

Spectroscopic, Spectrophotometric and Conductometric Analysis of Oxovanadium-Hydrazone Complex

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Abstract:- A simple and rapid spectroscopic, spectrophotometric and conductometric methods for the determination of Oxovanadium(IV) is developed in the presence of 2-methyl-4-(N-cyanoethyl) –N-benzenesulphonyl benzylidene-3-oxo-[N-(4-nitro-1-phenyl) propanamido] hydrazone (MNPH) under alcoholic medium. The metal ion forms dark blue coloured, λ_{\max} at 510nm. Beer's law is obeyed in the range 0-10 mg/ml. The stoichiometry of the complex has been determined by spectrophotometric and conductometric methods. 2-methyl-4-(N-cyanoethyl) –N-benzenesulphonyl benzylidene-3-oxo-[N-(4-nitro-1-phenyl) propanamido] hydrazone (MNPH) an biologically active compound forms 2:1 complex with molybdenum in alcoholic medium indicated by conductometric titration and is further verified by Job's methods of continuous variation as modified by Turner and Anderson. Analytical results also favour 2:1 ratio between ligand and metal, complex of hydrazone were synthesised with molybdenum, isolated in pure form dried and weighed. The yield of the complex so obtained is substantial. Analytical data agrees with the composition $[\text{VO.L}_2]$ (where L=different new synthesised hydrazones). The applicability of the method has been tested by analysis of a large number of different synthetic and commercial samples.

The characterization of these newly synthesized hydrazones and their metal complexes were done by IR, ¹H-NMR spectral studies and elemental analysis. The infrared data of these complexes revealed the bidentate nature of the ligands and coordination to imino nitrogen of the amido group and azomethinic-nitrogen atoms. The new products were synthesized and evaluated for anti-tuberculosis activity against Mycobacterium tuberculosis H₃₇R_v in L.J.medium. The biological screening data indicates that the metal chelates are more potent than the parent ligands.

Keywords: Spectroscopic, spectrophotometric, conductometric analysis, Job's methods, Oxovanadium - hydrazone complex.

I. INTRODUCTION

Hydrazones have interesting ligational properties due to the presence of several potential co-ordination sites and transition metal complex of these ligands have been studied extensively¹⁻⁵. Hydrazones also exhibit pharmacological activity⁶⁻⁹ and analytical application^{10,8,3}. In continuation of our earlier work on the metal complexes of different hydrazones¹¹⁻¹³, we report here reactions of 2-methyl-4-(N-cyanoethyl) –N-benzenesulphonyl benzylidene-3-oxo-[N-(4-nitro-1-phenyl) propanamido] hydrazone (MNPH) with salt of oxovanadium (IV). The coordination chemistry of oxovanadium (IV) with multidentate ligands is important due to its growing application in catalysis¹⁴ and therapeutics¹⁵. Vanadium in traces has multiple biological roles, therapeutic value in small doses and toxic in excess. Vanadium containing compounds have their utility as insulin mimetic¹⁶ and antiamebic agent¹⁷. It is also suggested that vanadium could be considered as a representative of a new class of non-platinum metal antitumour agents¹⁸. In the present investigation we describe the synthesis and characterization of some new hydrazones and their oxovanadium (IV) complexes.

A new spectrophotometric method has been developed based on the formation of a coloured complex of hydrazone with oxovanadium salt (vanadyl chloride). The stoichiometry of the complex has been determined. The results are further confirmed by conductometric analysis.

II. EXPERIMENTAL

Materials and Instrumentation: All reagents used were purchased from Merck and used as received. Melting points were taken in open capillary and are uncorrected. Elemental analyses, ¹H-NMR spectra were obtained on a Bruker FT-400 spectrometer using CDCl₃ as solvent and TMS as an internal standard. IR spectra were recorded on KBr disks, using a Jasco-410 FTIR spectrometer. All the hydrazides were prepared by the reaction of hydrazine hydrate with different esters.

3-oxo-[N-(4-chloro-1-phenyl) propanamido] hydrazide, 3-oxo-[N-(4-nitro-1-phenyl) propanamido] hydrazide¹⁹ and 2-methyl-4-(N-cyanoethyl) –N-benzenesulphonyl benzaldehyde²⁰ were prepared by reported methods.

Standard newly synthesised hydrazone (MNPH) solution (0.005M) was prepared by dissolving 259 mg. of pure newly synthesised hydrazone (MNPH) in methanol by heating on boiling water bath. After cooling, the volume was made to 100 ml. vanadyl chloride (VC) (0.005M) was prepared by dissolving 245 mg in 100 ml of methanol.

Spectral and absorbance measurements were made on Systronics spectrophotometer 106 and conductometric titration were performed using Systronics digital conductivity meter 306.

VERIFICATION OF BEER'S LAW

Equal instalments of standard ligand (MNPH) solution (100 mg/ml) were added to an excess of (VC) (metal salt), final volume raised to 10 ml and optical density measured at λ max 510 nm. The value of optical density was plotted against concentration of newly synthesised hydrazone (MNPH).

STOICHIOMETRIC STUDY

1. Mole ratio method: - A series of solutions were prepared where concentration of metal ion (VC) was kept fixed. Concentration of newly synthesised hydrazone (MNPH) was increased stepwise.

Exactly 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8 and 4.0 ml of ligand (MNPH) solution was transferred into separate 10 ml volumetric flasks. 1ml of VC was added to each flask and volume was made up to 10 ml. Optical densities were recorded. The method was carried out with equimolar and non-equimolar solutions of reactants.

2. JOB'S METHOD: - The sum of molar concentrations of newly synthesised hydrazone (MNPH) and VC was kept constant and volume of MNPH vs. VC was varied. Exactly 6.0, 5.5, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5 and 0.0 ml of standard ligand solution was transferred to separate 10ml flasks and 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 and 6.0 ml of VC was added to the above flasks. Total volume was kept constant optical densities were recorded and plotted volume of the variable component.

CONDUCTOMETRIC TITRATION

20ml of 0.005 M ligand (MNPH) solution was taken and diluted to 50 ml with conductivity water and stirred. After 5 min conductivity was observed as blanks. 0.005 M VC solution was added in instalments of 0.5 ml and conductivity observed after each addition till a constant value was obtained. Conductance values were plotted against the volume of VC added.

STOICHIOMETRIC STUDIES

1.MOLE RATIO METHOD :- A series of solutions with fixed metal ion concentration and gradually increasing ligand (MNPH) concentration were prepared. Total volume was kept 10 ml in each case and conductivities were recorded. Both equimolar and non-equimolar solutions were used for these determinations.

2.JOB'S METHOD: - Series of solutions were prepared as described above; total volume was left 10 ml and conductivity recorded and was plotted against the volume of the variable component.

III. RESULTS AND DISCUSSION

All compounds gave satisfactory results for elemental analysis, IR and ¹H-NMR spectra. The physical and analytical data of synthesized new hydrazones and their metal complexes are presented in table-1.

Table –1: Analytical Data of Synthesized hydrazones and their Metal Complexes

Compound s	Mol. Formula (Mol. Wt.)	M.P (°C)	Colour (yield %)	Elemental Analysis (%)			
				Calculated/ Found)			
				C	H	N	M
MNPH	C ₂₆ H ₂₄ N ₆ O ₆ S (548.58)	212	Yellow (75)	56.93 (56.87)	04.41 (04.35)	15.32 (15.28)	-
[VO(IV)- MNPH) ₂]	VO(IV)- (C ₅₂ H ₄₈ N ₁₂ O ₁₂ S ₂) (1164.10)	230	Dark Blue (70)	53.60 (53.55)	04.12 (04.08)	14.43 (14.37)	04.37 (04.30)

Infrared Spectra: Comparative study of the IR of hydrazones and metal complexes are helpful in evaluating the results.

Spectral interpretation of new hydrazones show characteristic bands i.e. ν (N-H) stretching: 3320-3060 cm⁻¹, ν (C=O) stretching: 1750-1650 cm⁻¹ and azomethine nitrogen: 1640-1610 cm⁻¹.

A strong band around 1630 cm⁻¹ indicates the formation of new hydrazone because this band appears due to condensation of hydrazide with aldehyde, when these hydrazones chelate with metals, the normal frequency of ν (C=O) stretching band is shifted towards lower frequency region.

The lowering by 10-30 cm⁻¹ in ν (C=N) azomethine nitrogen band frequency around 1700-1600 cm⁻¹ suggests the coordination of hydrazone ligand to the metal ion through imino nitrogen of the amido group and azomethine nitrogen. Some new

bands present in far infrared region ($690-650\text{ cm}^{-1}$ & $980-900\text{ cm}^{-1}$) shows the formation of some new [ν (V-N) and ν (V-O)] bands in the spectra of metal complexes.

In all the complexes of VO^{2+} , the V = O (oxovanadium) stretching frequency occurs in the range $975-960\text{ cm}^{-1}$. These values are in the range observed for monomeric VO^{2+} complexes²¹. The $d\pi - p\pi$ orbital overlap involved in a multiple bond. This strong multiple bonding with the oxygen appears to be responsible for the trans influence of the oxo ligand, which disfavors attachment of a ligand trans to O^{22} .

Table-2 Infrared absorption frequencies (cm^{-1}) of Hydrazones and their Metal Complexes

Compounds	ν (NH)	ν (C=N)	ν (V=O)	ν (V-N)
MNPH	3225 m	1627 s	-	-
[VO(IV)-(MNPH) ₂]	3210 m	1605 s	978 m	673 m

¹H-NMR Spectra: The ¹H-NMR spectra of new synthesized hydrazones MCPH and MNPH were recorded (Table-3). The spectra in comparison to the corresponding hydrazide, show the disappearance of NH_2 group signal, while that of the NH protons are shows low field to the range δ 8.90 – 11.80 ppm for the imino proton present in ligands²³ (hydrazones).

The proton of azomethine group (CH = N) sharp peak is observed at δ 8.50 – 8.80 ppm. Further two signals observed at δ 3.60 – 3.90 ppm are assigned to methylene protons²³. The multiplet due to aromatic protons appears in the δ 7.03 – 8.30 ppm region. The appearance of two doublets in the region δ 11.11 – 12.96 ppm coupled with signals at δ 3.60 – 3.90 ppm suggests enolization of hydrazones involving active methylene group with keto-enol equilibrium in the solution. Thus, the signal at δ 3.60 ppm may be attributed to methylene ($-\text{CH}_2-$) and that at δ 3.90 ppm to methane proton ($=\text{CH}-$).

The bonding of ligand to metal is further supported by ¹H-NMR spectral studies and NMR spectra (Table 3) recorded for [VO-(MNPH)₂]. The signals in the δ 11 – 13 ppm region are medium, broad and shifted upfield by about 0.38 – 0.45 ppm in the complex as compared to that in the free hydrazone in which they are relatively intense indicating that they arise due to secondary (imino) – NH protons²⁴. This suggests coordination of the imino nitrogen (amido group) atoms to the metal center. In the spectrum of oxovanadium complex of hydrazones (MNPH) position of δ – $\text{CH}=\text{N}-$ signal shifts down field by 0.49 – 0.65 ppm suggesting coordination of azomethine nitrogen atoms to the metal center.²⁴

Table-3 ¹H-NMR Spectral data of hydrazones and their metal complexes

Compounds	-N-H	-CH=N-	-CH ₂ -	Ar-H
MNPH	11.5 (1H,m)	8.7 (1H,s)	3.8 (2H,m)	7.15-8.10 (12H,m)
[VO(IV)-(MNPH) ₂]	11.9 (1H, m, bro.)	8.1 (1H,s)	3.7 (2H,m)	7.09-8.00 (12H,m)

IV. CONCLUSION

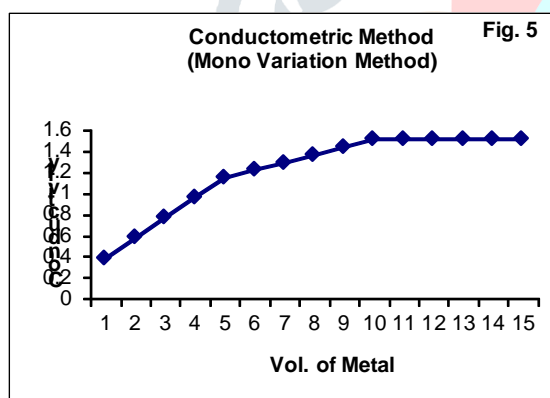
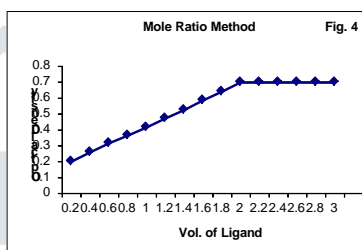
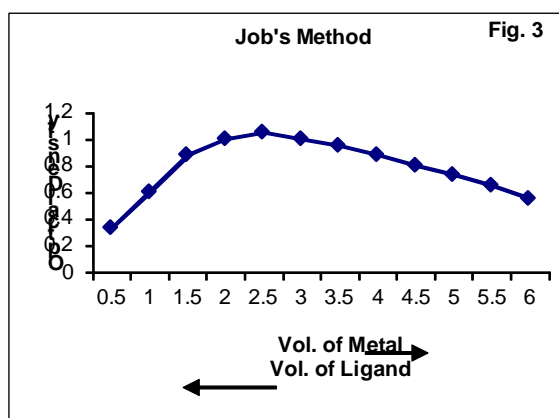
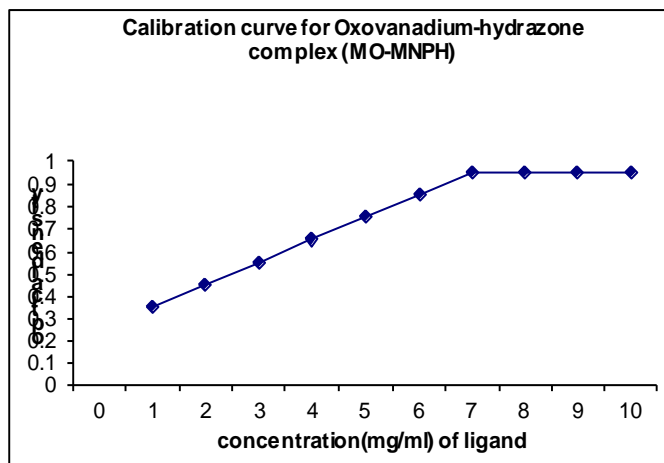
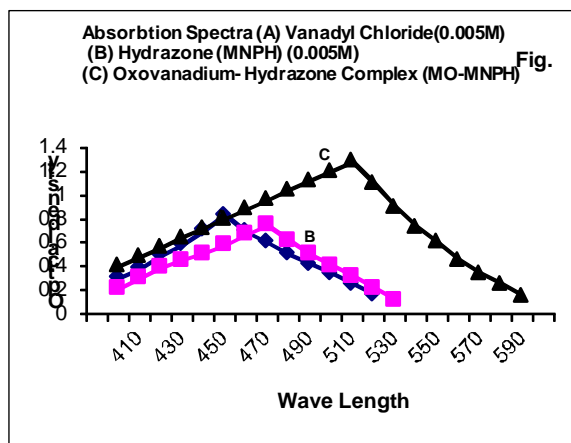
In this paper coordination chemistry of a newly synthesized hydrazone ligands, obtained from the reaction of 3-oxo-[N-(substituted -1-phenyl) propanamido] hydrazide and 2-methyl-4-(N-cyanoethyl)-N-benzenesulphonyl benzaldehyde, is described. Oxovanadium (IV) complexes have been synthesized using the above newly hydrazone ligands and characterized on the basis of analytical, IR ¹H-NMR spectral data. The observation of newly hydrazone ligand to the metal ion through imino nitrogen of the amido group and azomethine nitrogen and acts as a bidentate ligand. In all the synthesized metal complexes of vanadium metal attached oxygen atom to monomeric (VO^{+2}) form because of the $d\pi - p\pi$ orbital overlap involved in a multiple bond. This strong multiple bonding with the oxygen appears to be responsible for the trans-influence of the oxo-ligand, which disfavors attachment of a ligand trans to oxygen.

The biological screening data of indicate that the metal chelates are more potent than the parent ligands.

Yellow colour formed by addition of VC to newly synthesised hydrazone (MNPH) solution indicates the formation of a complex. The dark blue colour of the complex is stable for more than 5 h. Thus VC was found to be satisfactory reagent for complexation.

The λ max for Oxovanadium-hydrazone complex (MO- MNPH) was found to be at 510 nm [fig-1] and Beer's law was obeyed in the concentration range 0-10 mg/ml [fig-2]. Spectrophotometric studies were carried out using Job's method and mole ratio method. The plots for both these methods indicate the formation of only one complex between Oxovanadium and newly synthesised hydrazone (MNPH) under the condition of study and also confirmed a stoichiometric ratio 1:2 for the Oxovanadium-hydrazone (MO- MNPH) complex [fig-3,4&5]. Analytical data agrees with the composition [VO.L₂].

Conductometric measurements further confirm the above results. The proposed method is simple, rapid and economical and gives reproducible results; hence it can be used in routine laboratory analysis.



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