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A polymer grafted oxidomethoxidovanadium(V) complex of an ONO donor ligand mimicking peroxidase activity

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ABSTRACT

The reaction between $[V^{IV}O(acac)_2]$ and the ONO donor tridentate ligand H_2hap-iah (**I**) [H_2hap-iah = Schiff base obtained by the condensation of equimolar amounts of *o*-hydroxyacetophenone (hap) and indole-3-acetic hydrazide (iah)] in an equimolar ratio under an oxygen atmosphere in refluxing methanol gives $[V^{V}O(OMe)(\text{hap-iah})]$ (**1**). Treatment of **1** in methanol with H_2O_2 in the presence of KOH results in the formation of $K[V^{V}O(O_2)(\text{hap-iah})]$ (**2**). Complex **1** has been grafted into chloromethylated polystyrene cross-linked with 5% divinylbenzene {now abbreviated as PS-$[V^{V}O(OMe)(\text{hap-iah})]$ (**3**)} via covalent bonding through the imino nitrogen atom of the indole group. The two complexes have been characterized by various spectroscopic techniques (IR, electronic, ^{1}H, ^{13}C and ^{51}V NMR, ESI-MS), analytical and thermal studies. The polymer-grafted complex **3** has also been analyzed by field-emission scanning electron micrographs (FE-SEM) as well as energy dispersive X-ray (EDAX) studies. The polymer-grafted complex **3** has been used as a catalyst for the peroxidase-like oxidation of pyrogallol to purpurogallin in pH 7 buffer solution. Its high peroxidase mimicking ability, easy separation from the reaction medium and the reusability, without any considerable decrease in activity, suggest the practical utility of the catalyst.

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1. Introduction

Vanadium complexes are known for various catalytic oxidation reactions in the presence of oxidants like H_2O_2 and *tert*-butylhydroperoxide (TBHP) as they easily form intermediate species containing an electron rich peroxido group which is able to transfer oxygen to the organic substrate [1–3]. Our efforts in grafting these complexes into polymer matrices and using them as catalyst precursors [4–7] has the additional advantage in the direction of their technological usage because of their thermal stability, recyclability and high turnover rates, resulting in environmentally benign synthetic routes to fine chemicals. Recently we observed that inserting a spacer (an extra CH_2 group) between the polymer support and catalyst enhanced the catalytic performance of such grafted catalysts, possibly due to the presence of more catalytic centers on the surface of the polymer support which allow a better interaction of the catalytic center with the substrate and oxidant during the catalytic reaction [8,9]. Peroxidase-like activity, e.g.. the oxidation of 2,2′-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS), a classical chromogenic heme peroxidase substrate, catalyzed by vanadium haloperoxidases has been reported [10]. However, the catalytic applications of model vanadium complexes have rarely been examined for peroxidase-like activity [11]. Recently, peroxidase-like activity e.g., the oxidation of pyrogallol to purpurogallin, has been successfully achieved under mild reaction conditions with pH 7 buffered solutions in aqueous medium using homogeneous as well as heterogeneous model oxidovanadium(IV) complexes as catalysts [11]. These results encouraged us to design an oxidovanadium(V) complex with the ONO donor ligand H_2hap-iah (**I**, derived from *o*-hydroxyacetophenone and indole-3-acetic hydrazide). Its grafting into chloromethylated polystyrene (PS), characterization and catalytic potential toward the oxidation of pyrogallol to purpurogallin (a peroxidase mimicking activity) are reported here. The corresponding non-polymer-grafted oxidovanadium(V) complex has also been prepared to compare its catalytic performance.

2. Experimental

2.1. Materials

V_2O_5, acetylacetone (Sisco, India), *o*-hydroxyacetophenone, pyrogallol (Loba Chemie, India), indole-3-acetic hydrazide

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(Aldrich, USA) and 30% aqueous H_2O_2 (Rankem, India) were used as obtained. Chloromethylated polystyrene [18.9% Cl (5.35 mmol Cl per gram of resin)] cross-linked with 5% divinylbenzene was obtained from Thermax Limited, Pune, India. $[V^{IV}O(acac)_2]$ was prepared according to the method reported in the literature [12]. Other reagents and solvents were used as analytical reagent grade.

2.2. Physical methods and analysis

Microanalysis (C, H and N) was performed using an Elementar model Vario-EL-III. The vanadium content in the polymer-grafted complex was obtained by Inductively Coupled Plasma spectrometry (ICP; Labtam 8440 plasma lab). Thermogravimetric analysis of the complexes was carried out using a Perkin Elmer Pyris Diamond, having a weight sensitivity of 0.2 μg, under an oxygen atmosphere. The energy dispersive X-ray analysis (EDX) of the anchored complex was recorded on a FEI Quanta 200 FEG. The sample was coated with a thin film of gold to prevent surface charging, to protect the surface material from thermal damage by the electron beam and to make the sample conductive. Infrared spectra were recorded on a Nicolet NEXUS Aligent 1100 FT-IR spectrometer (having a resolution of 4 cm^{-1}) with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu 1601 UV–Vis spectrophotometer with 0.1 nm wavelength accuracy. Spectra of the non-polymer-grafted ligand and complexes were recorded in methanol and the spectrum of the polymer grafted complex was recorded in Nujol by layering a mull of the sample on the inside of one of the cuvettes while keeping the other one layered with Nujol as a reference. Using $BaSO_4$ as a background, the electronic spectrum of the polymer-grafted complex was also recorded after diluting the sample with $BaSO_4$. ^1H and ^{13}C NMR spectra (using a Bruker Avance III 500 MHz spectrometer) and the ^{51}V NMR spectrum (using a Bruker Avance III 400 MHz spectrometer) with common parameter settings were recorded in CD_3OD and DMSO-d_6, and the δ (^{51}V) values are referenced relative to neat V^VOCl_3 as an external standard. A high resolution mass spectrum (HRMS) in the positive ion electro spray ionization mass spectrum mode was obtained on a BrukermicrOTOF-Q II mass spectrometer in CH_3CN.

2.3. Synthesis

2.3.1. H_2hap-iah (**I**)

A mixture of indole-3-acetic hydrazide (3.78 g, 20 mmol) and *o*-hydroxyacetophenone (2.72 g, 20 mmol) in 100 mL of methanol was refluxed for 4 h. After reducing the solvent volume to ca. 15 mL and standing the solution in air for 24 h, an off-white solid precipitated, which was filtered off, washed with methanol and dried *in vacuo*. Recrystallization from methanol yielded the pure ligand. Yield: 5.5 g (89%). *Anal.* Calc. for $C_{18}H_{17}N_3O_2$ (307): C, 70.34; H, 5.58; N, 13.67. Found: C, 69.94; H, 5.53; N, 13.81%.

2.3.2. $[V^VO(OMe)$(hap-iah)] (**1**)

A methanolic (absolute) solution of $[V^{IV}O(acac)_2]$ (0.265 g, 1 mmol in 10 mL) was added to a solution of H_2hap-iah (**I**) (0.307 g, 1 mmol) dissolved in dry methanol (30 mL) and the obtained reaction mixture was heated at reflux for 6 h to give a dark brown solution. Slow evaporation of the solvent at room temperature under air gave a dark brown solid, which was filtered, washed with methanol and dried *in vacuo*. Yield: 0.285 g (70.7%). *Anal.* Calc. for $C_{19}H_{18}N_3O_4V$ (403.31): C, 56.58; H, 4.50; N, 10.42. Found: C, 56.81; H, 4.48; N, 10.60%. ^{51}V NMR (DMSO-d_6, δ/ppm): −520.8 (62%), −540.0 (9%), −549.5 (29%).

2.3.3. $K[V^VO(O_2)$(hap-iah)] (**2**)

Complex **1** (0.201 g, 0.5 mmol) was dissolved in methanol (20 mL) and then aqueous 30% H_2O_2 (1 mL) diluted in 2 mL MeOH and KOH (0.023 g, 0.5 mmol) dissolved in 2 mL MeOH were added with stirring. After 5 h of stirring a light pale yellow solid was filtered off, washed with methanol and dried in air. Yield: 0.130 g (59%). *Anal.* Calc. for $C_{18}H_{15}N_3O_5KV$ (443.37): C, 48.76; H, 3.41; N, 9.48. Found: C, 48.51; H, 3.32; N, 9.26%. ^{51}V NMR (DMSO-d_6, δ/ppm): −540.0 (55%), −551.0 (45%).

2.3.4. PS-$[V^VO(OMe)$(hap-iah)] (**3**)

Chloromethylated polystyrene (2.0 g) was suspended in DMF (15 mL) for 2 h. A solution of $[V^VO(OMe)$(hap-iah)] (2.0 g, 4.96 mmol) in DMF (15 mL) was added to the above suspension, followed by triethylamine (2.66 g) in ethyl acetate (15 mL), and the obtained reaction mixture was heated at 90 °C for 24 h with continuous but slow stirring. After cooling to room temperature, the polymer-grafted complex was separated by filtration, washed with hot DMF, followed by hot methanol. It was then further refluxed in methanol for ca. 12 h and dried in an oven in air at 110 °C. Recovery yield: 2.1 g.

2.4. Peroxidase mimetic activity: catalytic oxidation of pyrogallol

The catalyst PS-$[V^VO(OMe)$(hap-iah)] (**3**) was suspended in acetonitrile for 2 h before starting the reaction. The peroxidase mimetic activity was determined using a UV–Vis spectrophotometer by monitoring the absorbance increment at 420 nm (due to the formation of purpurogallin) up to 1.5 h [13]. Initially, 1 mL of a 2.5×10^{-2} M solution of 30% H_2O_2, 1 mL of 2.5×10^{-2} M pyrogallol solution and 0.015 g of the catalyst PS-$[V^VO(OMe)$(hap-iah)] were taken in 3 mL of phosphate buffer (1 M, pH 7) and the maximum measurable absorbance was recorded. In the second step, various parameters, such as different amounts of oxidant and catalyst and pH of the reaction medium, were optimized to evaluate the best reaction conditions for the maximum oxidation of pyrogallol. The steady state kinetics were performed by varying the concentration of pyrogallol (0.2–2.2 mM) for a fixed concentration of H_2O_2 (2.5×10^{-4} M/0.25 mM) in the presence of the catalyst PS-$[V^VO(OMe)$(hap-iah)] (0.010 g). The reaction was carried out in 2 mL of phosphate buffer (1 M, pH 7) and monitored spectrophotometrically by measuring the formation of purpurogallin from pyrogallol at 420 nm ($\varepsilon = 2640\ M^{-1}\ cm^{-1}$) in the time scan mode. The initial reaction rates were calculated and fitted to the Michaelis–Menten equation. Lineweaver–Burk linearizations were performed using Sigma-Plot software (Systat Software Inc.) with the enzyme kinetics module to calculate kinetic parameters.

3. Results and discussion

3.1. Synthesis and characterization

A solution of H_2hap-iah (**I**) reacted with $[V^{IV}O(acac)_2]$ in MeOH in a 1:1 M ratio under an aerobic atmosphere at reflux temperature to give the dark brown complex $[V^VO(OMe)$(hap-iah)] (**1**) [Eq. 1]. Its reaction with 30% aq. H_2O_2 in the presence of one equivalent of KOH in methanol gave the complex $K[V^VO(O_2)$(hap-iah)] (**2**) [Eq. 2].

$$2\left[V^{IV}O(acac)_2\right] + 2H_2\text{hap-iah} + 2MeOH + \frac{1}{2}O_2 \rightarrow 2\left[V^VO(OMe)(\text{hap-iah})\right] + H_2O + 4Hacac \quad (1)$$

$$\left[V^VO(OMe)(\text{hap-iah})\right] + H_2O_2 + KOH \rightarrow K\left[V^VO(O_2)(\text{hap-iah})\right] + MeOH + H_2O \quad (2)$$

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