

Synthesis and characterization of some vanadyl Schiff base complexes

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Abstract : Neutral tetradentate N_2O_2 type complexes of vanadium (IV) have been synthesized by metal ion catalyzed template process in which aromatic/aliphatic diamines such as orthophenylenediamine / ethylenediamine were allowed to undergo Schiff base condensation with salicylaldehyde having chlorine substitution at 3 or 5 position, in the presence of vanadyl sulphate in ethanolic medium, the stoichiometric ratio between amine, aldehyde and metal salt being 1:2:1. All the complexes were characterized on the basis of their micro analytical, spectral, magnetic and conductivity data. Micro analytical data indicate formula of the complexes to be of the type $[VO(SB^{1-4})]$ where SB stands for the binegative anion of the Schiff base H_2SB^{1-4} .

$H_2SB^1 = N, N' - bis(3-chloro\ salicylidene)$
ethylenediamine

$H_2SB^2 = N, N' - bis(3-chloro\ salicylidene)$
orthophenylenediamine

$H_2SB^3 = N, N' - bis(5-chloro\ salicylidene)$
ethylenediamine

$H_2SB^4 = N, N' - bis(5-chloro\ salicylidene)$
orthophenylenediamine.

Conductivity data supports non electrolytic nature of the complexes as the value lies in the range of 6 - 10 units.

Infra red spectral study suggests coordination to the vanadyl ion through azomethinic nitrogen and phenolic oxygen. Magnetic moment data along with electronic spectral bands corroborate square pyramidal geometry.

(Keywords : Spectral study, vanadyl complexes, Schiff base ligands, square pyramidal geometry)

Introduction

An important group of transition metal

complexes with Schiff base ligands are those of vanadium in different oxidation states (ranging from III to V). The biological role of vanadium is not yet fully recognized, but it is found in oxygenases, nitrogenase, phosphatase-metabolizing enzymes and phosphomutases¹⁻⁶. The biological activity of vanadium complexes includes anticancer, insuline-mimetic, anti-inflammatory and antibacterial^{7, 8}. Intense study on anti-tumoral effects of vanadium showed that it can disrupt cellular metabolism, affect the signal transduction pathways, can damage DNA but also can be used as a panacea for resistance to oncolytic immunotherapy⁹⁻¹⁵. Most of the biological and potential pharmacological effects of vanadium lie in inhibition of phosphotyrosine phosphatases (PTPs), e.g. PTP1B. PTPs are a large family of signalling enzymes that play an important role in signal transduction and regulation of cellular processes such as differentiation, cell growth and proliferation¹⁶. Several studies have provided evidence that vanadium compounds are strong inhibitors of tyrosine phosphatases strictly associated with their biological and pharmacological activities¹⁷⁻²⁰.

Experimental

2.1 Materials

All reagents and chemical purchased from Aldrich-Sigma were of analytical/spectroscopic grade and used without further purification. Chemicals and solvents used for the preparation of Schiff base ligands and metal complexes are salicylaldehyde, 3-chlorosalicylaldehyde, 5-chlorosalicylaldehyde, ethylenediamine, orthophenylenediamine,

oxovanadium(IV)sulphate hydrate, ethanol, methanol, chloroform, dimethylsulphoxide, toluene and dichloro-methane.

2.2 Preparation of Symmetrical Schiff Base

The ligands were prepared according to established procedures²¹. A typical procedure for the synthesis of the symmetrical Schiff base is as follows.

To a stirred solution of 0.08 moles of the chloro Salicylaldehyde in 60 ml absolute ethanol was added, drop wise, 0.04 mole of an ethylenediamine /orthophenylene diamine the mixture was then stirred for 2h at 50°C. Afterward the mixture was cooled to room temperature, or in ice and the products formed was collected by filtration. The crystals were washed with cold absolute ethanol and re-crystallized from

ethanol–chloroform (1.3v/v) mixture. The yellow crystals were dried in desiccators over silica gel.

2.3 Preparation of Oxovanadium (IV) Complexes

The following general procedure was used in the synthesis of all the oxovanadium (IV) complexes. Oxovanadium (IV) sulphate (6mmol, 0.978g) was dissolved in hot absolute methanol (30 ml) and a mixture of triethylamine (12mmol, 1.214 g) and the corresponding Schiff base (6 mmol), dissolved in methanol (20ml), were added with stirring, which resulted in an instant color change to green/orange. The mixture was stirred for 3h at 50°C and then concentrated to half of its volume using a rotary evaporator. The product was filtered and washed twice with cold absolute ethanol and allowed to dry in desiccators over silica gel.

Table – I: Physical properties and analytical data for the Schiff bases and Oxovanadium (IV) complexes

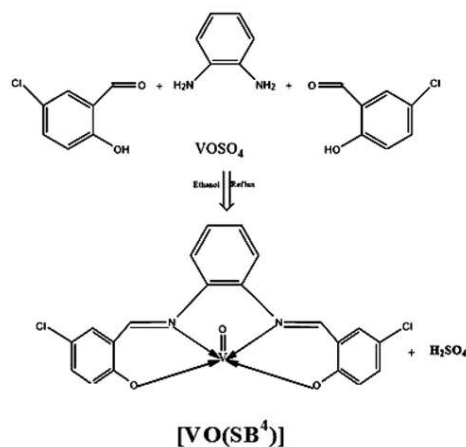
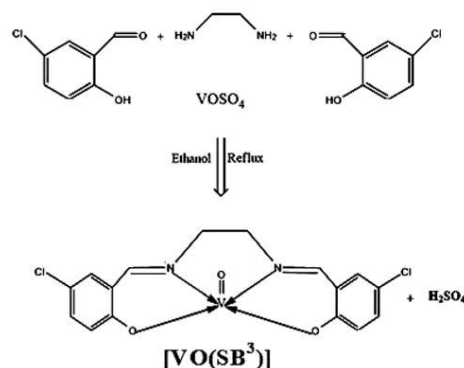
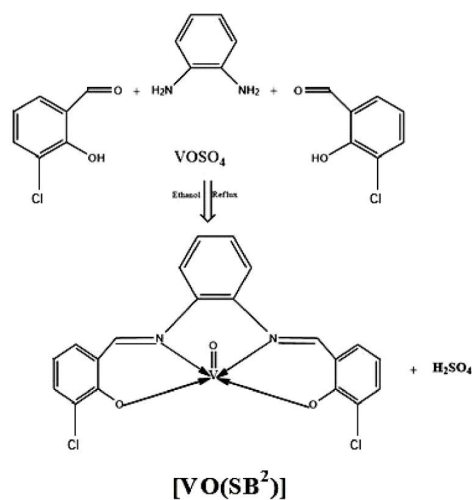
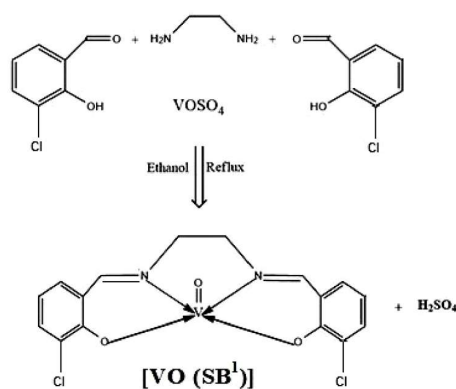
Comp.	Empirical Formula	Formula Weight	Yield	Color	M.P (°C)	Microanalysis Found (Cal)				
						%C	%H	%N	%Cl	%V
H ₂ SB ¹	C ₁₆ H ₁₄ N ₂ O ₂ Cl ₂	337	83.4	Yellow	165-166	56.88 (56.97)	4.14 (4.15)	8.28 (8.30)	21.01 (21.07)	—
H ₂ SB ²	C ₂₀ H ₁₄ N ₂ O ₂ Cl ₂	385	65.1	Orange	103-104	62.21 (62.33)	3.62 (3.63)	7.25 (7.27)	18.38 (18.44)	—
H ₂ SB ³	C ₁₆ H ₁₄ N ₂ O ₂ Cl ₂	337	80.2	Green	138-139	56.82 (56.97)	4.14 (4.15)	8.29 (8.30)	21.02 (21.07)	—
H ₂ SB ⁴	C ₂₀ H ₁₄ N ₂ O ₂ Cl ₂	385	79.7	Orange Yellow	72-73	62.20 (62.33)	3.62 (3.63)	7.26 (7.27)	18.00 (18.04)	—
VOSB ¹	C ₁₆ H ₁₂ N ₂ O ₂ Cl ₂	402	86.7	Green	>250	47.62 (47.76)	2.96 (2.98)	6.91 (6.96)	17.56 (17.66)	12.65 (12.68)
VOSB ²	C ₂₀ H ₁₂ N ₂ O ₂ Cl ₂	450	74.3	Brown	>250	53.12 (53.33)	2.67 (2.66)	6.18 (6.22)	15.32 (15.77)	11.23 (11.33)
VOSB ³	C ₁₆ H ₁₂ N ₂ O ₂ Cl ₂	402	91.6	Green	>250	47.58 (47.76)	2.95 (6.91)	6.92 (6.96)	17.50 (17.66)	12.66 (12.68)
VOSB ⁴	C ₂₀ H ₁₂ N ₂ O ₂ Cl ₂	450	75.5	Green	>250	53.08 (53.33)	2.65 (2.66)	6.21 (6.23)	15.21 (15.77)	11.18 (11.33)

The following factors were found to affect the course of the synthesis:-

- the sequence of addition of the reagents,
- temperature of the solution of the starting reagents (solution chilled to about 4°C)
- the nature of the diamines used and
- The reaction time.

A change in reaction time from four days to just three hours or the use of warm solution of the starting reagents produced mixed products. From the above observation it seems that the conden-

sation reactions occurred stepwise. The preparation of symmetrical Schiff base and their V (IV) complexes can be represented as follows.



Results and Discussions

3.1 ¹H NMR Spectra of the Schiff Bases

The ¹H NMR spectra (table II) of the symmetrical Schiff bases showed single peaks for each of the azomethine protons and phenolic protons. This is attributed to the symmetrical nature of these ligands.

3-Chlorosalicylaldiimine

In the ¹H NMR spectral of this series,

the signals due to the azomethine protons appeared as a singlet at 8.3-8.6 ppm while the O''H protons of the phenolic groups were observed at 12.7-12.9 ppm. The signal due to the chloro protons was observed as a singlet at 3.8 ppm. Three peaks were observed for the CH₂ protons at 2.2, 3.7 and 4.0 ppm, corresponding to a multiplet, a triplet and a singlet respectively.

Table – II
¹H NMR data for free ligands

Ligand	δ OH	δ Ar-H	δ N=CH
H ₂ SB ¹	12.7(s,2H)	6.7-7.3(m,6H)	8.3(s,2H)
H ₂ SB ²	12.7(s,2H)	6.9-7.7(m,10H)	8.6 (s,2H)
H ₂ SB ³	13.6 (s,2H)	6.7-7.3 (m,6H)	8.3 (s,2H)
H ₂ SB ⁴	13.1(s,2H)	6.8-7.3 (m,10H)	8.6 (s,2H)

5-Chlorosalicylaldehydeimine

The ¹H-NMR spectra of the Schiff bases in this series exhibit a multiplet Signals at 6.7-7.3 ppm which are attributed to the aromatic protons. The methyl protons of the chloro substituent were observed as a triplet at 1.5 ppm while its CH₂ protons appeared as a quadruplet at 4.1-4.2 ppm. The methyl protons of the methylethylenediamine bridged ligand were observed as a duplet at 1.4 ppm while its CH₂ protons were observed as a doublet at 3.9 ppm. The signals due the azomethine protons and the O-H protons of the phenolic groups were observed as a singlet at 8.3-8.6 and 13.1-13.8 ppm respectively.

The tentative assignments of the observed bands for the compounds were made by comparing the spectra with those reported in the literature on similar systems²²⁻²⁴.

The absorption bands due to the amino group disappeared in the IR spectra of all the ligands, which showed that the amino groups in the diamine condensed with the aldehyde/ketone. The band appearing at 1567-1640 cm⁻¹ due to azomethine group in the ligands is shifted to lower frequency at 1573-1634 cm⁻¹ in the metal(ii) complexes, indicating the participation of the azomethine nitrogen in interaction with the metal ion.

3.2 Infrared Spectra

The important infrared spectral bands of the ligands and the metal (ii) complexes are presented in table 4.3.1-4.3.2 and fig. 4.3.1-4.3.6.

Similarly, the ν (C-O) band of the ligands, which occurs at 1257-1334cm⁻¹, shifted to 1277-1366cm⁻¹ in the complexes indicated deprotonation coordination of the phenolic oxygen to the metal atom.

Table III:
Selected Infrared Spectral bands of the Schiff base and Oxovanadium (IV) Complexes

Complex	ν C=N	ν C-O	ν V=O	ν V-N	ν V-O
H ₂ SB ¹	1638	1285	-	-	-
H ₂ SB ²	1622	1272	-	-	-
H ₂ SB ³	1637	1275	-	-	-
H ₂ SB ⁴	1614	1283	-	-	-
VO SB ¹	1627	1277	979	491	573
VO SB ²	1599	1289	981	497	544
VO SB ³	1631	1313	976	483	611
VO SB ⁴	1602	1315	982	448	541

Thus, it can be concluded that the Schiff bases acted as tetradentate ligands coordination via the azomethine N and the phenolic O. Further conclusive evidence of the coordination of the Schiff bases with the metal ions was shown by the appearance new bands at 435-583 and 410-581 cm^{-1} assigned to the metal nitrogen (M-N) and the metal oxygen (M-O) vibrations, respectively. These bands were absent in the spectra of the uncomplexed Schiff bases, thus confirming participation of the O and N atoms in the coordination. It has been established that the metal-ligand Vibrational modes are very sensitive to substituent effects.

This was proposed on the basis of isotopic labelling studies (^{15}N - and ^{18}O -labelling). The substituent effects were based on the position of substitution rather than on the nature of substituents. The $\nu(\text{M-O})$ bands are observed to exhibit higher Vibrational frequencies than the $\nu(\text{M-N})$ bands for the meta-substituents while the order is reversed for the para-substituents regardless of the nature of the substituents. It was suggested that the transmission of the substituent effects in the Schiff bases complexes are propagated largely by a mesomeric mechanism. The important bands along with their assignments are listed in table III Oxovanadium (IV) complexes of Schiff bases can give rise either to monomeric structures with square pyramidal/ trigonalbipyramidal/octahedral coordination geometry or to polymeric structures, involving $\dots\text{O}=\text{V}\dots\text{V}=\text{O}\dots$ linkages, with a distorted octahedral geometry. However, on the basis of the location of the $\nu(\text{V}=\text{O})$ band it is possible to distinguish between monomeric and polymeric complexes. In the present work, most of the oxovanadium (IV) complexes exhibit a strong band in the region 959– 988 cm^{-1} . Which have been assigned to $\nu(\text{V}=\text{O})$ with a monomeric square pyramidal coordination geometry. All the orange-yellow coloured complexes, with the trimethylene bridge in which the $\nu(\text{V}=\text{O})$ appeared at 848-860 cm^{-1} , have been assigned polymeric species with $\dots\text{O}=\text{V}\dots\text{V}=\text{O}\dots$

interactions, which afforded a distorted octahedral coordination geometry.

3-Chlorosalicylaldiimines

The ligands exhibited the characteristic $\text{C}=\text{N}$ stretching frequency at 1622-1640 cm^{-1} and shifted to lower frequencies (1599-1634 cm^{-1}) upon complexation indicating the involvement of the nitrogen atom of the azomethine group in coordination. The phenolic C-O stretching frequency occurs in the 1272-1285 cm^{-1} for the ligands and in the 1277-1307 cm^{-1} region for the complexes. The C-O stretching frequency is generally shifted to a higher frequency, indicating the participation of phenolic oxygen in C-O-M bond formation.

A significant change observed in the infrared spectra of the complexes compared to their respective ligands is the appearance of strong absorption band due to $\text{V}=\text{O}$ stretching frequency in the complexes. All the complexes exhibited a strong $\text{V}=\text{O}$ stretching band at 979-981 cm^{-1} , which suggests monomeric square pyramidal structures. The $\nu(\text{V}=\text{O})$ stretching frequency of the trimethylene derivative occurs at 848 cm^{-1} , which is also consistent with polymeric system involving $\dots\text{O}=\text{V}\dots\text{V}=\text{O}\dots$ bridge. Other bands observed in the complexes in the regions 544-573 and 476-497 cm^{-1} are due to $\nu(\text{V-O})$ and $\nu(\text{V-N})$ respectively. These bands were absent in the spectra of the ligands.

5-Chlorosalicylaldiimines

The spectra of the Schiff bases show $\nu(\text{C}=\text{N})$ bands in the region 1614-1637 cm^{-1} , which is shifted to lower frequencies in the spectra of all the complexes (1602-1631 cm^{-1}) indicating the involvement of nitrogen in coordination to the metal ion. The $\nu(\text{C-O})$ band of the ligands, which occurs at 1272-1283 cm^{-1} , was slightly displaced to higher frequencies (1304-1315 cm^{-1}) on coordinated to the metal complexes. The characteristic $\nu(\text{V}=\text{O})$ stretching frequency in the oxovanadium (IV) complex appears as a strong band at 960-988 cm^{-1} , which

is consistent with monomeric square pyramidal structures. The nature of metal-ligand bonding is confirmed by the newly formed band at 541-614 and 448-483 cm^{-1} in the spectra of the complexes which are tentatively assigned to $\nu(\text{V-O})$ and $\nu(\text{V-N})$ respectively.

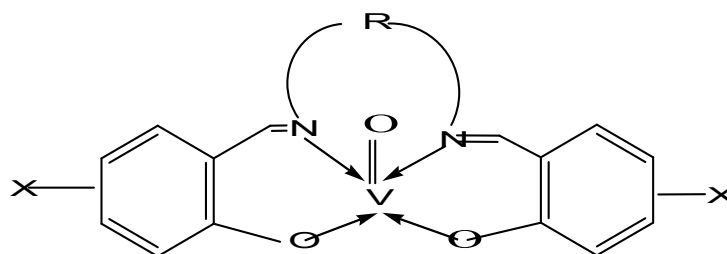
3.3 Electronic Spectra and Magnetic Moment Electronic Spectra of the Oxovanadium (IV) Complexes

The electronic absorption spectra are

often very helpful in the evaluation of results furnished by other methods of structural investigation. The electronic spectral measurements were used for assigning the stereochemistries of metal complexes based on the positions and number of d-d transition peaks. The electronic absorption spectra of metal (II) complexes were recorded in 10^{-3} M and 10^{-5} M solution of each complex in DMSO and chloroform in the range 200-1100 nm at room temperature. The results of the solution spectra are presented in table IV.

Table IV:
Electronic spectral bands of Oxovanadium (IV) complexes

Comp	Solvent	Band maxima/ cm^{-1} (/ $\text{cm}^{-1}\text{mmol}^{-1}$)		C.T	Ligand#
[VO(SB ¹)]	CHCl_3	16694(19)	24631 (10)	34722 (2660)	39370(4210)
	DMSO	16891(17)	25380 (1090)		37879(4270)
[VO(SB ²)]	CHCl_3		22422 (1790)	31348 (2590)	39370(3930)
	DMSO	15649	22624 (1790)	31646 (2500)	38023(3390)
[VO(SB ³)]	CHCl_3	16694(15)	25510 (620)	33333 (2280)	40984(3660)
	DMSO	17065(14)		26385 (650)	38760(3290)
[VO(SB ⁴)]	CHCl_3	16051 (7)	22831 (1180)	28818 (3040)	40650(3550)
	DMSO	16155 (9)	23641 (1410)	30395 (2990)	37879(2920)



Where $\text{R} = (-\text{CH}_2-)_2$ or $(-\text{C}_6\text{H}_4-)$, $\text{X} = 3\text{-Chloro}$ or 5-Chloro

Conclusion : On the basis of above discussions, square planar geometry as shown above has been proposed for the complexes. The ligands behave

in a dibasic, tetradentate manner utilizing both the azomethinic nitrogen and phenolic oxygen in coordination.

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