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Generation and Characterization of New Oxovanadium Complexes on Polymer Support

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2 Per cent divinyl benzene (DVB) crosslinked polystyrene support was synthesised and functionalised to get chloromethyl polystyrene. Polymeric ligands were prepared by anchoring ligand systems like Schiff base, ethylene diamine and dithiocarbamate on to the polymer backbone. A series of oxovanadium complexes were generated on the polymer support by polymer-analogous complexation reactions. Polymeric oxovanadium complexes containing S_2O_2, N_2O_2 and NO_3 chromophores were analysed by chemical and spectroscopic methods. Important spectral results from UV-Vis, IR and EPR analysis are discussed in detail. The results best explain the bonding pattern and stereochemistry of the complexes.

Key words : Polymer, Ligand, Complexes, Oxovanadium, EPR spectra.

INTRODUCTION

Oxovanadium complexes having chromophores S_4, O_4, N_4 and N_2O_2 were well studied by spectroscopic methods.[1–4] But complexes of the type VOS_2O_2 or $VONO_3$ cannot be prepared by usual methods. They can be prepared only by adjusting the structure of the ligand molecule, *i.e.*, by using tetradentate macrocyclic ligands. This strategy produces ligand dictate complexes that are sterically strained.[5] In the present work we tried to prepare oxovanadium complexes having chromophores S_2O_2, N_2O_2 and NO_3 by polymer supported strategy and analysed them by IR, UV and EPR methods. From the EPR of these complexes, correlation between g and A values was obtained and this result can be used for the analysis of vanadyl environment of unknown vanadyl complexes.

EXPERIMENTAL

General: Styrene and divinyl benzene were commercial samples and were purchased from Aldrich, USA. Solvents were obtained from E. Merck, India and purified by distillation before use. Stannic chloride, ethylene diamine, dithiocarbamate, etc. were purchased from Merck, Germany.

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IR spectra were recorded on Schimadzu IR-470 spectrophotometer operating in the range 4000–400cm^{-1}. Solid state electronic spectra were recorded on a Harry 2390 UV-Vis spectrophotometer and EPR spectra were recorded on a Varian E-12 spectrometer.

The polymer support used is 2% divinyl benzene (DVB) crosslinked polystyrene which was prepared by the suspension copolymerisation of styrene and divinyl benzene.[5] The polymer backbone was functionalised to get chloromethyl polystyrene by treating the polymer with chloromethylmethylether and stannic chloride in dichloromethane as the solvent.[6] Ligands like dithiocarbamate, ethylenediamine and Schiff bases were supported on to the polymer by following the literature procedure.[7]

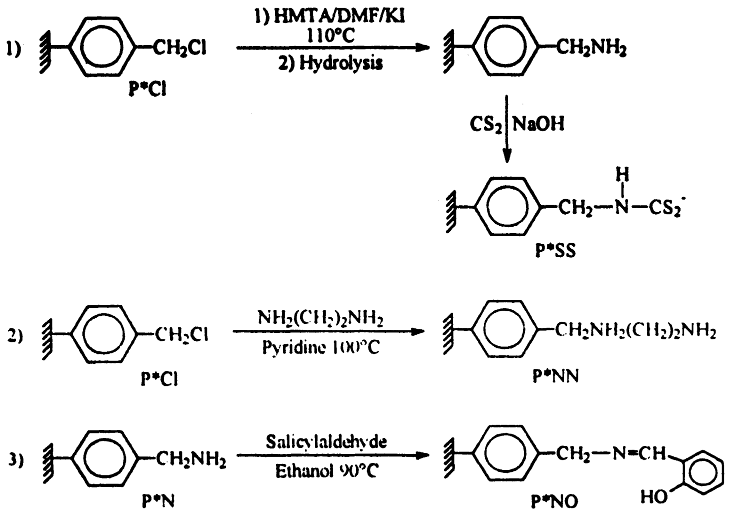
Preparation of polymer supported metal complexes

General procedure: Vanadyl complexes of the polymer supported ligands were prepared by mixing 1 g of the polymer supported ligand with 50 mL of 0.05 M $VOSO_4$ solution and stirring for 1 h. The polymer supported metal complex was filtered, washed with water and methanol and dried under vacuum.

RESULTS AND DISCUSSION

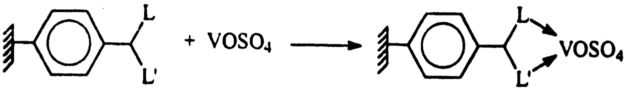
The chemistry of polymer supported ligands is a well-studied area and many researchers have contributed to this.[8] The systems involve hydrophilic and hydrophobic, aliphatic and aromatic and several amphiphilic supports also. The present study is aimed to generate a variety of ligands on a styrene-DVB copolymer support and study their ligation properties. The ligand functions chosen are N, NN, NO, OO and SS donor species as these contribute the major part in coordination chemistry.

The preparation of ligands is depicted in **Scheme 1**.



Scheme 1. Preparation of polymer supported ligands

The polymer supported ligands react with $VOSO_4$ to form the polymer supported metal complexes. The formation of the metal complexes can be represented generally as follows **(Scheme 2).**



Scheme 2. formation of polymer supported oxovanadium complexes

where L and L′ represents the coordination sites of the polymer supported ligands. The oxycation VO^{2+} may be formulated as containing V^{4+} and VO^{2+} always exist coordinated to other groups both in the solid state and in solution bringing the total coordination number of vanadium to five or six.

The polymer supported metal complexes were characterised by spectroscopic methods. In the IR spectra of these complexes a peak is observed at 960 cm^{-1}, which is attributed to the stretching vibration of the terminal V=O bond. Characteristic absorption peaks of ionic sulfate are present at 1120 and 620 cm^{-1} (Fig. 1). Dithiocarbamate and Schiff base are uninegative ligands, so the presence of anions suggest 1 : 1 ligand to metal ratio. The IR peaks show that the anions are present in the non-coordinated (ionic) form in these complexes.

The formation constant of $VOSO_4$ is small compared to that of VO $(H_2O)_5$; so the coordination of water molecule is more probable. The formation of 1 : 1 ligand to metal complexes may be attributed to the steric constraints imposed by the polymeric backbone.

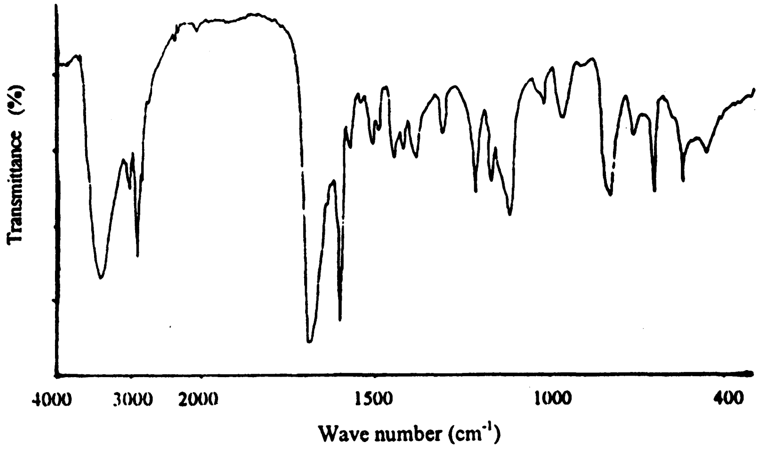


Fig. 1. IR spectrum of P*SS ($VOSO_4$)

The solid state electronic spectrum of vanadyl complexes exhibits peaks in the region 12000, 17000 and 25000 cm^{-1} (Fig. 2). Interpretation of the electronic spectra of oxovanadium complexes is a subject of continuing investigation and discussions. In the Ballhausen and Gray scheme[9] for the interpretation of the electronic spectra of aquated oxovanadium(IV) ions, ground level is the singly occupied nonbonding b_2 level and $e\pi^*$ orbital is considered to have less energy than b_1^* orbital and the energies for transition increases in the order $b_2 \rightarrow e\pi^* < b_2 \rightarrow b_1^* < b_2 \rightarrow a_1^*$. Selbin questioned the general applicability of BG scheme and concluded that b_1^* and $e\pi^*$ may be very close in energy and may cross one another from complex to complex.[10] The addition of a ligand to the sixth coordination position of vanadium decreases the energy of the $e\pi^*$ orbitals thereby shifting the $b_2 \rightarrow e\pi^*$ transitions to lower energies.

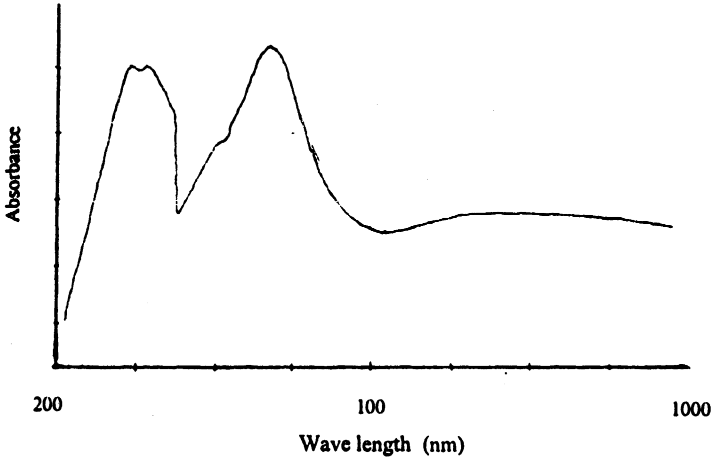


Fig. 2. Electronic spectrum of P*NN ($VOSO_4$)

In the $VO(H_2O)_5^{2+}$ molecule the vanadyl (V═O) bond is the strongest linkage and the four water molecules in the square plane are equivalent and are attached more strongly than the axial water molecule which has the weakest linkage of all. So generally the sixth coordination site of oxovanadium complexes is only weakly coordinated. Strongly coordinating solvents can get coordinated to sixth position thereby changing the energy level scheme. In the present system since 1 : 1 ligand to metal ratio exists the two coordination sites in the plane of the ligand molecules are coordinated strongly by water molecules. The sixth coordination site opposite to vanadyl oxygen is weakly coordinated by water.

Considering the above facts the electronic transitions of polymer supported oxovanadium complexes are assigned according to BG scheme as given in Table-1.

TABLE 1
ELECTRONIC TRANSITIONS (cm^{-1}) OF POLYMER SUPPORTED OXOVANADIUM COMPLEXES

Complex	$b_2 \rightarrow e\pi^*$	$b_2 \rightarrow b_1^*$	$b_2 \rightarrow a_1^*$
P*SS VOSO4	12886	17857	24509
P*NN VOSO4	12953	117730	24271
P*NO VOSO4	12850	17650	24740

The solid state EPR spectra of polymer metal complexes are anisotropic with two sets of resonance components, one each due to parallel and perpendicular features (Figs. 3–5). Each component splits into eight lines due to the coupling of unpaired electrons with the large moment of nearly 100% abundant V nucleus (I = 7/2).

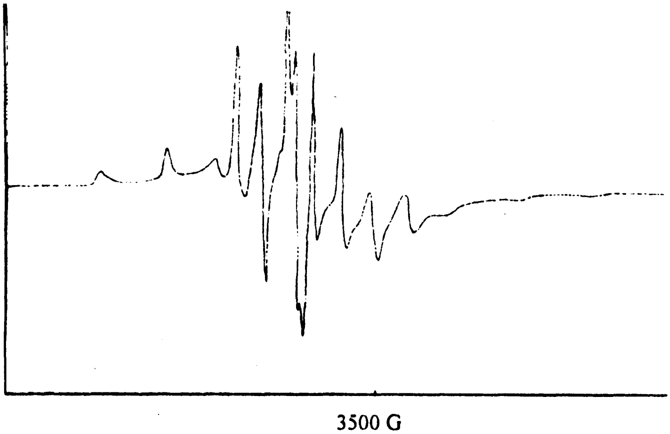


Fig. 3. EPR spectrum of P*SS ($VOSO_4$)

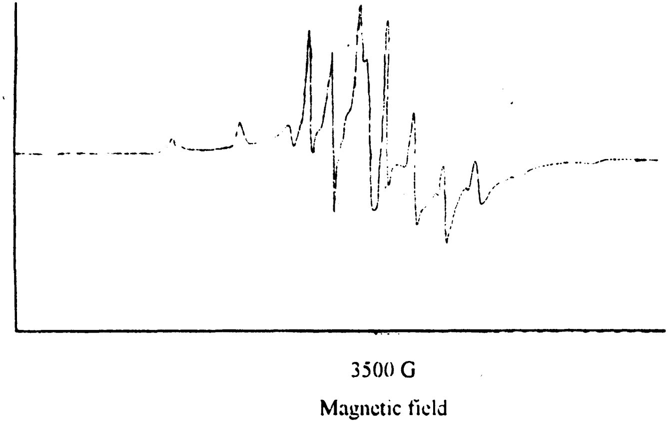


Fig. 4. EPR spectrum of P*NN ($VOSO_4$)

In the VO^{2+} complexes the unpaired electron resides in the b_2g^* orbital. This orbital is almost completely localised on vanadium in a d_{xy} atomic orbital (or the d_{xy} orbital is nonbonding). The unpaired electron resides in the b_2g^* orbital and the coefficient β_2^2 for this orbital is a measure of the inplane bonding of the metal ligand bond. β_2^2 is calculated using the equation proposed by Kivelson and Lee.[11]

$$A_{11} = P\left[-\beta_2^2\left(\frac{4}{7} + K\right) + g_{\|} - 2.002 + \frac{3}{7}(g_{\perp} - 2.002) + D_{\|} + \frac{3}{7}D_{\perp}\right]$$

The value of P is 128 for V^{2+} (the effective charge on vanadium is +2 owing to charge transfer from oxygen) $D_{\|}$ and $D_{\perp}$ are roughly estimated to be –0.005 and –0.0005 respectively. The value of K (isotropic contact term) is taken to be 0.8.

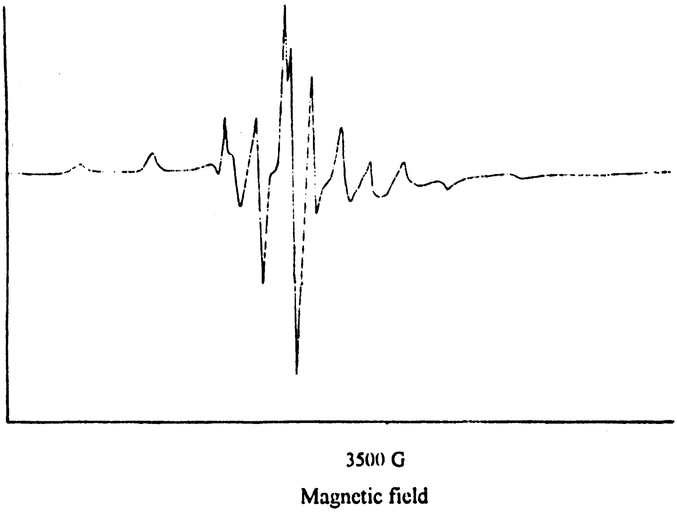


Fig. 5. EPR spectrum of P*NO ($VOSO_4$)

Rearranging eqn. (1)

$$\beta_2^2 = \frac{\left[\frac{-A_1}{P} + g_{\|} - 2.002 + \frac{3}{7}(g_{\perp} - 2002) + 0.0052\right]}{\left(\frac{4}{7} + K\right)}$$

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

$$g_{\|} = \frac{2.002 - 8\beta_2^2\beta_1^2\varepsilon}{\Delta E_{x^2-y^2}}$$

$$g_{\perp} = \frac{2.002 - 8\beta_2^2 e\pi^2\varepsilon}{\Delta E_{xzyz}}$$

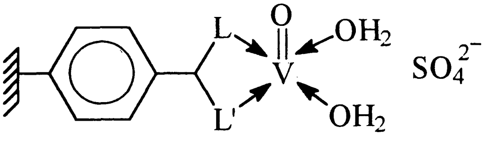
β_2^2, β_1^2 and $e\pi^2$ are the unpaired spin density in the d_{xy}, $d_{x^2-y^2}$ and d_{xz}, d_{yz} orbitals respectively. ε is the spin orbit coupling constant whose value is 170 for VO^{2+}. The EPR parameters calculated for the metal complexes are given in Table-2.

TABLE 2
EPR PARAMETERS OF POLYMER SUPPORTED VANADYL COMPLEXES

Complex	$g_{\|}$	$g_{\perp}$	$A_{\|}$	$A_{\perp}$	β_2^2	β_1^2	$e\pi^2$
P*SS $VOSO_4$	1.9285	1.9848	191.4	73.5	1.029	0.843	0.880
P*NN $VOSO_4$	1.9260	1.9860	195.0	74.2	1.050	1.000	—
P*NO $VOSO_4$	1.9456	1.9880	175.0	64.2	0.949	0.746	0.531

The inplane σ bonding represented by β_1^2 varies from compound to compound and decreases as the covalency of the bond increases. The same is true for out of plane π bonding represented by $e\pi^2$. The values of β_2^2, β_1^2 and $e\pi^2$ suggest that the inplane bonding is ionic but the inplane σ bonding and out of plane bonding are appreciably covalent.

From the above discussions the following general structure can be assigned to the complexes.



So polymer supported strategy generates chromophores S_2O_2, N_2O_2 and NO_3 on polymer supports. The preparation of these chromophores in homogeneous conditions is difficult and macrocyclic ligands result in strained molecules. From the EPR parameters g_0 and A_0 are calculated using equations

$$g_0 = \frac{g_{\parallel} + 2g_{\perp}}{3} \quad \text{and} \quad A_0 = \frac{A_{\parallel} + 2A_{\perp}}{3}$$

and the g_0 and A_0 values are given in Table-3.

TABLE-3

g_0 AND A_0 VALUES OF DIFFERENT VANADYL CHROMOPHORES

Complex	Chromophore	g_0	A_0
P*SS $VOSO_4$	S_2O_2	1.966	112.8
P*NN $VOSO_4$	N_2O_2	1.965	114.4
P*NO $VOSO_4$	NO_3	1.973	101.1

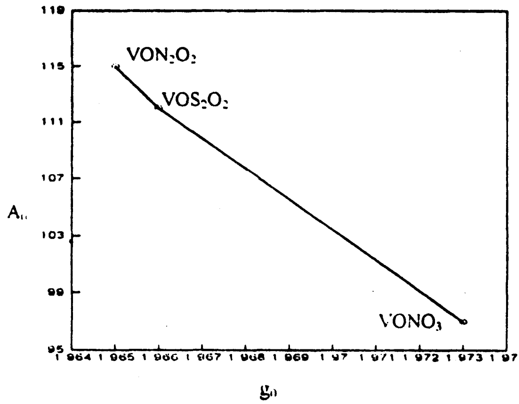


Fig. 6. Correlation plot for vanadyl complexes

A correlation between g_0 and A_0 values can be obtained (Fig. 6) and it is seen that the plot of g_0 against A_0 is roughly linear. This plot may be used to find out the environment of unknown vanadyl complexes.

Polymer supported strategy can be used to prepare metal dictated vanadyl complexes having different chromophores and the correlation plot may be extended, which may find application in the characterisation of vanadyl complexes.

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