



Synthesis and Biological Activities of Oxovanadium(IV) Complexes of Schiff Bases

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Schiff bases like N-benzoyl-1-N-2-furan thiocarbohydrazone (A), thiophine-2-aldehyde *o*-phenylene diamine (B) and thiophene 2-aldehyde *m*-phenylene diamine are formed by the condensation of different carbonyl and amino compounds. The oxovanadium(IV) complexes of these Schiff bases have been characterized on the basis of elemental analysis, molar conductance, magnetic susceptibility, electronic, IR and ESR spectra.

Key Words: Schiff bases, Synthesis, Oxovanadium(IV), Biological activities.

INTRODUCTION

The chemistry of oxovanadium(IV) has received considerable attention¹ as the VO²⁺ unit can readily coordinate four, 5 and 6 donor atoms to form VOL₄, VOL₅ and VOL₆ type of complex², respectively. Additional interest has been generated, due to discoveries of the increasing biological importance of vanadium³. Several types of invertebrate accumulate vanadium in their blood. Thus, the ascidian seaworm phallusion mammilata has a blood concentration of vanadium upto 1900 ppm, which represents more than a 10 fold concentration with respect to the sea water in which it lives⁴. In this instance, vanadium is believed to play a role in the oxygen transport cycle⁵. Vanadium is also known to be an essential nutrient in higher life forms^{3,6} where it is involved in phospholipids oxidation, sulphur metabolism and cholesterol biosynthesis⁷.

Recently, two types of vanadium enzymes were discovered^{8,9} *i.e.*, vanadium nitrogenase and vanadium bromoperoxidase. The discovery that vanadium is involved in the nitrogenous and bromoperoxidase as low molecular weight complex (amovadin)¹⁰ led to renewed interest in the chemistry of the model compounds with varying N/O coordination sites. In another report¹¹, oxovanadium(IV) with coordinated N-O donor ligand was shown to be the active site in vanadium bromoperoxidase.

Vanadium has been a subject of investigation with regard to its association with insulin and its role in the body¹² control of glucose levels in plasma has been achieved *in vitro* and *in vivo* by means of vanadium administration in the form of inorganic salts¹³. As these salts are poorly absorbed the required high doses have been associated with undesirable side effects.

In order to achieve better absorption and so to reduce the doses of the element it seemed appropriate to administer it in the form of an organic matrix¹⁴. The reported¹⁵ structurally documented^{14,16} *bis*(maltolato) oxo-vanadium(IV) (BMOV) has been found to be effective, in the regulating glucose levels in the plasma of diabetic rats. It lowered cholesterol and triglyceride and ameliorated the cardiac disfunction normally observed in diabetic patients. It exhibited no significant toxic effect or hepatic and kidney function^{17,18}.

EXPERIMENTAL

All chemical used were of analytical grade. The ligands were prepared by different carbonyl and amino compounds. The carbonyl compound used were carboxy methyl-2-furan dithioate and thiophene-2-aldehyde and amino compounds used were benzoic acid hydrazide, *o*- and *m*-phenylene diamine. The ligands form complexes with methanolic solution of vanadyl sulphate at 7.0 pH on refluxation. Elemental analysis were carried out of RSIC CDRI, Lucknow. Conductivity measurement were carried out at Philips Conductivity bridge model PR 9500 with a dip type conductivity cell in methanol, DMF and DMSO solution at 25 °C. Magnetic susceptibility of the complexes were determined by Gouy method at the Department of Chemistry, Bareilly College, Bareilly. The sample tube was calibrated with CuSO₄. The IR spectra of complexes were recorded with Perkin Elmer spectrometer model 651 in KBr or in nujol phase at RSIC, CDRI, Lucknow. The visible spectra were recorded with Beckmann DU-2. Spectrophotometer in the range of 750-300 cm⁻¹ at Chemistry Department, Bareilly College, Bareilly.

Preparation of ligands: The Schiff bases were prepared by the condensation of carbonyl and amino compound. The amino compound was dissolved in methanol and refluxed for 0.5 h. Now requisite amount of carbonyl compound was added to the flask and this mixture was refluxed for about 6 h and kept for 24 h. The crystals of ligand were obtained and purified by recrystallization. The purity of ligands were checked by elemental analysis and m.p.

Preparation of oxovanadium(IV) complex: The aqueous methanolic solution of vanadyl sulphate (0.01 nmol) and the corresponding ligand (0.390 g, 0.01 mol) was refluxed as a water bath for about 5-6 h. The pH of a solution was adjusted to 7 by dropwise addition of 10 % methanolic sodium acetate solution. The metal chelates separated out on cooling. The product was washed repeatedly with methanol and finally with petroleum ether (60-80 °C) and dried *in vacuo*.

RESULTS AND DISCUSSION

Elemental analysis (Table-1) reveals that the oxovanadium complexes have the compositions with complex A $C_{12}H_8N_2O_3SVCl_2H_2O$, complex B has $C_{22}H_{24}N_4S_2O_2VCl_4$ and complex C has $C_{22}H_{24}N_4S_2O_2VCl_4$. The electrolytic nature and oxovanadium(IV) complex measured in DMF and DMSO. The electrolytic nature for complex A was 1:2 and for complex B and C were 1:4.

The oxovanadium complexes are paramagnetic in nature. The value of magnetic moment varies from 1.69-1.71 BM which is very close to the calculated value for d^1 system. The oxovanadium complexes appears to have octahedral geometry. The electronic spectral band of the oxovanadium(IV) complexes exhibits three distinct absorption bands. The low intensity absorption peaks in long wave length region are possible due to first crystal field transition $2B_2 \rightarrow 2E_1$ ($d_{xy} \rightarrow d_{xz}, d_{yz}$). This transition is spread over 13555 cm^{-1} region. The second crystal field transition is observed at 18500 cm^{-1} due to transition $2B_2 \rightarrow 2B_1$ ($d_{xy} \rightarrow d_{x^2-y^2}$). The third peak lie at 2800 cm^{-1} and is due to transition $2B_2 \rightarrow 2A_1$ ($d_{xy} \rightarrow d_{z^2}$).

The IR spectrum of ligand A show bands at 3125 and 3100 cm^{-1} which may be due to presence of two N-H groups. The bands at $1640, 1460, 1325, 1000$ and 835 cm^{-1} are assigned to $\nu(C=O)$, thioamide, $I[\beta NH + \nu CN]$ thioamide II $\gamma(CN) + \beta(NH)$, $\nu(N-N)$ and $\nu(C=S)$, respectively. The spectrum of the complex shows only one peak at 3125 cm^{-1} due to $\nu(N-H)$ suggesting the loss of one hydrazenic proton *via* enolization. A strong band in the spectrum of the ligand at 1640 cm^{-1} [due to $\nu(C=O)$] is found to be absent in the spectrum of the complex and in the place of this a new band appears which may be due to $\nu(N=C)$ of N CO suggesting that enolic oxygen is involved

in bonding. The spectrum of the complex shows a negative shift of 20 cm^{-1} in $\nu(C=S)$ suggesting an additional bonding through thio sulphur.

The spectrum of the complex shows a positive shift of 20 cm^{-1} in $\nu(N-N)$, this indicates that one hydrazenic nitrogen is also involved in bonding. Further the band at $1460, 1325$ and 1000 cm^{-1} due to thioamide I, II and $\nu(N-N)$ undergo positive shift of $25, 15$ and 20 cm^{-1} , respectively showing the involvement of thiolato sulphur. It appears therefore the ligand is acting in bidentate manner co-ordinating through thiolato sulphur, both the hydrazenic nitrogen and enolic oxygen¹⁹.

The IR spectrum of the complex exhibits a new band at 3400 cm^{-1} which may be due to the presence of water molecule. The appearance of a band at 810 cm^{-1} may be assigned to wagging modes of coordinated water molecule. This is further supported by the TGA which indicates the percent weight loss corresponding to the loss of two water molecules.

The IR spectra of the compound B exhibited a strong band at 1600 and 700 cm^{-1} which may be assigned to $\nu(C=N)$ and C-S (thiophene), respectively. Other sharp band at 3320 and 3120 cm^{-1} were absent. These bands have assigned to asymmetric and symmetric of NH_2 group, respectively²⁰. The IR spectra of the complex showed a downward shift of 15 cm^{-1} in the $\nu(C=N)$ vibrations due to the reduction of electron density, this indicates the involvement of nitrogen atom of azomethine group in coordination.

The $\nu(C-S)$ band exhibited an upward shift at 10 cm^{-1} indicating the coordination through sulphur atom of thiophene ring. The C-S stretching frequency was shifted to higher value on account of an increased $d\pi-d\pi$ contribution between sulphur atom and ring p system²¹. The $\nu(NH_2)$ band remain unaltered which shows the non involvement of amino group in the complex formation. Thus the ligand is behaving in a bidentate manner coordinating through azomethine nitrogen and thiophene ring sulphur atom. The IR spectra of the complex shows new bands at 3140 cm^{-1} which may be due to the presence of coordinated water molecule. The rocking and wagging mode of water molecule appears at 810 cm^{-1} .

The IR spectra of ligand C shows important bands at 1625 cm^{-1} which may assign to $\nu(C=N)$ at 700 cm^{-1} (thiophene C-S) at 3330 and 3110 cm^{-1} due to asymmetric and symmetric NH_2 group²².

The IR spectra of the complex show a band at 1610 cm^{-1} indicating coordination through nitrogen atom of azomethine group. This downward shift may be due to the reduction of electron density in the azomethine link. The $\nu(C-S)$ band showed an upward shift of 15 cm^{-1} indicating involvement of

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF COMPLEXES

Name of complex	m.f.	Colour	m.p. (°C)	Composition (%)					Solubility	Magnetic moment (B.M.)
				C	H	N	Cl	Br		
A	$C_{12}H_8N_2O_3SVCl_2H_2O$	Light brown	375	35.82 (35.46)	2.98 (2.72)	6.96 (6.58)	7.96 (7.74)	–	DMSO	1.71
B	$C_{22}H_{24}N_4S_2O_2VCl_2$	Deep colour	240	41.71 (41.60)	3.79 (3.62)	8.84 (8.26)	10.11 (10.00)	22.43 (22.11)	DMSO	1.71
C	$C_{22}H_{24}N_4S_2O_2VCl_4$	Black	2.45	41.71 (41.60)	3.79 (3.58)	8.84 (8.71)	10.11 (10.02)	22.43 (22.38)	DMSO	1.72

sulphur atom in co-ordination. The upward shift may be due to the increased d_{π} - d_{π} contribution between sulphur atom and ring π system²⁰. The stretching vibration of NH_2 group remain unaltered in the spectra of the complex thus the ligand is behaving in bidentate manner co-ordinating through sulphur and nitrogen atom.

The IR spectra of the complex shows new band at 3410 cm^{-1} which may be due to presence of co-ordinated water molecule, the rocking and wagging modes of water molecule appears at 810 cm^{-1} .

ESR spectra of oxovanadium: At the room temperature polycrystalline ESR spectrum was nearly identical with the spectrum of the frozen glass. The solution ESR spectrum clearly shows an equidistant 8 line pattern characteristic of mononuclear VO^{2+} complexes. The frozen glass or polycrystalline spectrum reveals that there are totally 16 lines with the narrow 8 line perpendicular bunch enveloped with in the eight line parallel bunch. The resolution of the ESR spectra in to parallel and perpendicular regions even in room temperature poly crystalline ESR spectrum may be due to a large inter molecular distance offered by the macromolecule quadridentate nature of the schiff bases causing negligible intermolecular dipolar broadening²².

Biological activity: The ligand and its polychelates were screened for antimicrobial activity by disc diffusion method^{23,24} against *E. coli*, *Klebsiella*, *Salmonella typhi* and *Bacillus*¹⁹. The results indicate that the ligand is active towards *E. coli* and *Bacillus* while *S. typhi* and *Klebsiella* show a poorer inhibitory effect. *S. typhi* is highly inhibited by oxovanadium(IV) chelate. However, there is moderate effect of all other polychelates *Klebsiella* is moderately inhibited by oxovanadium(IV) chelates.

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