

***Synthesis and Characterization of Oxovanadium Complexes
Incorporating Bidentate ligand***

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CERTIFICATE

This is to certify that the dissertation entitled “*Synthesis and Characterization of Oxovanadium Complexes Incorporating Bidantate ligand*” submitted by *Ms Sangeeta Sethy* of Department of Chemistry, National Institute of Technology, Rourkela for the degree of Master of Science in Chemistry is based on the result obtain in the bonafide project work carried out by her under my guidance and supervision. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

I further certify that to the best of my knowledge she bears a good moral character.

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ABSTRACT

Two new oxovanadium(V) complexes, $[\text{VO}(\text{L}_1^{\text{I}})_2(\text{OEt})]$ and $[\text{VO}(\text{L}_2^{\text{S}})_2(\text{OEt})]$ (**1-2**) have been reported which are obtained from the reaction of the Schiff bases ($\text{L}_1^{\text{I}}\text{H}_1$, $\text{L}_2^{\text{S}}\text{H}_1$), (Where $\text{L}_1^{\text{I}}\text{H}_1$ = isonicotinyldrazone of benzaldehyde, $\text{L}_2^{\text{S}}\text{H}_1$ = salicylaldehydrazone of acetophenone) with $\text{VO}(\text{acac})_2/\text{VOSO}_4$ in 2:1 molar ratio in ethanolic medium. All the synthesized ligands and the metal complexes are successfully characterized by elemental analysis, IR, UV-vis and NMR spectroscopy. This study indicates that both the complex (**1** and **2**) is monomeric in solid state while complex **2** may have dimeric nature in solution.

1. INTRODUCTION

Over the past decades the chemistry of vanadium and its coordination complexes have received much interest over the other transition metals because of its biological [1] and catalytic activity [2]. Vanadium is a very essential element found in remarkably high concentration in various marine organisms and plants [3]. Due to the discovery of the fact that certain haloperoxidases [4-6], nitrogenases [7], amavadin [8] isolated from *Amarnitamuscaria* contain vanadium in the form of vanadate ion (VO_3^+) in a nonporphyrinic O/N donor environment [9-10], interest in this field has been increased. Vanadium is found to exist in seven oxidation state (V^{V} to V^{-1}) [11], which makes its chemistry more complicated than the other 1st row transition metals. It has the ability to interact with biomolecules both in cationic and anionic forms which is very uncommon. This may be the reason behind its various biological effect [12-13]. It is found to show activity like insulin-mimetic [14], anti-carcinogenic [15], anti-leishmanial [16] etc. In recent time the insulin mimetic effect of vanadium is of great interest and various approaches are made to develop new drug containing vanadium with high thermodynamic stability, with an adequate balance of hydro/lipophilicity, and with low toxicity. To achieve these goals, various factors like donor property, hydrophilic / lipophilic property of ligand, position of substituent in ligand are to take care. From literature it is well known that vanadium complexes of composition VOL_2 with bidentate chelating ligand often show insulin mimetic action [17].

Keeping these observations in mind, I have continued my work on oxovanadium complex incorporating bidentate ligand systems. In this dissertation I have reported the synthesis, full characterizations of two bidentate ligands and its corresponding oxo-vanadium(V) complexes. All the synthesized ligands and corresponding metal complexes have been characterized by several spectroscopic techniques. The X-ray studies of the synthesized vanadium complexes are under process.

2. EXPERIMENTAL

2.1. Work plan:

This proposal is concerned with the design of various bidentate ligands synthesized from acid hydrazides and different carbonyl compounds and the synthesis of oxovanadium complexes by the reaction of bidentate ligands with $\text{VO}(\text{acac})_2$.

2.2. Synthesis of the Ligands:

The synthesis of our final ligand consists of two steps.

Step-1: Synthesis of acid hydrazide

The four acid hydrazides were prepared as follows.

To the solution of (0.01 mole) methyl ester, (0.1 mole) hydrazine hydrate was added. To it catalytic amount of ethanol was added and left for refluxing for 4hrs. After cooling the solution in the refrigerator, white compound is obtained which indicates the formation of the product. It was filtered and washed thoroughly with ethanol and ether, then dried over fused CaCl_2 .

Step-2: Synthesis of Schiff's base ligand

All the four Schiff's base ligands used in this study were prepared by stirring carbonyl compounds and the respective hydrazide in equimolar ratio. A typical synthesis is describe below. Schiff base ligand, anthraniloylhydrazone of benzaldehyde ($\text{L}_1^{\text{A}}\text{H}_1$) was prepared by reacting anthraniloylhydrazide (1.51g/10mmol) and benzaldehyde (1.01ml/10mmol) in stirring ethanol (15 ml) for 3 h. The resulting white compound was filtered and washed with ethanol and dried over fused CaCl_2 .

2.3 Synthesis of the Metal complexes:

I have synthesized eight different ligands but due to shortage of time the full characterization of two ligands and their corresponding complexes have been given. The complexes are synthesized as follows.

2.3.1. Complex 1, $[VO(L_1^I)_2 OEt]$:

0.225 g (1.00-mmol) sample of ligand $L_1^I H_1$ was dissolved in minimum volume of ethanol. In hot condition the ligand is completely soluble giving a light yellow color solution. To it 0.133 g (0.5-mmol) of vanadium (IV) acetylacetonate was added. Color of the solution slowly changed to dark green. After 3 h of reflux, the solution was filtered. Slow evaporation of the filtrate over 4 days produced black solid. The characterization of the solid product was done systematically. Complex 2 was also prepared by the similar method as above by taking $L_2^S H_1$ as ligand and $VOSO_4$ as starting precursor. $[VO(L_1^I)_2 OEt](1)$: Yield: 49%. Found (Calc. for $C_{32}H_{23}N_6O_2V$): C 57.43 (57.35), H 4.58 (4.60), N 17.51 (17.57). $[VO(L_2^S)_2 OEt](2)$: Yield: 45%. Found (Calc. for $C_{32}H_{31}N_4O_6V$): C 58.41 (58.35), H 4.27 (4.20), N 9.01 (9.06).

3. RESULTS AND DISCUSSION:

Spectral characteristics:

3.1. IR Spectra:

The IR spectra of the ligand ($L_1^I H_1$) show stretching vibration of N-H and C=O at 3193 and 1686 cm^{-1} respectively. The C=N stretching may be merged with that of C=O because of which we are getting a broad band at 1686-1645 cm^{-1} region. These bands are absent in the spectra of complex 1 (Figure 3.1.1). The disappearance of N-H and C=O stretching band unambiguously confirms that the ligand coordinates with the vanadium in the enol form. Also the C=N stretch of the ligands has been shifted to 1599 cm^{-1} in the spectra of the complexes, suggesting the coordination of the imine nitrogen to the

vanadium moiety. A new band at 942 cm^{-1} is characteristic of vanadium oxo absorptions [18].

$[VO(L_2^S)_2OEt](2)$: $\nu(\text{C}=\text{N})\ 1602\text{ cm}^{-1}$, $\nu(\text{C}=\text{C})\ 1572\text{ cm}^{-1}$, $\nu(\text{V}=\text{O})\ 991\text{ cm}^{-1}$.

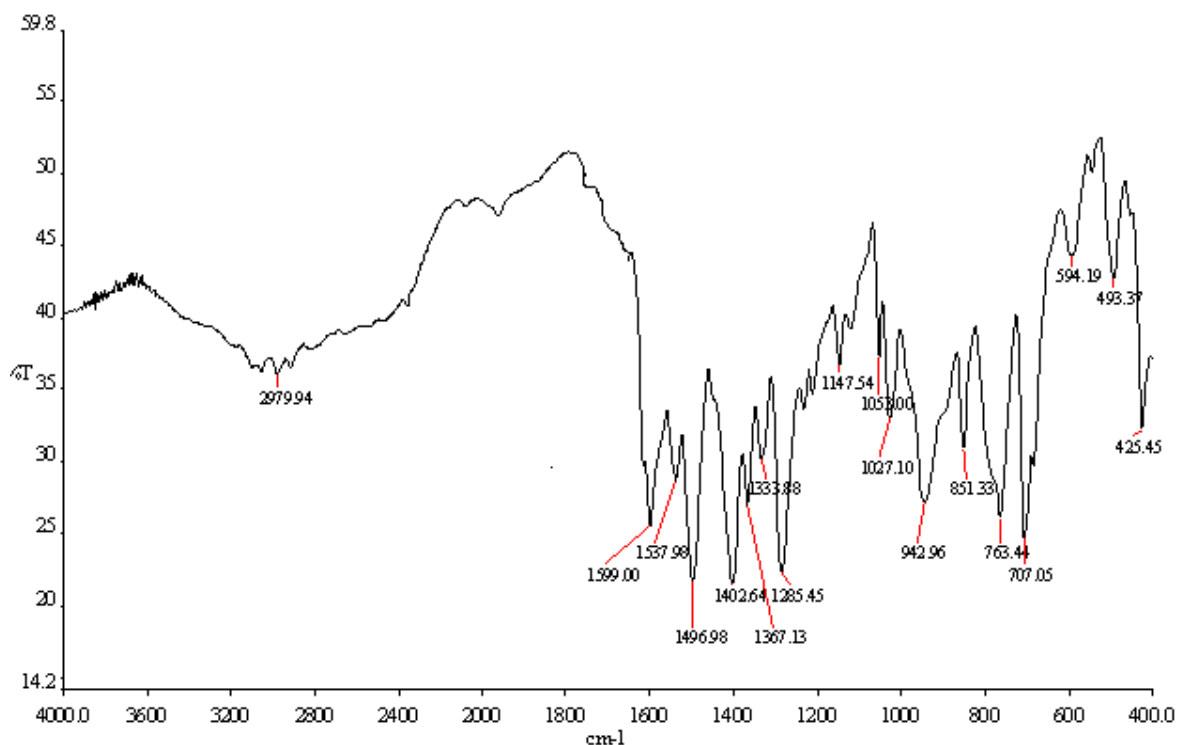


Figure 3.1.1. IR spectra of complex **1** $[VO(L_1)_2OEt]$:

3.2. Electronic Spectra:

The electronic spectra of all the ligand as well as complexes were taken in DMSO. Presence of strong electronic band at 403, 398 nm in complex **1** and **2** respectively is assignable to ligand to metal $[L-V(d\pi), LMCT]$ charge transfer whereas the band in high energy region (305 – 259 nm) of the ligand as well as the complex are due to the intraligand charge transfer. The spectra of ligands ($L_1^I H_1$) and complexes **1** are shown in Figure 3.2.1- 3.2.2.

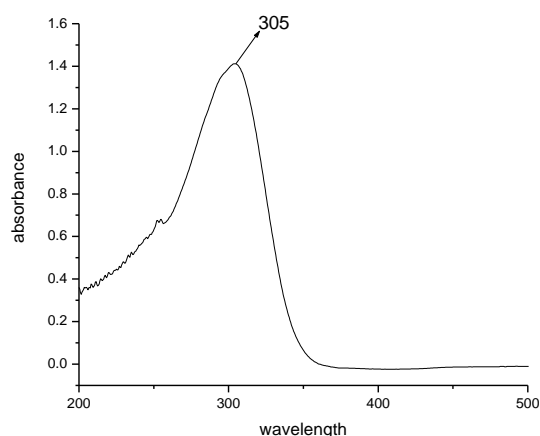


Figure 3.2.1. UV-Vis spectra isonicotinyldiazene of benzaldehyde(L_1H_1)

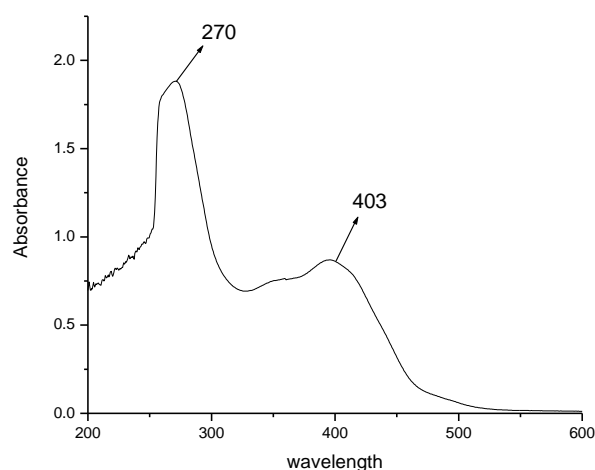


Figure 3.2.2. UV-Vis spectra of complex 1 [$VO(L_1)_2 OEt$]

3.3. NMR Spectra isonicotinyldiazene of benzaldehyde (L_1H_1)

In the 1H NMR spectra of the free ligand, the resonance for (-NH) proton is observed at 12.22, (-CH) at 8.79 and aromatic protons in the range of 7.39 - 8.81 ppm respectively. This data suggests the formation of the ligand. The conclusion was also supported by the results of ^{13}C NMR spectra as expected of the free ligand. ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 164.6, 161.96, 150.72, 150.44, 149.59, 141.25, 134.49, 130.86, 129.36, 127.73, 123.92, 122.21, 121.88.

3.4. NMR spectra of salicylaldehyde of acetophenone ($L_2^S H_1$)

In the 1H NMR spectra of the free ligand, the resonance for (-NH) proton is observed at 11.83 ppm, (-OH) at 11.35 ppm, aromatic protons in the range of 6.97 – 8.03 ppm and (CH_3) proton at 2.33 ppm respectively. This data suggests the formation of the ligand. The conclusion was also supported by the results of ^{13}C NMR spectra as expected of the free ligand.

3.5. ^{51}V NMR Spectra of complexes

The 1H NMR spectra of the complexes were taken in $DMSO-d_6$ but as it is difficult to explain without having X-ray structure. Corresponding ^{51}V NMR spectra is only included for discussion. The ^{51}V NMR spectra of complex **1** display a singlet at -511 ppm and that of complex **2** display two peaks at -555 and -593 ppm. These chemical shifts are usual for complexes containing the oxovanadium(V) unit [19], which indicate the complex has been formed.

4. CONCLUSION:

Several bidentate hydrazone ligands were synthesized and successfully characterized by IR, UV-vis and elemental (C, H, N) analyzer. The basic and electronic property of these ligands has been nicely explored in the syntheses of various oxovanadium(V) complexes. Complex **1** and **2** reported here has been fully characterized by IR, UV-visible, NMR spectroscopy and C, H, N analysis. This study indicates that both the complex (**1** and **2**) is monomeric in solid state while complex **2** may have dimeric nature in solution. Actual structure of the complexes will be known from single crystal X-ray study which is under process.

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