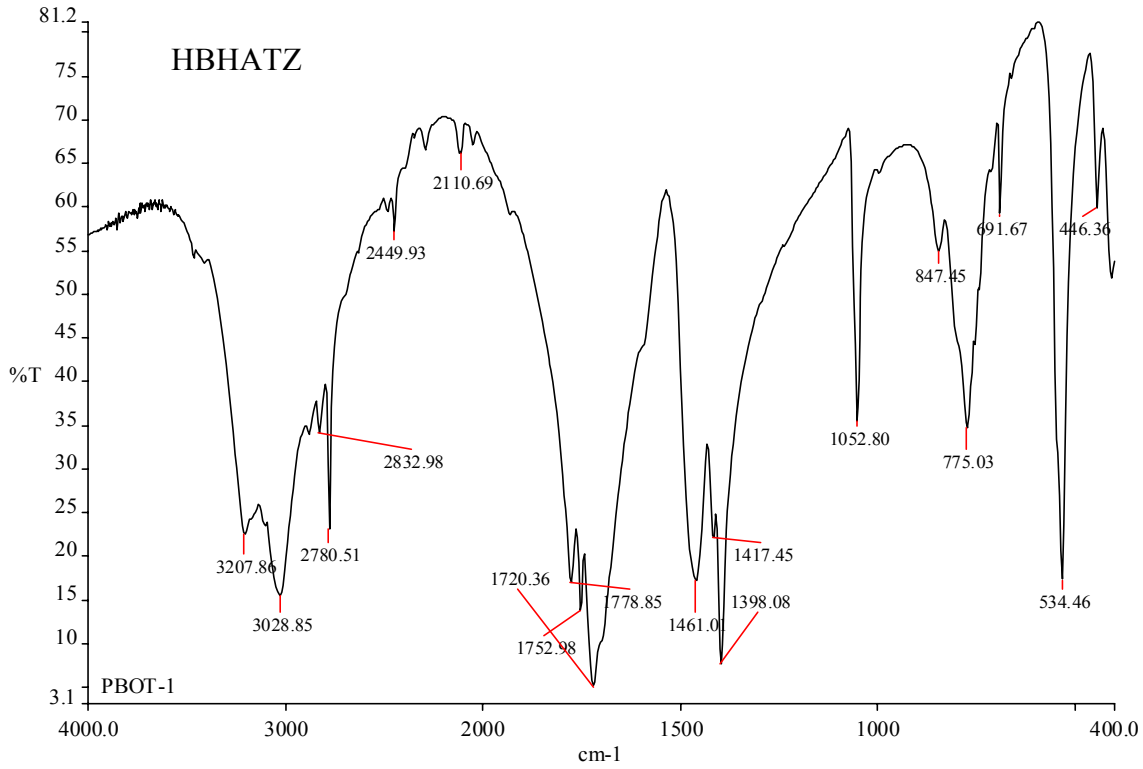
7.4. Spectra

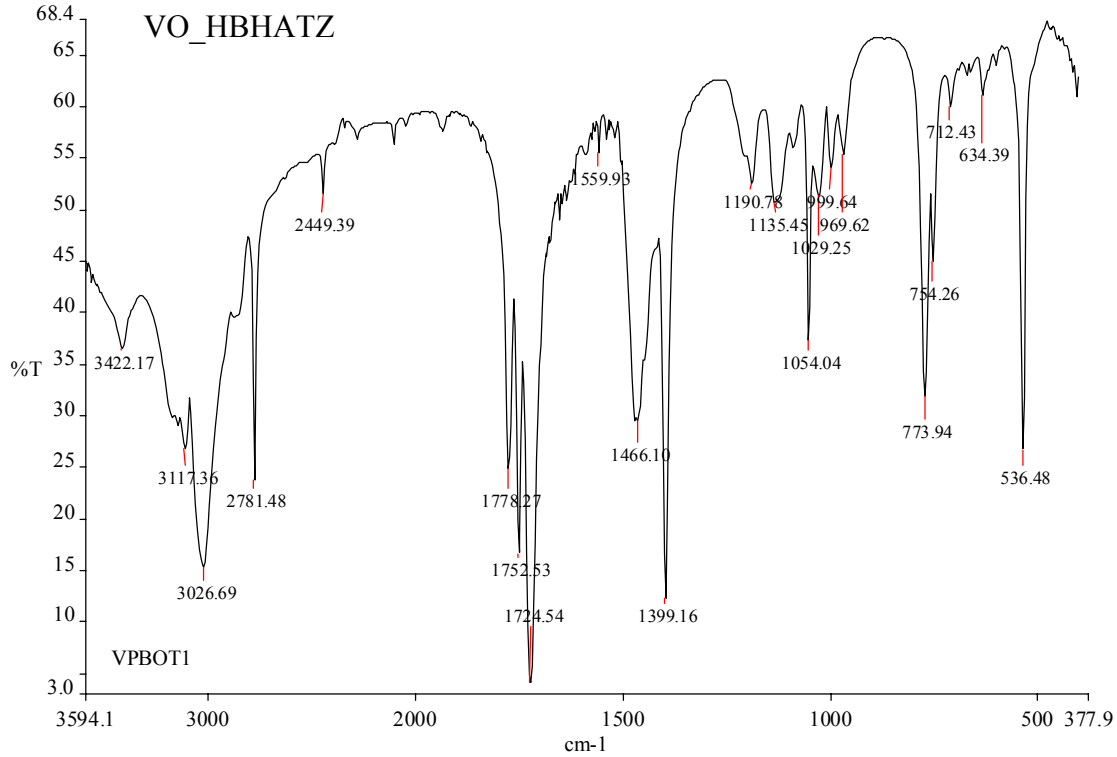
7.5.1 IR spectrum of HBHTZ and VO(II)-HBHTZ



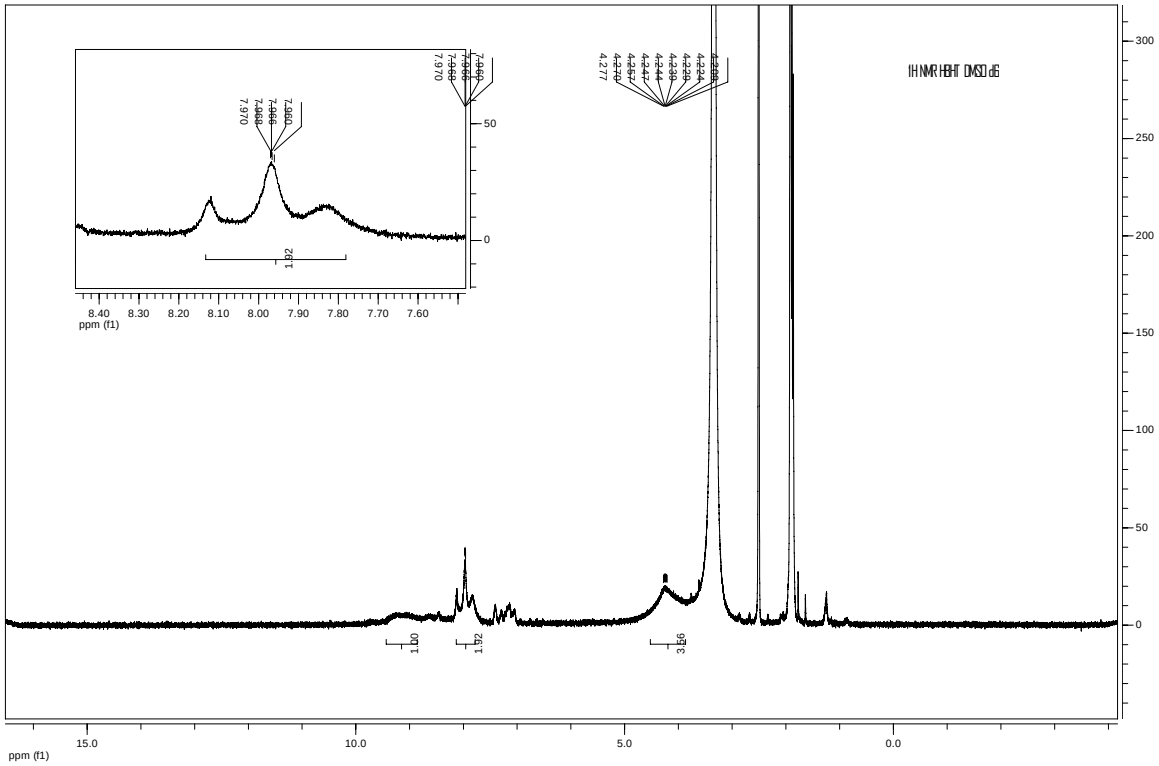


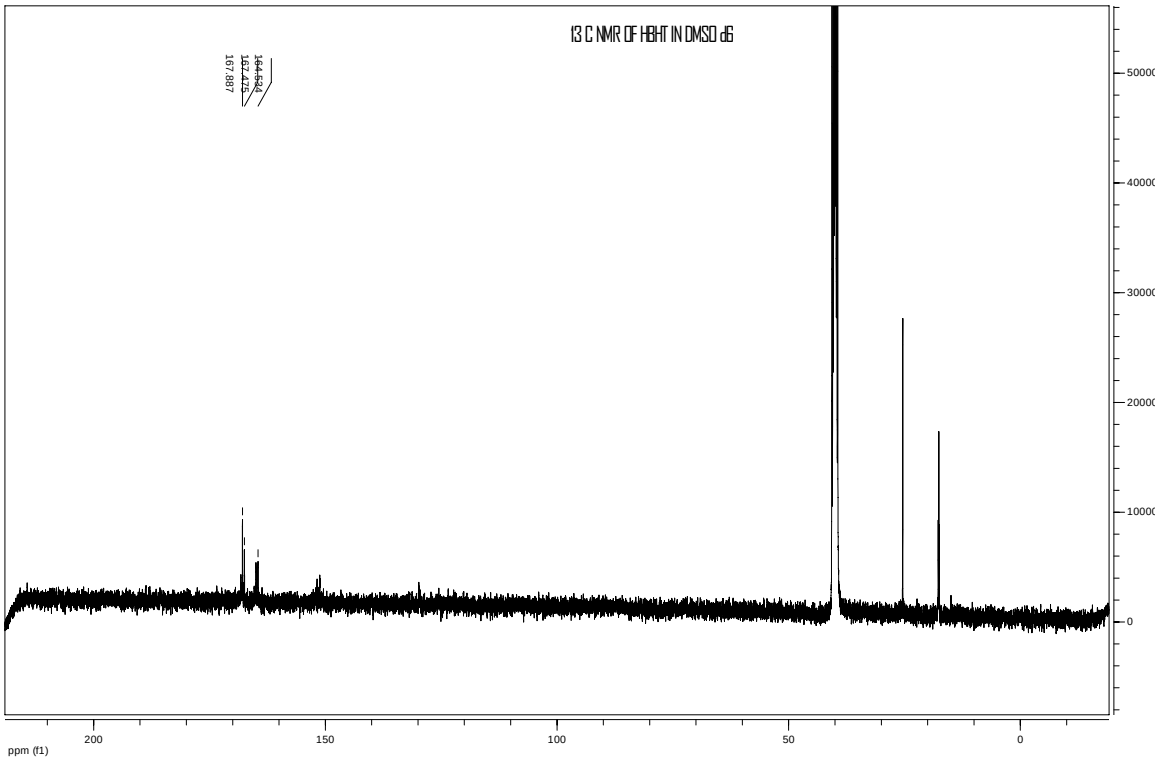
7.4.2 IR spectrum of HBHATZ and VO(II)-HBHATZ



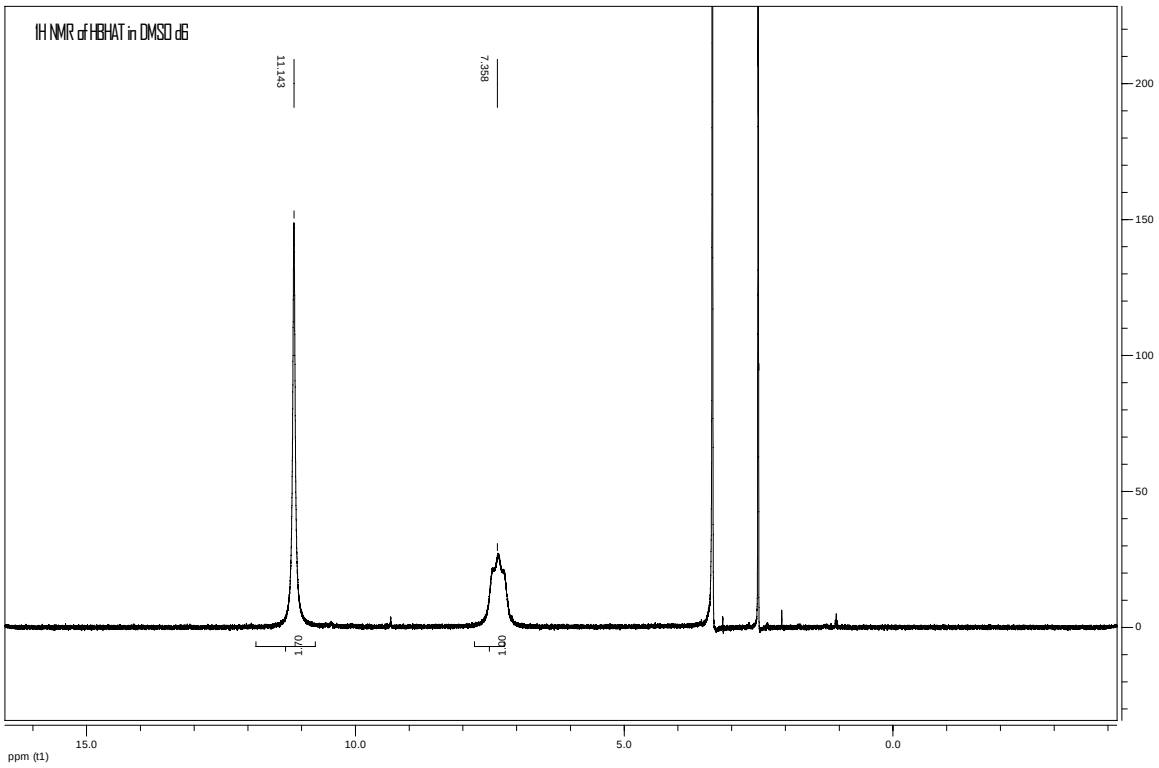


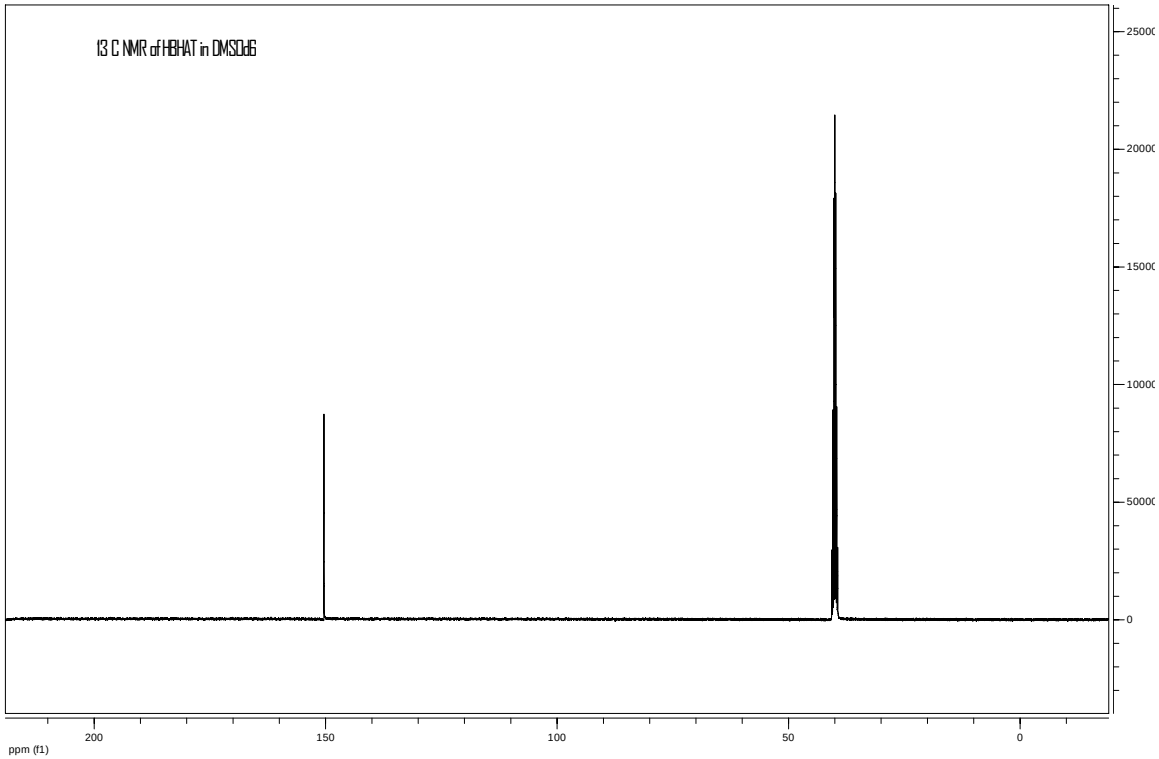
7.4.3 ^{1}H NMR Spectrum and ^{13}C NMR Spectrum of HBHTZ



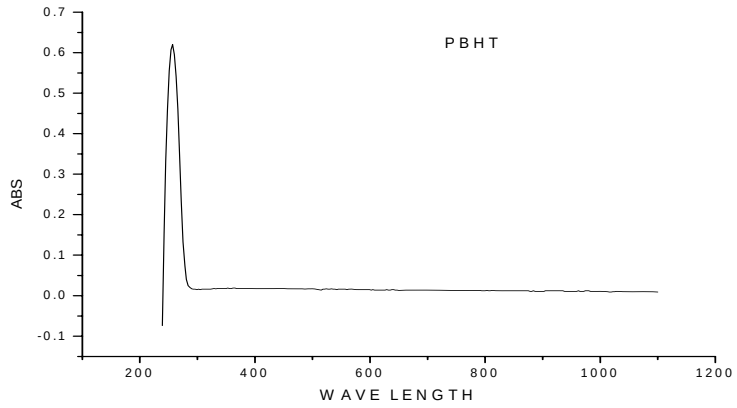


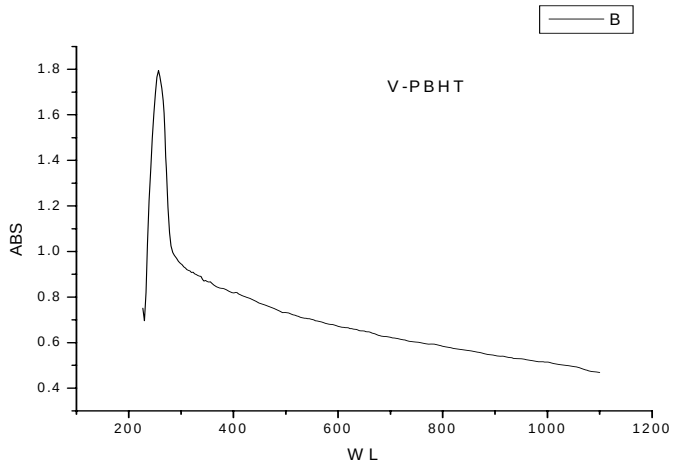
7.4.4 ^{1}H NMR Spectrum and ^{13}C NMR Spectrum of HBHATZ

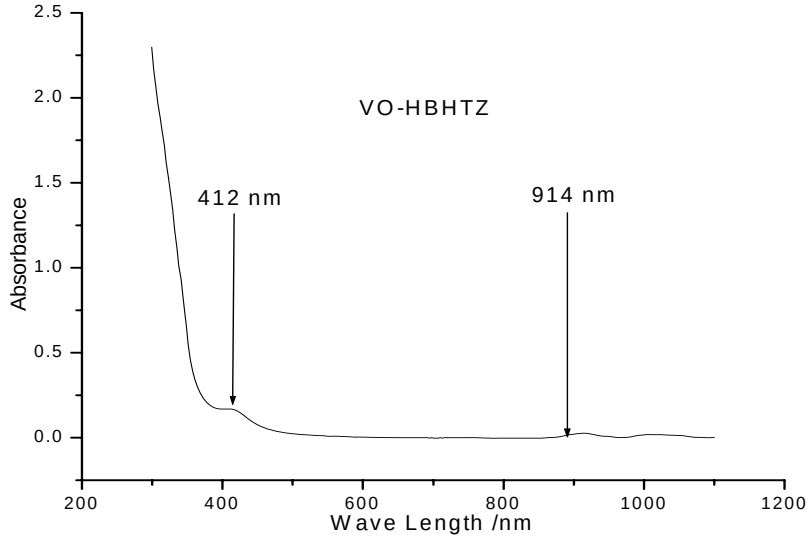




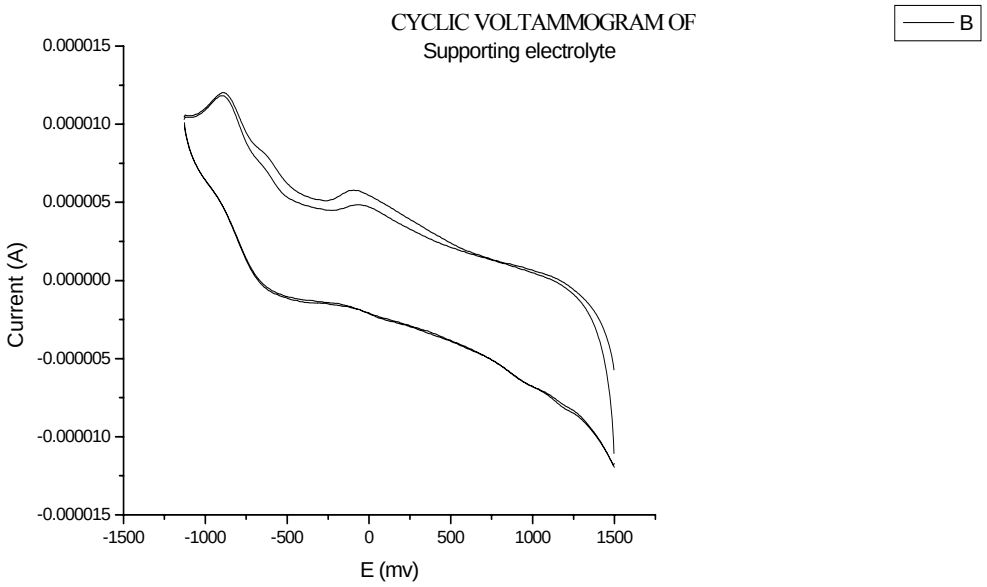
7.4.5 UV-Vis Spectrum of HBHTZ and VO(II)-HBHTZ

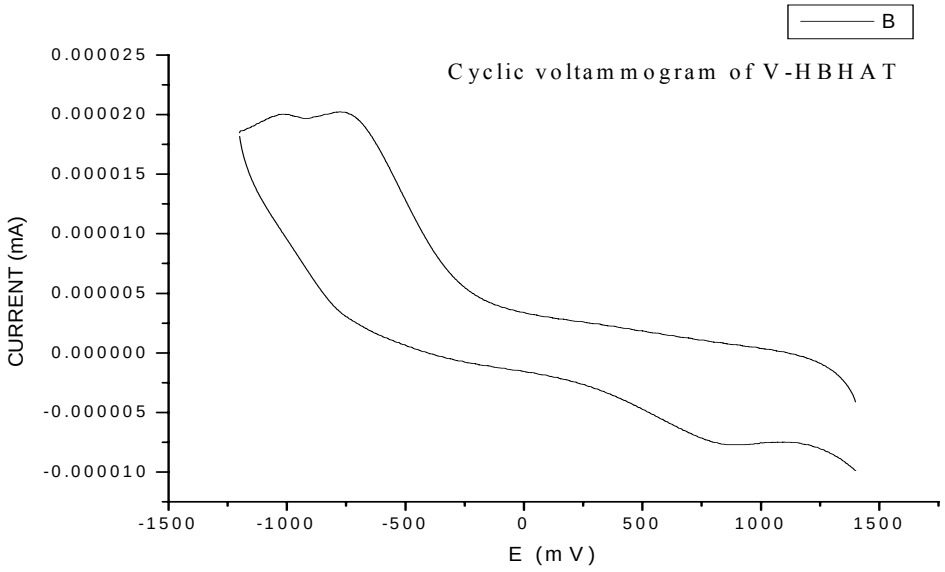


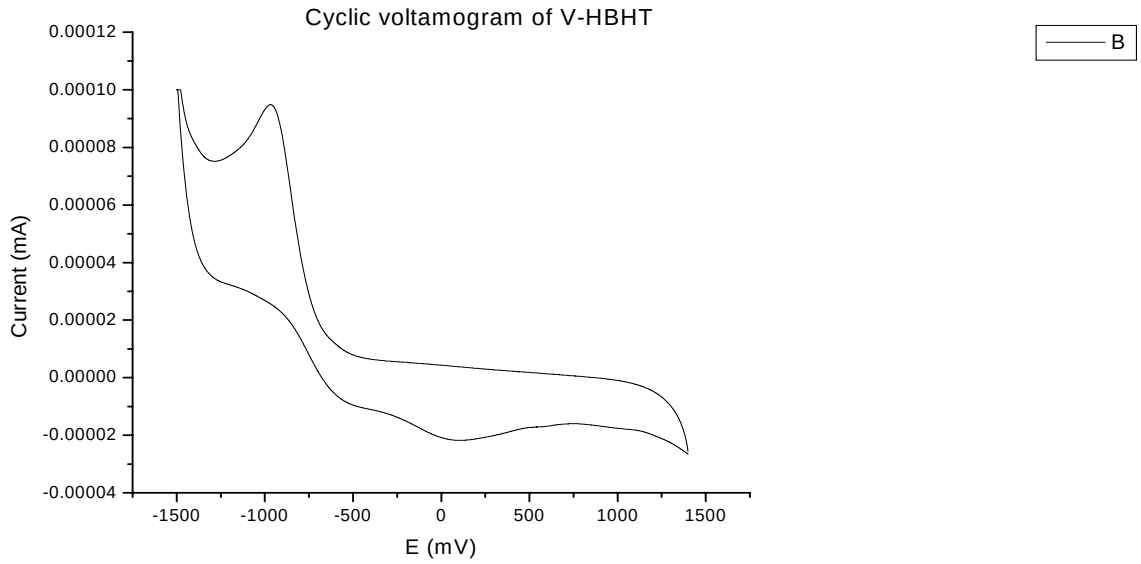


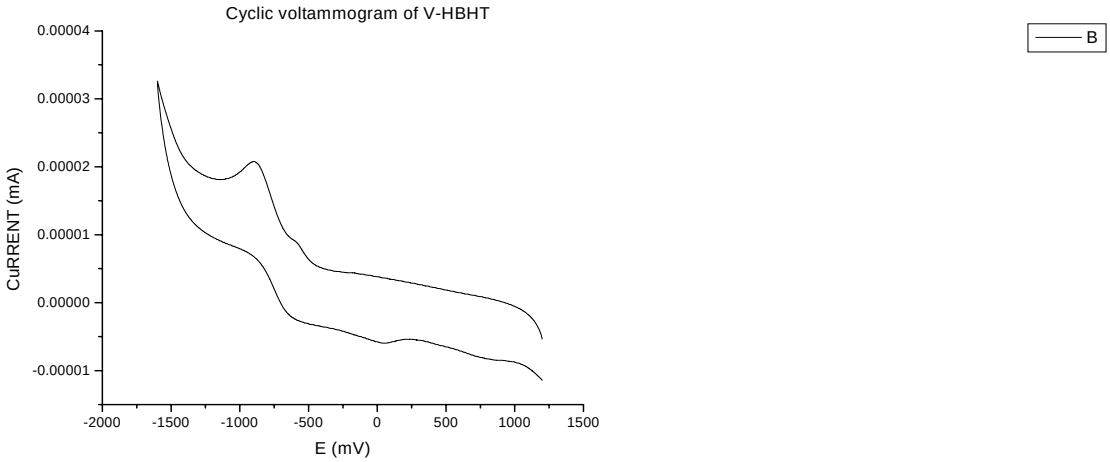


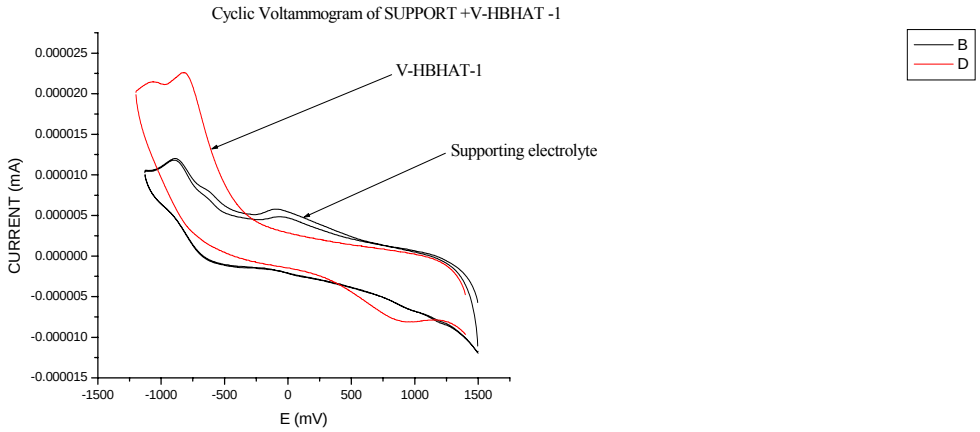
7.5 Cyclic voltammogram of VO(II)-HBHTZ and VO(II)-HBHATZ

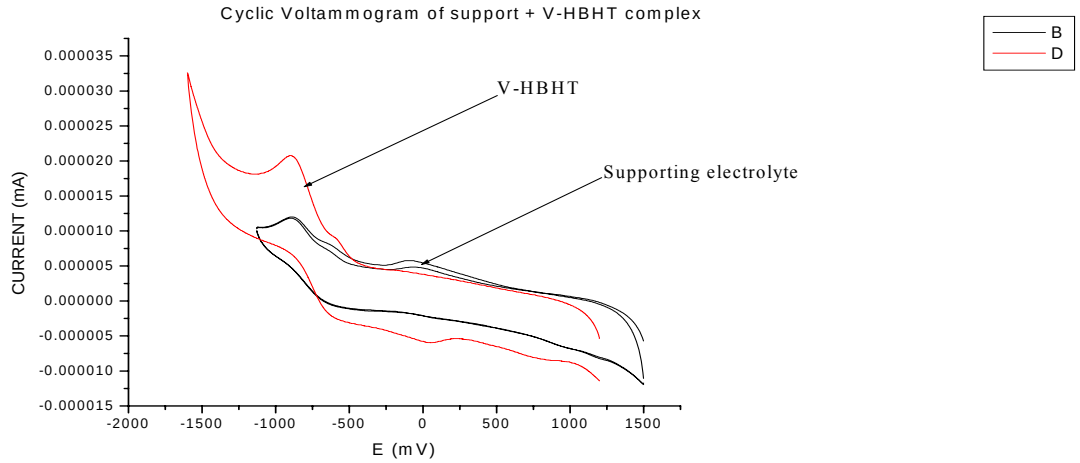





Cyclic voltamogram of V-HBHT
B
Current (mA)
0.00012
0.00010
0.00008
0.00006
0.00004
0.00002
0.00000
-0.00002
-0.00004
-1500
-1000
-500
0
500
1000
1500
E (mV)


Cyclic voltammogram of V-HBHT
B
CuRRENT (mA)
0.00004
0.00003
0.00002
0.00001
0.00000
-0.00001
-2000
-1500
-1000
-500
0
500
1000
1500
E (mV)


Cyclic Voltammogram of SUPPORT +V-HBHAT -1
B
D
V-HBHAT-1
Supporting electrolyte
CURRENT (mA)
E (mV)
0.000025
0.000020
0.000015
0.000010
0.000005
0.000000
-0.000005
-0.000010
-0.000015
-1500
-1000
-500
0
500
1000
1500


Cyclic Voltammogram of support + V-HBHT complex
B
D
V-HBHT
Supporting electrolyte
CURRENT (mA)
E (mV)
0.000035
0.000030
0.000025
0.000020
0.000015
0.000010
0.000005
0.000000
-0.000005
-0.000010
-0.000015
-2000
-1500
-1000
-500
0
500
1000
1500