

Covalently Linked Five-Coordinate Schiff-base Complexes on Polymer Supports—VO(IV) Systems

7.1 Introduction

Vandium is widely distributed¹ in rocks, soils, plants, animals and to lesser extent in waters and has been shown to be present in the marine animal, phallusia mamillata (Sea Squirt)² and land plants Amanita muscaria (mushroom).^{3,4} Most importantly oxovanadium (IV) is concentrated in the solid asphaltic fraction of petroleum⁵ with porphyrin⁶ ligands. More and more data on the spectral properties of the Oxovanadium (IV) complexes are needed to establish correlation between the spectral parameters and the ligand type. There have been effort from different corners for identifying ligands for oxovanadium (IV) present in the geological^{7,8} and biological systems.^{9,10}

Reactivity of transition metal complexes with Lewis-bases hence the formation of adduct with the two has already been discussed by several investigators.^{11,12} Oxovanadium (IV) complexes with square pyramidal structure react with Lewis bases to form stable adducts, in which the base occupies the sixth coordination position in an octahedral complex.¹¹

Villarego et al.¹² reports cyclohexylamine and morpholine adducts of oxovanadium (IV) dithiocarboxylates and discusses various spectral results obtained thereon. Structure of the monomer adduct molecule put forward by them are given in the Figure 7.1.

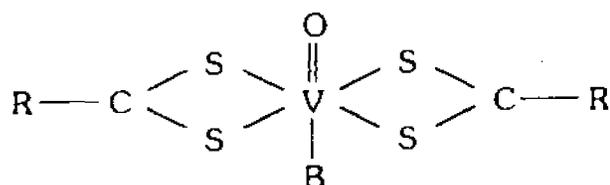


Figure 7.1. Monomeric structure proposed for adducts of Bis (R-dithiocarboxylato) oxovanadium (IV).
(B - base cyclohexylamine or morpholine; R - n-pentyl, n-hexyl, cyclohexyl, phenyl, iso-octyl).

Adduct formation between $\text{VO}(\mathbf{45})_2$ and various coordinating species has been studied by W. L. Linert et al.¹³ Electronic, IR and far IR spectra supports solvate formation. The complex forms 1:1 adducts with pyridine, N,N-dimethyl formamide, N,N-dimethyl acetamide and dimethyl sulphoxide. These adducts were obtained in crystalline form. So several oxovanadium (IV) complexes interact with various donor solvents, exhibiting solvatochromic behaviour.¹⁴ The solvation reaction always leads to a colour change which indicates electronic modification.^{15,16} $[\text{VO}(\mathbf{45})_2]$ presented in Figure 7.2 as **I** interact with solvents form the adduct (**II**).¹³ But depending on the solvent used there will be **I** and **II** in different concentration. This can be noticed from the absorption maxima and corresponding shift in the absorption.¹² The shift of the band is due to the changing intensities of the two overlapping bands associated with the changing concentration of the two species. Larger shifts are seen for hydroxylic solvents like water or methanol as can be expected from their more pronounced acceptor properties.

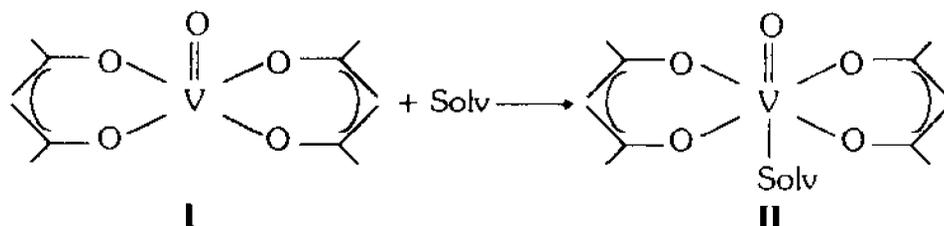


Figure 7.2.

Far IR spectra also provides an intensity ratio which directly relates to the ratio of concentration of non-coordinated to strongly coordinated species. The far IR spectra of $\text{VO}(\text{acac})_2$ in pyridine solution shows a splitting of its bands, a fact which can be attributed to a cis-trans-equilibrium in solution, as has been found in solid adducts of $\text{VO}(\text{acac})_2$ with a series of substituted pyridines.¹⁷ From the intensities of both peaks, the reporters¹³ concluded that a ratio of about 2:1 for the concentration of species (III) and (IV) as in Figure 7.3 is present in pyridine solution.

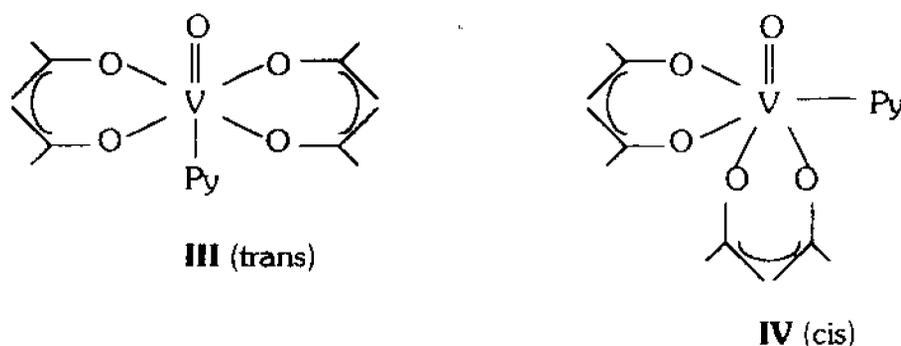


Figure 7.3

In this chapter one of the work included is the coordination of different SB oxovanadium (IV) complexes on polymer support **D** and **C**. Complexes of oxovanadium (IV) with some other ligands were also synthesised and could succeeded in anchoring on above mentioned supports. Analogous works with different coordinating ligands are there but the significance here is that the

coordinating functions are on a crosslinked polymer support. Thus the complexes anchored on the polymer supports facilitates various spectral studies in the solid state—especially EPR technique. Another achievement is the modification of usual structure of the complexes with polymer support.

The polymer support **A(3)H** is changed into different SBs by reacting with primary amines and it is used to synthesise asymmetric mono Schiff-base complexes of oxovanadium (IV) bearing anionic functions.¹⁸⁻²¹ Similar species was also generated by using N-supported polymer matrix. The polymer supports employed are **B(10)H**, **B(20)H** and **B(30)H**.

Asymmetric oxovanadium (IV) complexes without anions were generated by reacting solutions of different monomer complexes of oxovanadium (IV) with polymer supported SBs. Yellow coloured supports change to green on metallation and not washable by solvents.

Tetradentate SBs were also generated on polymer support in a view to synthesise neutral oxovanadium (IV) complexes on polymer support. But the result shows the formation of mono SB complexes with anions on the support. Spectral features were tried to analyse the structure of the complex species.

7.2 Mono-Schiff-base complexes of oxovanadium (IV) bearing anionic functions

Here enlightens the route to generate asymmetric mono-Schiff-base complexes of oxovanadium (IV) with anionic functions using polymer supports. Polymer support used for this work is **A(3)H** and different SB anchored PS generated from it by treatment with primary amines. It is then allowed to react with vanadyl sulphate in aqueous alcohol gives metallated polymer having green colour.

7.2.1 Experimental

Synthesis of polymer supports employed for this work is already described in chapter 3. SB anchored polymer support and that of metallated sample were generated exactly in the same way as illustrated in chapter 3. The resins were well washed with ethyl alcohol and methyl alcohol and dried in an oven at 100°C.

7.2.2 Results and discussion

All polymer supported species are thoroughly washed with solvents and dried in an oven at 100°C. Chloromethyl polystyrene, 2,4-dihydroxy benzaldehyde anchored polymer support **A(3)H**, corresponding SB formed from it by treatment with primary amine were characterised by IR spectroscopy. Polymer supported SB on treatment with vanadyl sulphate solution yields green coloured metallated polymers. This gives a very strong absorption at 1120 cm⁻¹ region due to the presence of ionic sulphate²² in the polymer support. Table 7.1 gives various IR absorption bands observed. An absorption at 980 cm⁻¹ is observed characteristic of V=O stretching frequency.^{16,23} Absorption at 3420 cm⁻¹ shows the presence of coordinated water in the metallated species.²²

Table 7.1. Relevant IR bands (cm⁻¹).

Compound	$\gamma_{C=N}$	$\gamma(SO_4^{--})$	$\gamma_{V=O}$
A(4) VO(SO ₄) _{1/2}	1640	1120	978
A(5) VO(SO ₄) _{1/2}	1620	1120	980
A(6) VO(SO ₄) _{1/2}	1630	1120	980
A(7) VO(SO ₄) _{1/2}	1635	1120	980

Electronic spectra

Electronic spectra of the metallated polymer samples were taken and their spectral features were found to be similar. These samples give characteristic absorption band in the range 12000-13500 cm^{-1} , 14000-15500 cm^{-1} and at 18000-19500 cm^{-1} . Absorptions obtained above 28000 cm^{-1} are assigned to charge transfer spectra. Electronic transitions showed by various samples are given in Table 7.2.

Table 7.2. Ligand field energies of polymer supported oxovanadium complexes.

Metallated polymer support	Electronic transitions (cm^{-1})
A(4) VO(SO ₄) _{1/2}	12500, 15649, 18963
A(5) VO(SO ₄) _{1/2}	12406, 14947, 19157
A(6) VO(SO ₄) _{1/2}	12674, 15479, 18975
A(7) VO(SO ₄) _{1/2}	16366, 20964
A(8) VO(SO ₄) _{1/2}	13210, 19801
A(9) VO(SO ₄) _{1/2}	15500, 18518

The energy level scheme for vanadyl system has been considered by Jorgensen²⁴ and Furlani,²⁵ both using simple crystal field model. Furlani's calculation considered only the $C_{\infty v}$ symmetry at VO^{2+} alone, and therefore cannot hope to account for all the observed levels. By considering VO^{2+} in aqueous solution as a tetragonal $\text{VO}(\text{H}_2\text{O})_5^{2+}$ molecule ion, with axial destabilisation, Jorgensen obtains an energy level scheme which qualitatively accounts for the crystal field part of the spectrum. If the tetragonal perturbation results in axial compression, as in $\text{VO}(\text{H}_2\text{O})_5^{2+}$, the axial a_1 orbital is less stable than b_1 , but the ordering of the e and b_2 orbitals depends on the relative values of splitting parameters.²⁶ The ground state configuration of the one d electron in

VO^{2+} is placed in the b_2 orbital. The predicted transitions are $b_2 \rightarrow e$, $b_2 \rightarrow b_1$ and $b_2 \rightarrow a_1$ as shown in Figure 7.4.

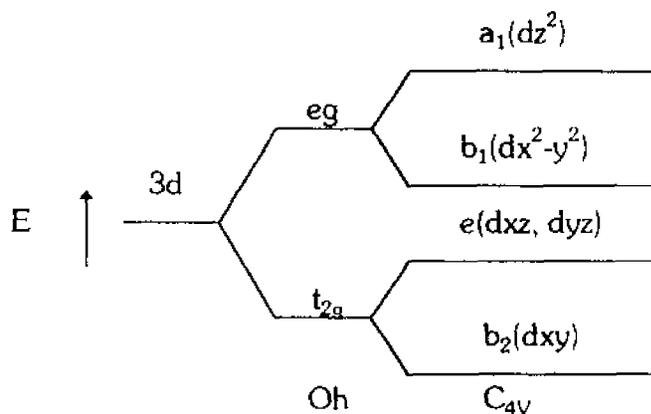


Figure 7.4. Energy levels in crystalline fields of Oh and compressed C_{4v} symmetry.

The spectrum of $VOSO_4 \cdot 5H_2O$ in aqueous solution shows two crystal field bands at 13000 cm^{-1} and 16000 cm^{-1} , which can be assigned to the transitions $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$, respectively. The $b_2 \rightarrow a_1$ transition is expected at higher energies.²⁶ The electronic spectra of metallated species give absorption in the range $12000\text{--}13500\text{ cm}^{-1}$, $14000\text{--}16500\text{ cm}^{-1}$ and $18500\text{--}21000\text{ cm}^{-1}$ and these are assigned to $b_2 \rightarrow e$, $b_2 \rightarrow b_1$ and $b_2 \rightarrow a_1$ respectively.

EPR spectra

EPR spectra of the samples were recorded in solid state and it is given in Figure 7.5. The resolution of the spectra are fairly good so that spin Hamiltonian parameters of the samples could be measured from it and they are given in Table 7.3.

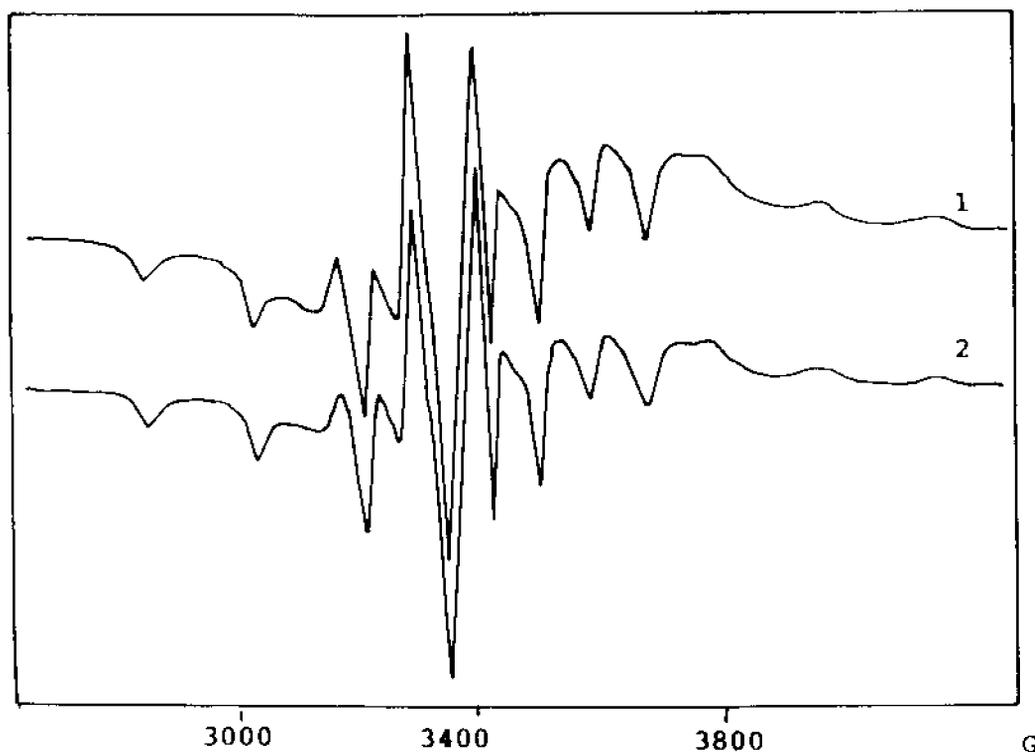


Figure 7.5. EPR spectra of (1) $A(7)VO(SO_4)_{1/2}$ and $A(9)VO(SO_4)_{1/2}$.

Table 7.3. Magnetic parameters of polymer supported metal complexes.

Compound	A_{\parallel}	g_{\parallel}	A_{\perp}	g_{\perp}
$A(7)VO(SO_4)_{1/2}$	195	1.9368	75	1.9861
$A(8)VO(SO_4)_{1/2}$	196	1.9404	74.2	1.9942
$A(9)VO(SO_4)_{1/2}$	193.57	1.9395	74.3	1.9849

EPR spectra of oxovanadium (IV) complex generated on polymer support are typical of that expected from an electron interacting with a vanadium nucleus ($I=7/2$). In all the cases it is seen that $g_{\perp} > g_{\parallel}$. In-plane π bonding of the complexes can be calculated from the equation.²⁷

$$B_2^2 = \left[-\frac{A_{\parallel}}{p} + (g_{\parallel} - 2.0023) + \frac{3}{7} (g_{\perp} - 2.0023) + 0.0053 \right] \left/ \left(\frac{4}{7} + K \right) \right.$$

B_2^2 value calculated for the samples are given in Table 7.4.

Table 7.4. In-plane π bonding of polymer supported metal complexes.

Compound	$(B_2^*)^2$
A(7) VO(SO ₄) _{1/2}	1.062
A(8) VO(SO ₄) _{1/2}	1.073
A(9) VO(SO ₄) _{1/2}	1.055

In-plane π bonding $(B_2^*)^2$ gives a measure of π bonding interaction between ligand and metal ion.

7.3 Mono-Schiff-base complexes of oxovanadium (IV) bearing anionic functions

The polymer supports used for this work are **BH**₂ and SBs derived from this. Their synthesis and characterisation were already discussed in chapter 4. SB anchored polymer supports employed are **B(10)**H, **B(20)**H and **B(30)**H. These supports are used for the synthesis of asymmetric mono-Schiff-base oxovanadium (IV) complexes with anion on the support. On complexation, yellow coloured SB anchored polymer supports are changed to green. Analogous work with Cu(II) ion is described in section 4.2. But these supports coordinates more oxovanadium than Cu(II) ions. Polymer supports became intensely green coloured after treatment with vanadyl salt solution.

7.3.1 Experimental

Synthesis of SB anchored polymer supports **B(10)H**, **B(20)H** and **B(30)H** were already described in section 4.2. The support is converted to their metallated species by mixing aqueous alcohol solution of vanadyl sulphate with the SB anchored polymer support. This is also described in section 4.2 with Cu^{2+} complexation.

7.3.2 Results and discussion

Aminomethyl polystyrene **BH₂** and the SB anchored support derived from it were characterised by IR analysis. The intensely deep green coloured metallated species were subjected to IR analysis and it shows strong absorption for ionic sulphate in the region²² 1120 cm^{-1} and absorption corresponding to $\text{V}=\text{O}$ stretching²³ at 980 cm^{-1} . The IR spectral results are given in Table 7.5.

Table 7.5. Relevant IR bands (cm^{-1}).

Compound	$\gamma(\text{C}=\text{N})$	$\gamma(\text{SO}_4^-)$	$\gamma(\text{V}=\text{O})$
B(10)VO(SO₄)_{1/2}	1620	1108	980
B(20)VO(SO₄)_{1/2}	1625	1118	984
B(30)VO(SO₄)_{1/2}	1620	1124	982

Electronic and EPR spectra

Electronic spectra of metallated samples give two main transitions in the range 16000 cm^{-1} and 21000 cm^{-1} and they are assigned $b_2 \rightarrow b_1$ and $b_2 \rightarrow a_1$ transitions. Electronic spectra of the samples are given in Figure 7.6. All samples are found to be EPR active and give anisotropic spectra. Some of their EPR spectra are given in Figure 7.7. Some Hamiltonian parameters of the samples are given in Table 7.6.

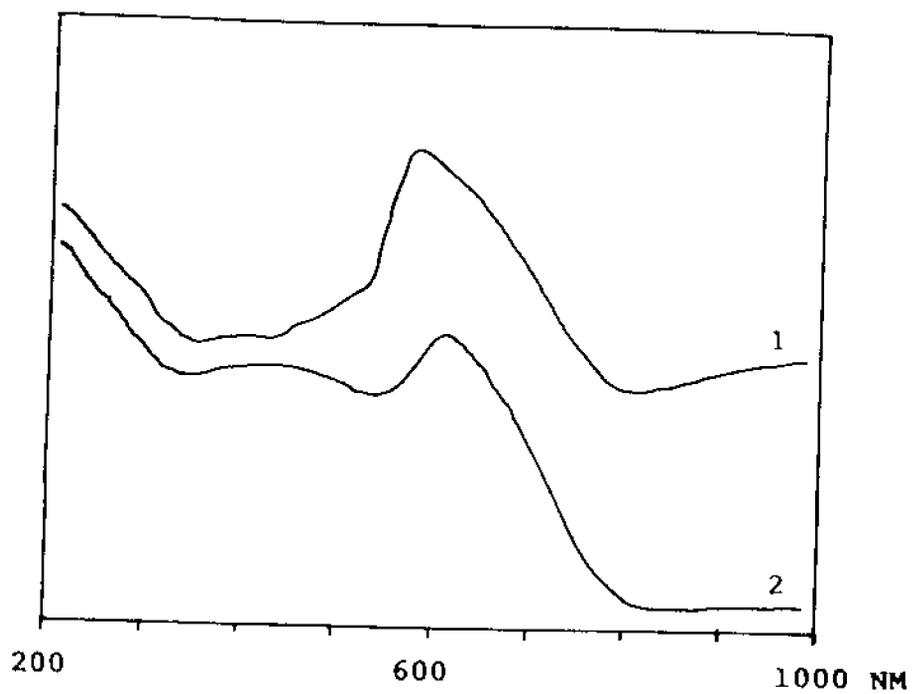


Figure 7.6. Electronic spectra of (1) $\text{B(20)VO(SO}_4\text{)}_{1/2}$ and $\text{B(30)VO(SO}_4\text{)}_{1/2}$.

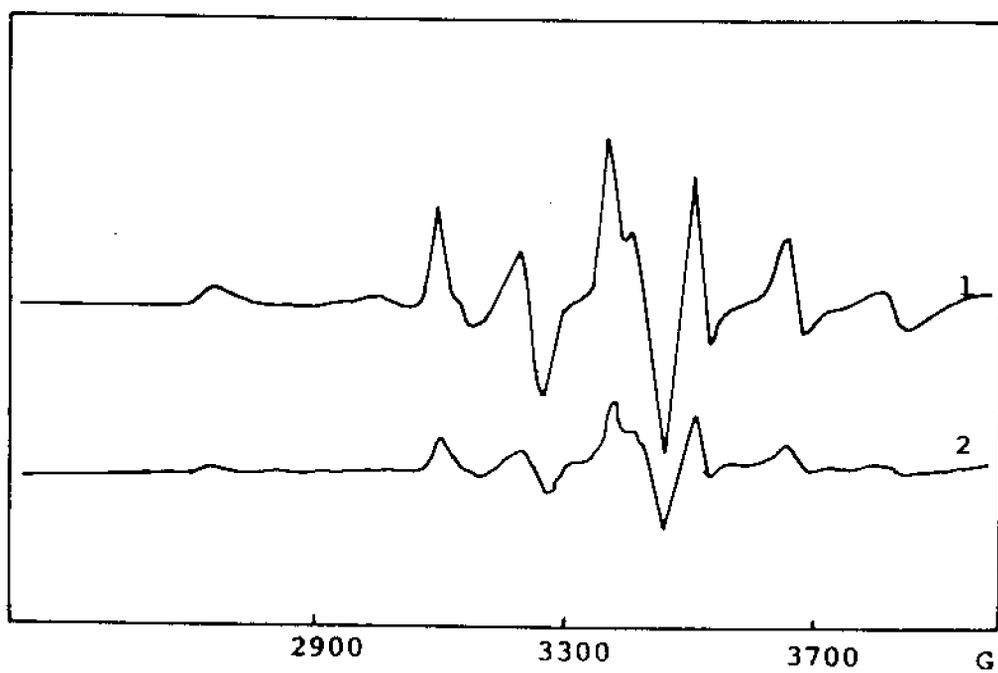


Figure 7.7. EPR spectra of (1) $\text{B(20)VO(SO}_4\text{)}_{1/2}$ and $\text{B(30)VO(SO}_4\text{)}_{1/2}$.

Table 7.6. Magnetic parameters of polymer supported metal complex.

Compound	A_{\parallel}	g_{\parallel}	A_{\perp}	g_{\perp}	B_2^2
B(20) VO(SO ₄) _{1/2}	182.5	1.9411	60	1.9829	0.9927
B(30) VO(SO ₄) _{1/2}	185	1.9388	67.5	1.970	1.003

$(g_{\perp} - g_{\parallel})$ value for **B(20)**VO(SO₄)_{1/2} and **B(30)**VO(SO₄)_{1/2} species are found to be 0.0418 and 0.0312 respectively so a higher in-plane ligand field is observed in **B(30)**VO(SO₄)_{1/2}. Same result is observed in **B(30)**Cu(NO₃) species also.

7.4 Polymer supported asymmetric Bis-SB complexes of oxovanadium

Vanadyl ion surrounded by different types of ligands were generated with the help of a polymer support. Polymer support bears SB moiety formed by condensing aminomethyl polystyrene with salicylaldehyde **B(10)**H. This polymer support was treated with chloroform/THF solution of Bis-Schiff-base oxovanadium complexes and some other types of oxovanadyl complexes like vanadyl acetyl acetonate, vanadyl benzoyl acetonate and vanadyl 8-hydroxy quinolate. One of the bidentate ligand from the monomeric complex in solution with the vanadyl metal ion forms asymmetric complex with the SB moiety on the polymer support. It is a convenient method for synthesising asymmetric complexes of oxovanadyl on polymer support. SB moiety on the support can be tuned and it is possible to synthesise different asymmetric vanadyl complexes. So structurally modified asymmetric oxovanadyl complexes can be synthesised by this method.

7.4.1 Experimental

A series of bis-bidentate SB oxovanadyl complexes, vanadyl acetyl acetonate, vanadyl benzoyl acetonate and vanadyl 8-hydroxy quinolinate were synthesised. Preparative method employed for bis-bidentate SB vanadyl^{28,30} complexes and vanadyl acetyl acetonate³¹ complexes were already reported.

Preparation of vanadyl benzoyl acetonate

2.5 g (0.01 mole) of vanadyl sulphate was dissolved in 500 ml of aqueous alcohol and to this 2 g of sodium acetate was added and stirred well. The solution was filtered and to the filtrate 6.5 g (0.02 mole) of benzoyl acetone in 50 ml of alcohol was added and the mixture was refluxed on a water bath for one hour. On cooling crystals of vanadyl benzoyl acetonate separates and it was filtered and gently washed with alcohol.

Vanadyl (8-hydroxy quinolinate)

2.5 g (0.01 mole) of vanadyl sulphate was dissolved in 50 ml of aqueous alcohol and to this 2 g of sodium acetate was added and stirred well. Precipitate was filtered out and to the clear solution 3.1 g of 8-hydroxy quinoline in 80 ml of alcohol was added and stirred well. The solution was heated on a water bath for an hour and kept overnight. The separated crystals were taken out and washed slightly with alcohol.

Asymmetric vanadyl complex on polymer support

Vanadyl complexes prepared for this work are all uniformly soluble in chloroform or THF. 500 mg of the complex was dissolved in 30 ml of chloroform/THF and the clear solution was poured into 250 mg of **B(10)H** polymer support kept in 20 ml of chloroform. The resultant mixture was well stirred and heated on a water bath for one hour with constant shaking. Yellow

colour of the polymer support turned to green indicates complexation on polymer support. This colour is intact to solvents, like CHCl_3 or alcohols.

7.4.2 Results and discussion

Polymer supports discussed in this section were characterised by IR, UV and EPR methods. Characterisation of aminomethyl polystyrene and SB anchored support formed from it on treatment with salicylaldehyde are discussed in the previous sections. IR spectrum of **B(10)H** gives a peak at 1625 cm^{-1} characteristic of azomethine ($\nu_{\text{C=N}}$) and it is shifted to 1620 cm^{-1} in the metallated sample. Relevant IR bands are recorded in Table 7.7.

Table 7.7. Relevant IR bands (cm^{-1}).

Compound	$\nu_{\text{C=N}}$	$\nu_{\text{C=C}}$	$\nu_{\text{V=O}}$
B(10)VO(11)	1620	1580	998
B(10)VO(12)	1624	1580	994
B(10)VO(13)	1620	1570	1000
B(20)VO(11)	1620	1600	980
B(10)VO(45)	1628	1600	988
B(10)VO(55)	1630	1570	970

A series of asymmetric complexes are generated on the polymer support and a shift of azomethine absorption is observed in many cases. A peak in the range $960\text{-}1000 \text{ cm}^{-1}$ is observed in all metallated species and it is assigned to V=O stretching frequency.²³ The V=O stretching frequency of VO(45)_2 in noncoordinated solvents like CCl_4 is 1008 cm^{-1} while the asymmetric complex

generated **B(10)VO(45)** shows $V=0$ stretching frequency at 990 cm^{-1} . The $V=O$ stretching force is decreased by replacement of one acetyl acetonate group by a bidentate Schiff-base moiety.

Electronic spectra

Solid state UV spectra of some of the asymmetric complexes generated on polymer support is given in Figure 7.8. These complexes show mainly three absorptions in the range around 11000 cm^{-1} , 18000 cm^{-1} and 20000 cm^{-1} except charge transfer spectra occurring at higher frequencies. The values are given in Table 7.8.

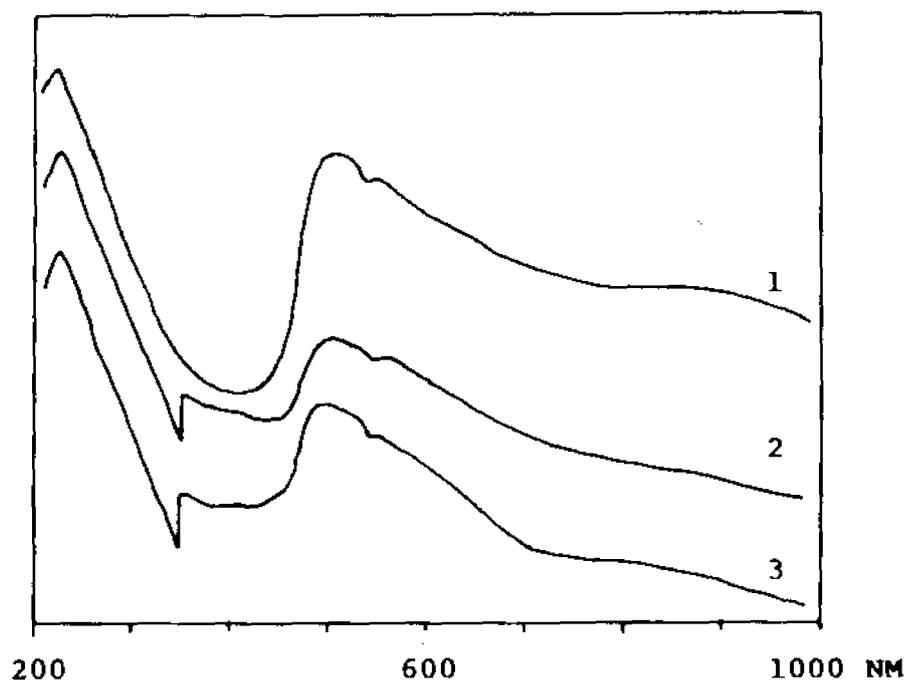


Figure 7.8. Electronic spectra of (1) **B(10)VO(45)**, (2) **B(10)VO(55)** and (3) **B(10)VO(65)**.

Table 7.8. Ligand field energy transitions of asymmetric complexes generated on polymer support.

Compound	Electronic transitions (cm^{-1})
B(10)VO(11)	41376, 18761, 24630
B(10)VO(12)	11198, 16420, 23809
B(10)VO(13)	11600, 17574, 24390
B(10)VO(14)	11235, 17064, 24000
B(10)VO(45)	11230, 18315, 19841
B(10)VO(55)	11709, 18115, 20202
B(10)VO(65)	11402, 18315, 20161

The $b_2 \rightarrow b_1$ and $b_2 \rightarrow e$ transitions are not much affected by different substituents but $b_2 \rightarrow a_1$ transitions for SB complexes were much higher than other complexes like acetyl acetonate, 8-hydroxy quinolate and benzoyl acetonate complexes.

EPR spectra

All the mixed ligand oxovanadyl complexes synthesised are found to be EPR active and gives anisotropic spectra. EPR spectra of some of the samples are given in Figure 7.9. Hamiltonian parameters of the complexes formed on the support could be obtained from the EPR spectra and it is tabulated in Table 7.9.

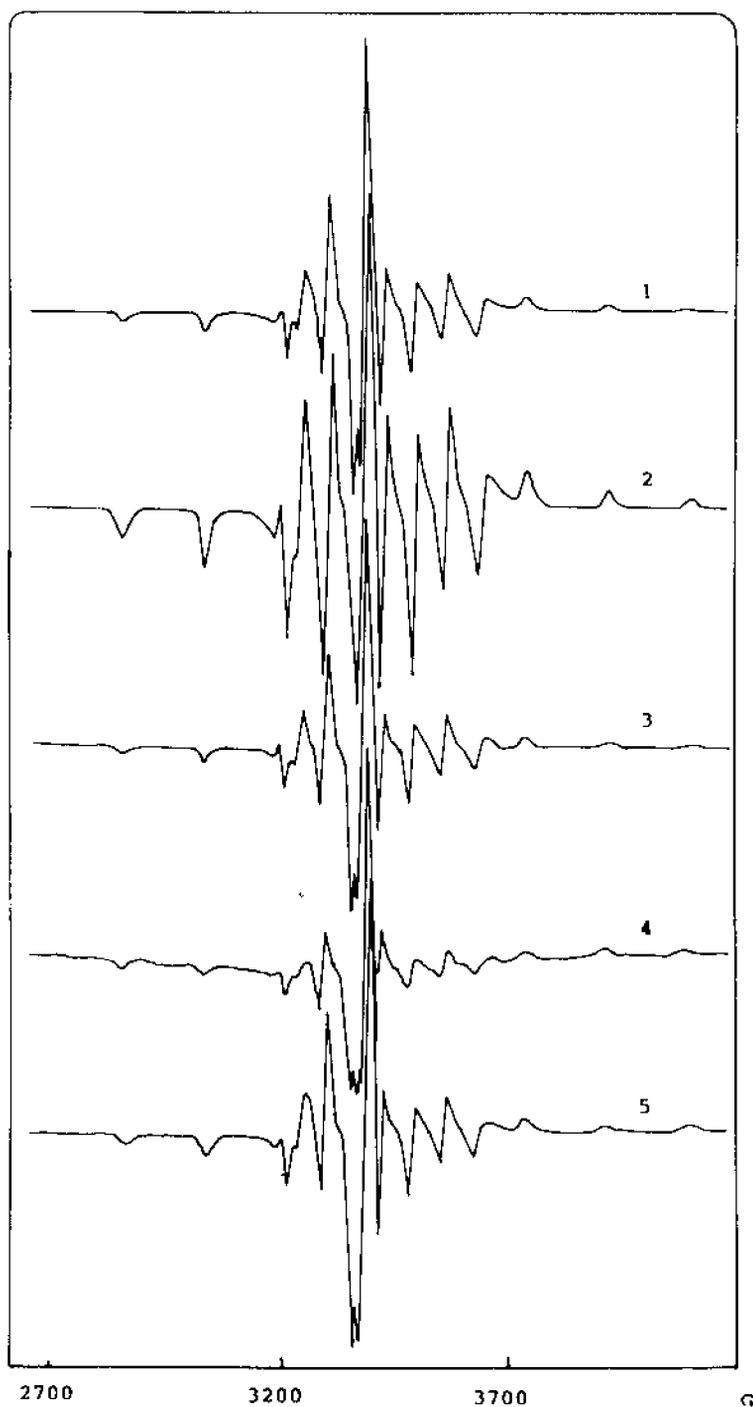


Figure 7.9. EPR spectra of (1) **B(10)VO(11)**, (2) **B(10)VO(45)**, (3) **B(10)VO(65)**, (4) **B(10)VO(55)** and (5) **B(20)VO(11)**.

Table 7.9. Magnetic parameters of asymmetric complexes generated on polymer support.

Compound	A_{\parallel}	g_{\parallel}	A_{\perp}	g_{\perp}	B^2
B(10)VO(11)	176.42	1.9503	61.42	1.9892	0.9668
B(20)VO(11)	175	1.9537	62.14	1.9892	0.9612
B(10)VO(45)	176.42	1.9433	61.43	1.99834	0.9598
B(10)VO(55)	179.28	1.9453	71.42	1.9776	0.9754
B(10)VO(65)	177.14	1.9492	61.42	1.9910	0.9706

The Hamiltonian parameter ($g_{\perp}-g_{\parallel}$) for **B(10)VO(11)** is 0.0389 and that for **B(20)VO(11)** is 0.0355 and the lesser value in the anisotropy of g in **B(20)VO(11)** shows higher donor strength of the extended conjugation in 2-hydroxy naphthalene 1-carbaldehyde comparing to salicylaldehyde. Similar value for VO(45)_2 in toluene medium is²⁷ $(1.996-1.944) = 0.052$ and that in the mixed ligand complex **B(10)VO(45)** formed on the support is $(1.9834-1.9433) = 0.0401$. Here higher donor strength is experienced in mixed ligand complex **B(10)VO(45)** formed on the polymer support **B(10)H**. The ($g_{\perp}-g_{\parallel}$) value of **B(10)VO(45)** and **B(10)VO(65)** are 0.0401 and 0.0418 respectively. Higher donor strength is in **B(10)VO(45)** as expected due to $p\pi$ ring current in the benzene ring.

7.5 Bivanadyl complexes of SBs derived from diamines

Studies on transition metal complexes of tetradentate Schiff-base ligands are available in the literature.^{32,33} When dipositive transition metal ion complexes with this type of ligands, the complex formed usually will be neutral. Synthesis and various spectral analysis of oxovanadium (IV) complexes with

tetradentate ligands are available from the literature.³⁴ In this work two different tetradentate SBs are generated on a polymer support and allowed to react with oxovanadium salt solution. Similar to the behaviour of tetradentate SB solution, a neutral oxovanadium complex from the polymer supported SBs was expected. But it was observed that the metallated species bears anion in one of the polymer support. The polymer support used for this purpose was chloromethyl polystyrene and the tetradentate SB ligand synthesised are those derived from 2,4-dihydroxy benzaldehyde with ethylene diamine salen (OH)₂ or with O-phenylene diamine salphen (OH)₂. The polymer supported SB species are **A(1)H₂** and **A(2)H₂**. On treating with water the vanadyl complex species of **A(1)H₂**, loses the anion (sulphate) completely. A broad peak at 980 cm⁻¹ corresponding to V=O stretching frequency was observed for this species. While, the support **A(2)H₂** gives sulphate anion after metallation. In this case behaviour of both polymer supported SBs are found to be different towards metallation.

7.5.1 Experimental

Synthesis of SB using 2,4-dihydroxy benzaldehyde and ethylene diamine [salen (OH)₂] and 2,4-dihydroxy benzaldehyde with O-phenylene diamine [salphen (OH)₂] were described in chapter 4 section 4.4. The process by which these tetradentate SBs in solution are immobilised on the support is also mentioned there. These supports are represented as **A(1)H₂** and **A(2)H₂**, respectively.

7.5.2 Results and discussion

Characterisation of SB anchored supports **A(1)H₂** and **A(2)H₂** were already discussed in section 4.4. The metallated samples of these supports were subjected to IR analysis. Metallated sample of support **A(1)H₂** gives no band

corresponding to sulphate ion whereas it gives well defined absorption characteristic of $V=0$ stretching frequency at 980 cm^{-1} . But metallated sample of $\mathbf{A(2)H_2}$ gives characteristic absorption of sulphate ion indicating neutral complex of oxovanadyl is not formed with this polymer supported SB. The $V=0$ stretching frequency at 980 cm^{-1} is also observed. So the SB anchored support $\mathbf{A(1)H_2}$ gives $\mathbf{A(1)VO}$ complex with no sulphate ion whereas $\mathbf{A(2)H_2}$ gives $\mathbf{A(2)(VO)_2SO_4}$ complex species. This indicates the involvement of C-C distance in diamine, where NH_2 groups are attached has its own influence in complex formation. Polymer support also has its influence in choosing the structure with metal ion.

Electronic and EPR spectra

Electronic spectra of metallated species are recorded in the solid state and are presented in Figure 7.10. These two species give electronic transitions mainly in the 12000 cm^{-1} , 18000 cm^{-1} and 23000 cm^{-1} region. The transition in the range 12000 cm^{-1} is assigned to ${}^2b_2 \rightarrow {}^2e_1$, that at 18000 cm^{-1} is due to ${}^2b_2 \rightarrow {}^2b_1$ and still higher energy transition occurring at 23000 cm^{-1} is that of ${}^2b_2 \rightarrow {}^2a_1$.

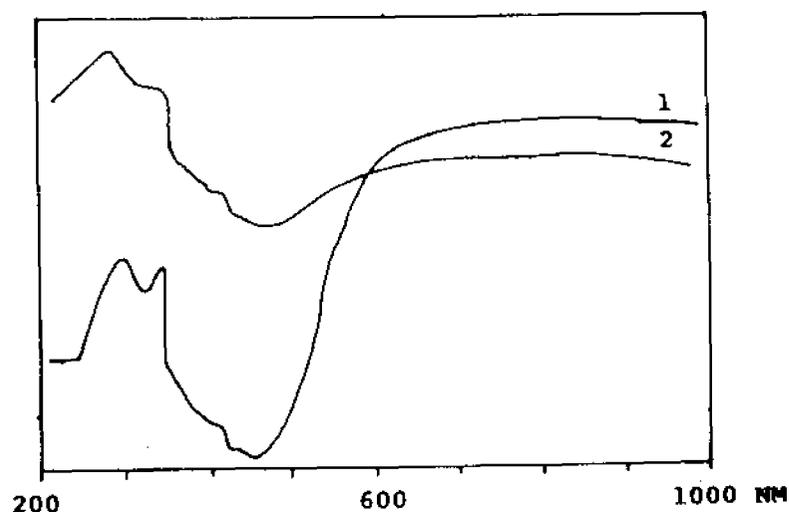


Figure 7.10. Electronic spectra of (1) $\mathbf{A(2)(VO)_2SO_4}$ and (2) $\mathbf{A(1)(VO)}$.

The values of ${}^2b_2 \rightarrow {}^2b_1$ and ${}^2b_2 \rightarrow {}^2a_1$ transitions in neutral tetradentate vanadyl SB complexes in solution are available from early reporters.³⁰ The SBs used are salen and salphen. The values corresponding to the above transitions reported are 16950 cm^{-1} and 17000 cm^{-1} respectively.

Electronic transitions in polymer supported SB complexes described in this section are higher than those of neutral oxovanadium tetradentate SB complexes in solution. Asymmetric SB complexes on polymer supports were described earlier. The energy transition for ${}^2b_2 \rightarrow {}^2b_1$ and ${}^2b_2 \rightarrow {}^2a_1$ are found to be higher than the respective transitions in tetradentate oxovanadium complexes in solutions. The d orbital splitting in polymer supported complexes is greater than unsupported oxovanadium complex in solution. The ${}^2b_2 \rightarrow {}^2b_1$ energy transitions for polymer supported oxovanadium complexes and oxovanadium complex in solution are given in Table 7.10.

Table 7.10. ${}^2b_2 \rightarrow {}^2b_1$ energy transition for polymer supported and unsupported oxovanadium complex.

VO salen	VO salphen	A(1)VO	A(2)(VO) ₂ SO ₄
16950 cm^{-1}	17000 cm^{-1}	18268 cm^{-1}	18867 cm^{-1}

EPR spectra of the species are distinctly anisotropic and characteristic of one species. The spectra are given in Figure 7.11. Some paramagnetic data observed from spectra are recorded in Table 7.11.

Table 7.11. Magnetic and bond parameter values of polymer supported oxovanadium complexes.

Compound	A_{\parallel}	g_{\parallel}	A_{\perp}	g_{\perp}	B^2
A(1)VO	197.26	1.9741	86.105	2.0328	1.116
A(2)(VO) ₂ SO ₄	196.47	1.976	86.88	2.031	1.113

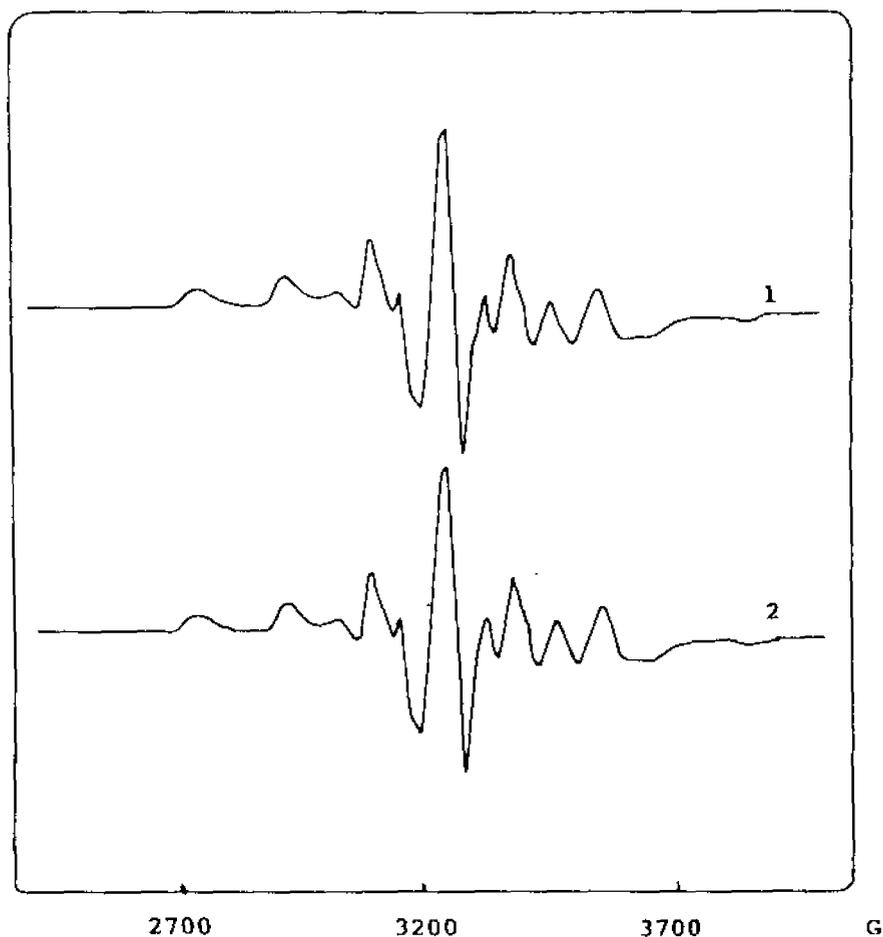


Figure 7.11. EPR spectra of (1) $A(1)(VO)$ and (2) $A(2)(VO)_2SO_4$.

Magnetic parameters of oxovanadium SB complexes in solution and the same SB anchored polymer supported oxovanadium complexes are given in Table 7.12. Anisotropy in the g values, i.e., $(g_{\perp} - g_{\parallel})$, gives a measure of the in-plane ligand field strength. The values $(g_{\perp} - g_{\parallel})$ are found to be smaller in symmetric tetradentate oxovanadium SB complexes than corresponding polymer supported oxovanadium complexes.

Table 7.12. Anisotropy value ($g_{\perp}-g_{\parallel}$) for tetradentate oxovanadium (IV) complex and corresponding values for polymer supported oxovanadium complex.

Oxovanadium (IV) complex	$g_{\perp}-g_{\parallel}$	Polymer supported complex	$g_{\perp}-g_{\parallel}$
VO salen	1.987-1.955 = 0.032	A(1) VO	2.0328-1.9741 = 0.0587
VO salphen	1.988-1.957 = 0.031	A(2) VO ₂ SO ₄	2.0312-1.9761 = 0.0551

Smaller value of ($g_{\perp}-g_{\parallel}$) means larger in-plane ligand field strength. So in-plane ligand field strength is found to be higher for tetradentate SB oxovanadium (IV) complexes than the SB anchored polymer supported complexes.

7.6 Bis-bidentate Schiff-base and other five-coordinated complexes of VO(IV)

In this work a series of bis-bidentate SB oxovanadium (IV) complexes with different N-substituents and another complex, vanadyl acetyl acetonate were prepared. These complexes have a residual tendency to be coordinated or linked upon Lewis base. The amino and pyridine functions on the polymer supports bond with vanadyl complexes and forms six coordinated species. References are available regarding these oxovanadium (IV) complex species which forms adducts with Lewis base molecules.^{12,13} But generating such species on a crosslinked polymer matrix is a new strategy and provides a means to get EPR spectra of vanadyl complexes in the solid state and a way for the modification of their usual structure.

7.6.1 Experimental

Preparation of vanadyl SB complexes

Primary alkyl amine-salicylaldehyde SB vanadyl complexes were prepared by the standard method²⁸ and aromatic primary amine SB complexes were prepared by the method adopted by Pandeya et al.³⁰

In this piece of work, methylamine, ethylamine and butylamine SBs with salicylaldehyde were used for synthesising oxovanadium (IV) complexes. 0.025 mol of vanadyl sulphate was dissolved in 30 ml of alcohol and to this 0.05 mol of anhydrous sodium acetate was added and the mixture was stirred and filtered. Separately, 0.025 mol of salicylaldehyde and slightly excess primary amine were mixed in 50 ml of alcohol and refluxed on a water bath for 30 min. The resulting yellow solution of SB was added slowly to the magnetically stirred filtrate containing vanadyl acetate. The mixture was refluxed for four hours while stirring. The precipitate was collected, washed several times with alcohol and dried in a vacuum desiccator at 30°C.

5 g (0.05 mol) of freshly distilled aniline was mixed with 6.1 g (0.05 mol) of salicylaldehyde in 60 ml of alcohol. The contents were shaken and were refluxed for about half an hour. The yellow coloured SB solids separated was collected and washed gently with alcohol. This ligand (0.002 mol) was taken in 25 ml of alcohol and an aqueous solution of vanadyl sulphate (0.001 mol) were mixed with it. Green coloured solutions obtained were diluted with water while the solids separates quickly. These were filtered, washed with water and dried in a vacuum desiccator.

Preparation of oxovanadium (IV) acetyl acetate

Vanadyl acetyl acetate complex was synthesised by mixing solution of 0.01 mol of vanadium sulphate in water and 0.06 mol (6 g) of acetyl acetone

followed by 20 g of urea.²⁹ The reaction mixture was covered with a watch glass and heated overnight on a steam bath. As the urea hydrolyses to release ammonia, the complex separates. The crystals were washed with water and dried in air.

Anchoring the complex on polymer matrix

The complexes prepared by above methods were anchored on polymer matrices, aminomethyl polystyrene and polyvinyl pyridine by identical methods. 500 mg of the complex was dissolved in 40 ml of chloroform/THF and it was mixed with 200 mg of pre-swollen polymer support. Then the mixture was refluxed on a water bath for 24 h. Then the polymer was washed well with chloroform and alcohol and dried in a vacuum desiccator.

7.6.2 Results and discussion

Polymer supports employed in this work are aminomethyl polystyrene **C** and polyvinyl pyridine **D** and they were characterised by IR measurements. Oxovanadium complexes anchored on these polymer supports give well defined peaks characteristic of $V=O$ stretching frequency in the region $950-1000\text{ cm}^{-1}$. **DVO(12)₂** sample gives a peak at 1620 cm^{-1} due to the shifting of absorption peak originally present at 1600 cm^{-1} for the free polymer-support.^{35,36} This supports the anchoring of complex on the polymer backbone. The absorption peaks due to the $\gamma_{C=C}$, δ_{CH} (in-plane), CH (out of plane) of PVP also shift to higher wavenumber by $6-7\text{ cm}^{-1}$ in the complex anchored support also help us to confirm the coordination of complex on PVP.³⁷ The IR absorption of aminomethyl polystyrene in the region $1580-1700\text{ cm}^{-1}$ and that of the polymer supported metal complex differs indicating the coordination between complex and support as mentioned in earlier cases. $V=O$ stretching frequency in PVP

anchored metal complex $\text{DVO}(\mathbf{11})_2$ is observed at 984 cm^{-1} while that in aminomethyl polystyrene it is 970 cm^{-1} . In the case of the unappended metal complex the corresponding value is 980 cm^{-1} . This is in accordance with the variation observed by Gutmann's rule.³⁸ The VO stretching frequency observed in oxovanadium complex bonded to different Lewis bases were studied and it showed that the frequency is higher for Lewis base pyridine than aliphatic amine. Some IR bands are recorded in Table 7.13.

Table 7.13. Relevant IR bands (cm^{-1}).

Compound	$\gamma_{(\text{C}=\text{N})}$	$\gamma_{\text{C}=\text{C}}$	$\gamma_{\text{V}=\text{O}}$
D.VO(11) ₂	1600, 1640	1545	984
D.VO(12) ₂	1600, 1630	1540	978
D.VO(13) ₂	1600, 1635	1545	980

Electronic spectra

Oxovanadium complex coordinated to polyvinyl pyridine sample is well washed with THF and chloroform and it is dried in an oven at 80°C . This sample is then subjected to UV analysis in the solid state. Different vanadyl SB complexes and oxovanadium acetyl acetonate were tried in this way. In all the cases reproducible spectra are obtained with mainly four absorptions in the region $10,000\text{ cm}^{-1}$, $12,000\text{ cm}^{-1}$, $16,000\text{ cm}^{-1}$ and $23,000\text{ cm}^{-1}$. Various transitions shown by different samples are given in Table 7.14.

Table 7.14. Ligand field energies of oxovanadium (IV) complexes supported on **D**.

Polymer supported metal complex	Electronic transition (cm ⁻¹)
D.VO(11) ₂	10570, 11454, 17094
D.VO(12) ₂	10438, 12738, 16666
D.VO(13) ₂	10548, 11560, 16393
D.VO(14) ₂	10405, 11579, 16129
D.VO(45) ₂	10582, 11764, 17985

Here the three transitions occurring in the range (10000-11000 cm⁻¹), (11000-12500 cm⁻¹) and 16000-17000 cm⁻¹ is assigned to ²b₂→²e₂, ²b₂→²b₁ and ²b₂→²a₁ respectively.^{39,40} Due to the interaction between ring current of pyridine and metal d orbitals the separation of energy levels were found to be reduced. Electronic spectra of same oxovanadium (IV) complexes on aminomethyl polystyrene were tried and their spectra were also found to be similar. Electronic spectra of some of the sample are given in Figure 7.12. Ligand field energies of **C** supported oxovanadium (IV) complexes are given in Table 7.15.

Table 7.15. Ligand field energies of **C** supported oxovanadium (IV) complexes.

Sample	Electronic transitions (cm ⁻¹)
C.VO(11) ₂	11709, 16611, 22573
C.VO(12) ₂	10660, 18587, 20325
C.VO(13) ₂	10660, 18416, 20040
C.VO(14) ₂	11402, 17921, 20080
C.VO(45) ₂	12121, 16666, 21141

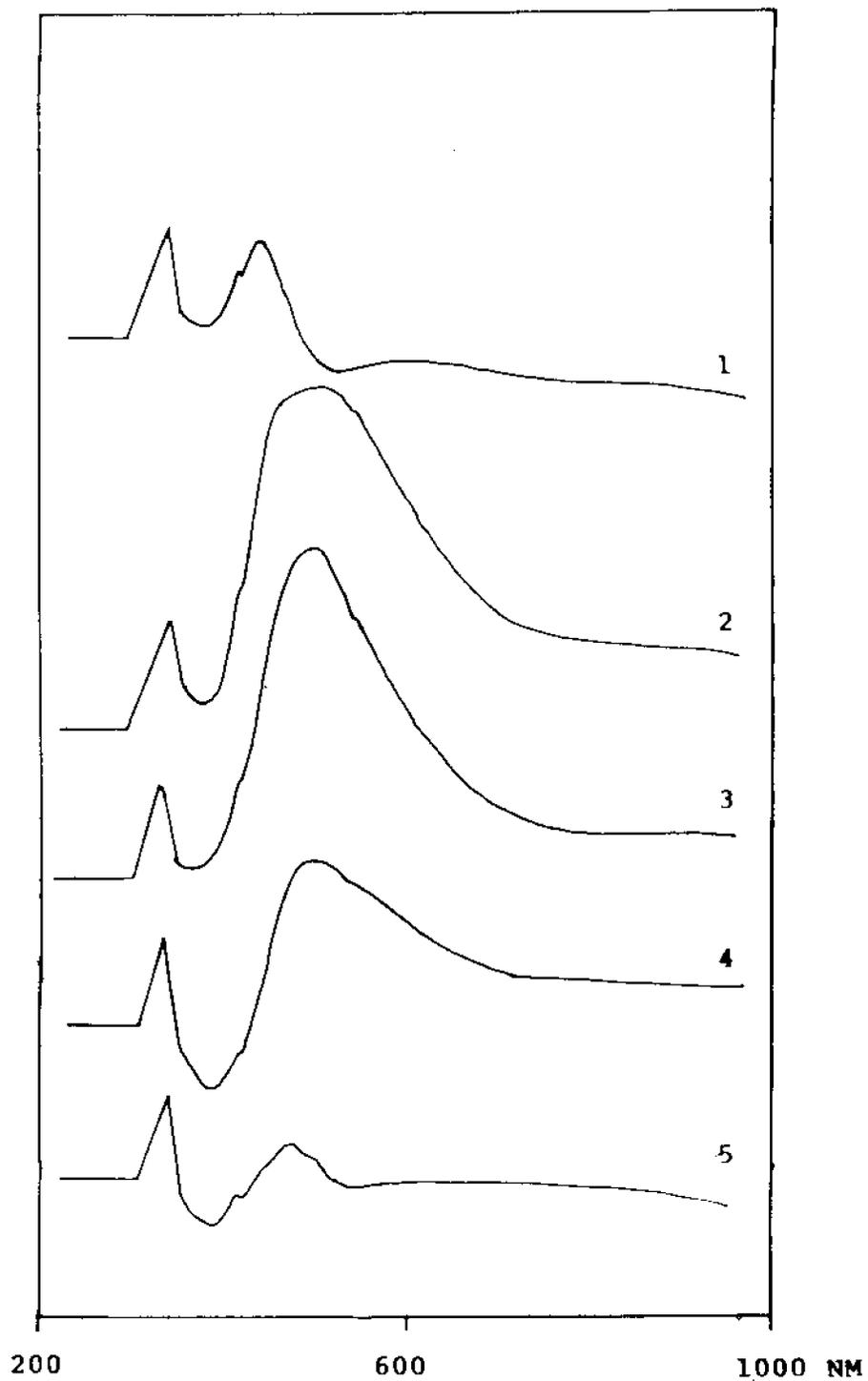


Figure 7.12. Electronic spectra of (1) C.VO(11)_2 , (2) C.VO(12)_2 , (3) C.VO(13)_2 , (4) C.VO(14)_2 , and (5) C.VO(45)_2 .

In this case the low energy transition occurring in the range 10000-12500 cm^{-1} is assigned ${}^2b_2 \rightarrow e^2$ and that in the range 16000-18000 cm^{-1} is assigned to ${}^2b_2 \rightarrow {}^2b_1$ and the third transition at 21000 cm^{-1} range is attributed to ${}^1b_2 \rightarrow {}^2a_1$. The σ donor of nitrogen in amino function of **C** support interact with dz^2 orbital of metal and splits its energy more than as compared to similar case of anchoring of oxovanadium complex to **D** support.

EPR spectra

Both polymer supported (**D** and **C**) oxovanadium (IV) complexes are found to be EPR active and gave anisotropic spectra. Some of the spectra of the species supported on **D** and **C** are given in Figures 7.13 and 7.14, respectively.

Hamiltonian parameters of the species measured from the spectra are given in Table 7.16 and Table 7.17. Table 7.16 gives A_{\parallel} , g_{\parallel} , A_{\perp} and g_{\perp} values of oxovanadium complex supported on **D** and Table 7.17 gives corresponding value of same complexes while supported on **C**.

Table 7.16. Magnetic parameters of **D** supported oxovanadium (IV) complexes

D supported oxovanadium complexes	A_{\parallel}	g_{\parallel}	A_{\perp}	g_{\perp}
D.VO(11) ₂	177.78	1.9506	80.08	1.9765
D.VO(12) ₂	178.96	1.9529	76.53	1.9861
D.VO(13) ₂	180.14	1.9437	77.7	1.9861
D.VO(14) ₂	178.96	1.953	76.53	1.9561
D.VO(45) ₂	181.32	1.9483	78.88	1.967

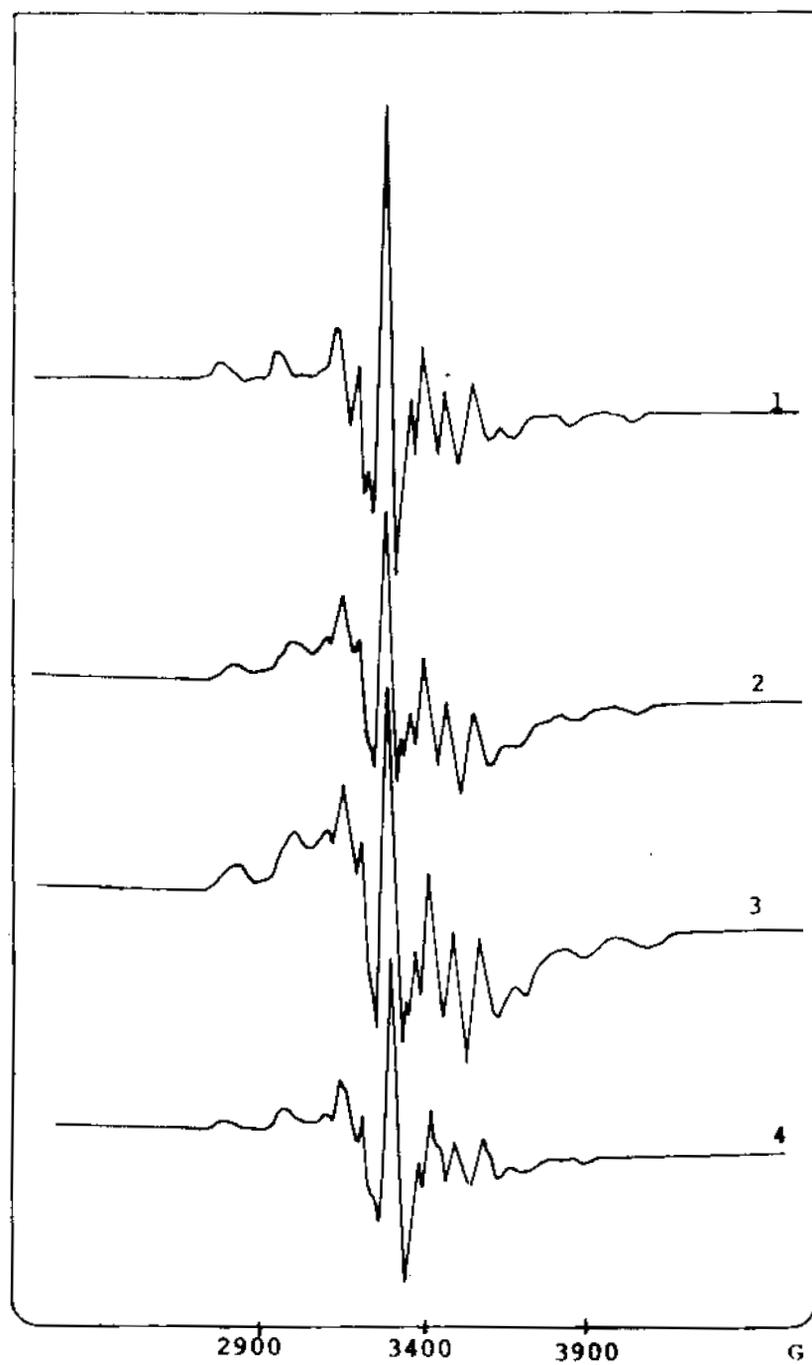


Figure 7.13. EPR spectra of (1) D.VO(11)_2 , (2) D.VO(12)_2 , (3) D.VO(13)_2 , and (4) D.VO(45)_2 .

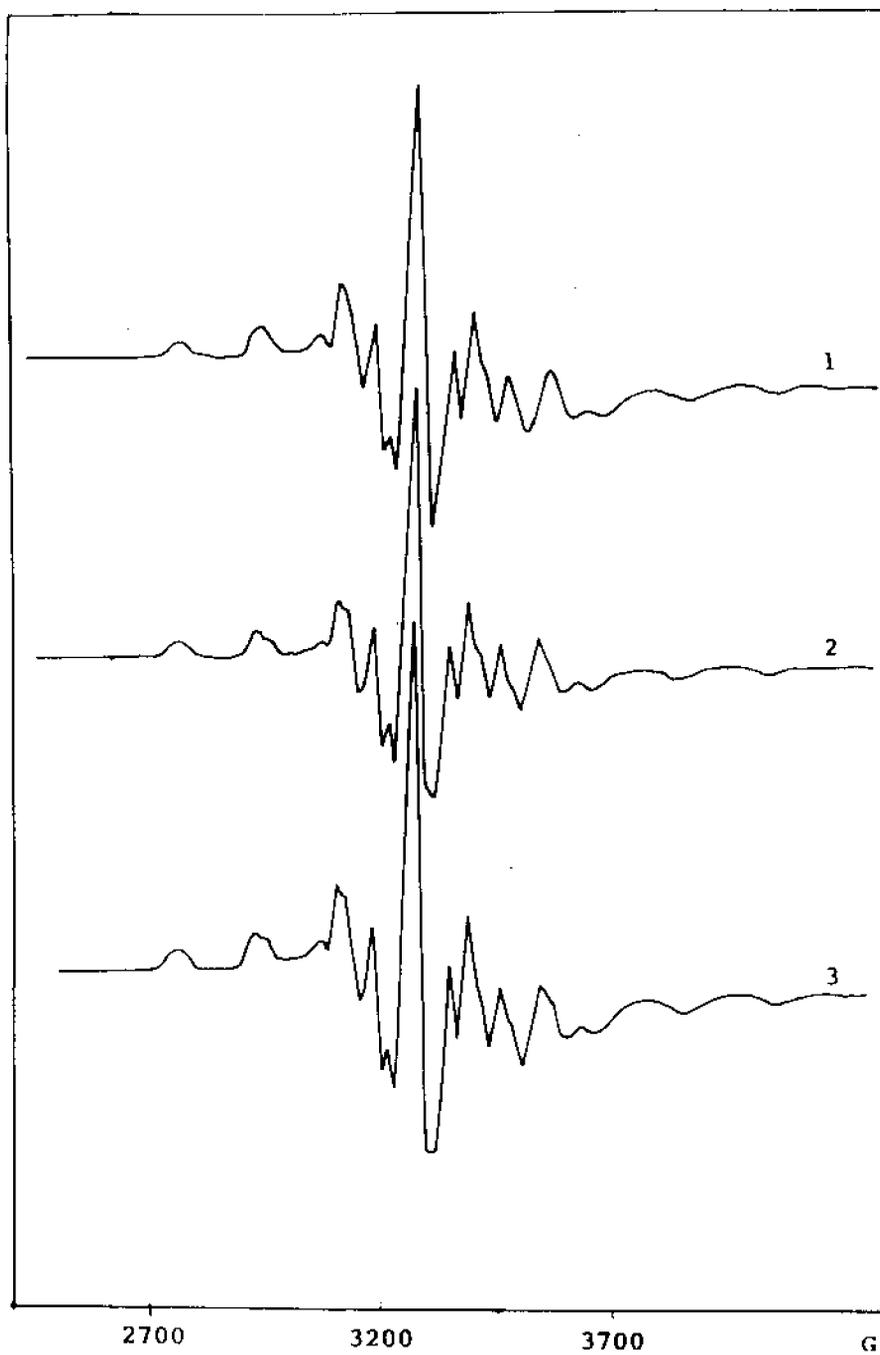


Figure 7.14. EPR spectra of (1) C.VO(11)_2 , (2) C.VO(12)_2 , and (3) C.VO(13)_2 .

Table 7.17. Magnetic parameters of C supported oxovanadium (IV) complexes

C supported oxovanadium complexes	A_{\parallel}	g_{\parallel}	A_{\perp}	g_{\perp}
C.VO(11) ₂	177.78	1.967	74.17	1.990
C.VO(12) ₂	175.43	1.9717	77.7	1.9861
C.VO(13) ₂	151.58	1.9209	85.95	1.967
C.VO(14) ₂	178.96	1.953	73	1.9837
C.VO(45) ₂	183.67	1.9576	77.7	1.9813

g-Values and electronic transition energies

The g-factors are related to the optical transition energies through the equations.³⁰

$$g_{\parallel} = 2.002 - \frac{8(B_2^*)^2(B_1^*)^2 \epsilon}{\Delta E_{x^2-y^2}} \quad (1)$$

$$g_{\perp} = 2.002 - \frac{2(B_2^*)^2(E_n^*)^2 \epsilon}{\Delta E_{xz,yz}} \quad (2)$$

$(B_2^*)^2$ is calculated from the equation.³⁴

$$(B_2^*)^2 = \left[\frac{-A_{\parallel}}{P \times 10^4} + (g_{\parallel} - 2.002) + \frac{3}{7}(g_{\perp} - 2.002) + 0.0052 \right] \frac{4}{7} + K$$

$10^4P = 128$; K, the isotropic contact term, is related to the amount of unpaired electron density at vanadium nucleus is taken as 0.8 in this calculations. $(B_2^*)^2$, $(B_1^*)^2$ and $(E_n^*)^2$ are the unpaired electron metal orbital populations in the

xy , x^2-y^2 and xz , yz orbitals respectively.^{7,41} Since the orbital containing the unpaired electron, d_{xy} , has zero electron density at the vanadium nucleus and does not mix with the metal 4s orbital, there is no direct way of putting the unpaired electron density on the nucleus. The nonzero value of K is due to an indirect mechanism, like spin polarisation mechanism.⁴² The unpaired electron in the d_{xy} orbital formally creates unpaired electron density in filled 2s and 3s orbitals of vanadium. In the absence of covalent bonding and 4s mixing, spin polarisation should remain constant for all vanadium complexes and be equal to free ion value K_0 .

$(B_1^*)^2$ is the bonding coefficient for dx^2-y^2 orbital. The value of in-plane σ -bonding coefficient $(B_1^*)^2$ generally follows σ -donor strength of the ligand and $(B_1^*)^2$ decreases as the covalent bonding increases. The value $(B_1^*)^2$ and in-plane π bonding $(B_2^*)^2$ calculated for oxovanadium complexes supported on **D** and **C** are given in Tables 7.18 and 7.19.

Table 7.18. $(B_1^*)^2$ and $(B_2^*)^2$ values of **D** supported oxovanadium (IV) complexes.

D supported complexes	$(B_2^*)^2$	$(B_1^*)^2$
D.VO(11) ₂	0.9178	0.4480
D.VO(12) ₂	0.9822	0.4770
D.VO(13) ₂	0.9821	0.5071
D.VO(14) ₂	0.9822	0.4273
D.VO(45) ₂	0.9862	0.4736

Table 7.19. $(B_1^*)^2$ and $(B_2^*)^2$ values of **C** supported oxovanadium (IV) complexes.

C supported complexes	$(B_2^*)^2$	$(B_1^*)^2$
C.VO(11) ₂	0.9869	0.4368
C.VO(12) ₂	0.9738	0.4294
C.VO(13) ₂	0.7969	-
C.VO(14) ₂	0.9815	0.6618
C.VO(45) ₂	1.0110	0.5418

The values of in-plane σ -bonding coefficient decreases as the covalent bonding increases. The $(B_1^*)^2$ values of the complexes comes in the range (0.40-0.68) and in-plane π bonding $(B_2^*)^2$ comes in the range (0.90-1.1). Alkyl amine-salicylaldehyde SB vanadyl complexes anchored on **C** support possesses higher in-plane covalency while arylamine-salicylaldehyde SB vanadyl complex on **D** support has higher in-plane covalency. Same result is observed in copper SB complexes anchored on **C** and **D** support.

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