

# Oxovanadium(IV) based coordination polymers and their catalytic potentials for the oxidation of styrene, cyclohexene and *trans*-stilbene

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## Abstract

Reaction between 5,5'-methylenebis(salicylaldehyde) or 5,5'-dithiobis(salicylaldehyde) and 1,2-diaminocyclohexane in equimolar ratio leads to the formation of new polymeric chelating ligands  $[-CH_2(H_2sal-dach)-]_n$  (**I**) and  $[-S_2(H_2sal-dach)_2-]_n$  (**II**). These ligands react with  $[VO(acac)_2]$  in DMF to give coordination polymers  $[-CH_2\{VO(sal-dach)\cdot DMF\}-]_n$  (**1**) and  $[-S_2\{VO(sal-dach)\cdot DMF\}-]_n$  (**2**). Both complexes are insoluble in common solvents and exhibit a magnetic moment value of 1.74 and  $1.78\mu_B$ , respectively. IR spectral studies confirm the coordination of ligands through the azomethine nitrogen and the phenolic oxygen atoms to the vanadium. These complexes exhibit good catalytic activity towards the oxidation of styrene, cyclohexene and *trans*-stilbene using *tert*-butylhydroperoxide as an oxidant. Concentration of the oxidant and reaction temperature has been optimised for the maximum oxidation of these substrates. Under the optimised conditions, oxidation of styrene gave a maximum of 76% (with **1**) or 85% (with **2**) conversion having following products in order of selectivity: benzaldehyde > styreneoxide > 1-phenylethane-1,2-diol > benzoic acid. A maximum of 98% conversion of cyclohexene was obtained with both the catalysts where selectivity of cyclohexeneoxide varied in the order: **2** (62%) > **1** (45%). With the conversion of 33% (with **1**) and 47% (with **2**), oxidation of *trans*-stilbene gives benzaldehyde, benzil and *trans*-stilbeneoxide as major products.

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**Keywords:** Coordination polymers; Oxovanadium(IV) complexes; Catalyst; Epoxidation reaction

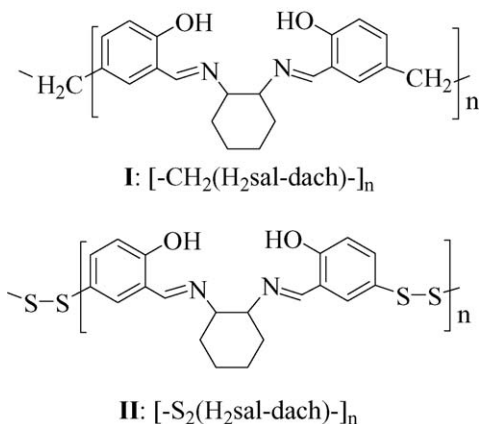
## 1. Introduction

The potential catalytic abilities of vanadium compounds have lead to an increasing interest in vanadium coordination chemistry in recent years [1]. In the presence of hydrogen peroxide or organic hydroperoxides, vanadium complexes are able to accelerate the oxidative halogenation of organic compounds [2–7] and the oxidation of aliphatic as well as aromatic substrates including the oxidation of (prochiral) organic sulfides to (chiral) sulfoxides [8–16]. Coordination polymers, i.e. polymeric metal complexes derived from simple or polymeric coordinating ligands are generally insoluble in common solvents and have added advantage, over monomer analogues, of easy separation from the catalytic reaction mixture leading to operational flexibility and recyclability [17,18]. Recently reported oxovanadium(IV) based coordination polymers by Ando et al. [19] are insoluble

in common solvents and their catalytic oxidation reactions are heterogeneous in nature [19].

We have also designed oxovanadium(IV) based coordination polymers of polymeric Schiff bases derived from 5,5'-methylenebis(salicylaldehyde) and diamines that exhibited potential catalytic activity and selectivity for the liquid-phase hydroxylation of phenol to catechol. The oxidative bromination of salicylaldehyde, a reaction similar to that exhibited by functional models of enzyme vanadate-dependent haloperoxidases (V-HalpO), has also been carried out with these complexes [18]. The objective of the present work is to synthesize polymeric oxovanadium(IV) complexes of the ligands **I** and **II** formed from 5,5'-methylenebis(salicylaldehyde) or 5,5'-dithiobis(salicylaldehyde) and 1,2-diaminocyclohexane, Scheme 1 and study catalytic potential for the oxidation of styrene, cyclohexene and *trans*-stilbene using *tert*-butylhydroperoxide (TBHP) as an oxidant. Different types of catalysts have been tested for the oxidation of styrene [20–25], cyclohexene [26–33] and *trans*-stilbene [34–38].

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Scheme 1. Structure of ligands.

## 2. Experimental

### 2.1. Materials and physical methods

$\text{V}_2\text{O}_5$  (Loba chemicals, India), trioxane (Spectro chemicals, India), salicylaldehyde, acetylacetone, 1,2-diaminocyclohexane, 70% (w/v) *tert*-butylhydroperoxide (TBHP) (E. Merck, India) and sulfur monochloride (Aldrich Chemical Co., U.S.A.) were used as supplied. All other chemicals and solvents were of AR grade and were used without purification. 5,5'-Methylenebis(salicylaldehyde) [39], 5,5'-dithiobis(salicylaldehyde) [40], and  $[\text{VO}(\text{acac})_2]$  [41] were prepared following the known methods.

Elemental analyses of the ligands and complexes were performed by the sophisticated analytical instrumental facilities section of the Central Drug Research Institute, Lucknow, India.  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance 200 MHz spectrometer in  $\text{DMSO}-d_6$ . Thermogravimetric analyses of the catalysts were carried out using a TG Stanton Redcroft STA 780. IR spectra were recorded as KBr pellets on a Nicolet NEXUS Aligent 1100 FT-IR spectrometer. Electronic spectra were recorded in Nujol on a Shimadzu 1601 UV-vis spectrophotometer by layering the mull of one sample to the inside of one of the cuvettes while keeping another one layered with Nujol as reference. The magnetic susceptibility measurements were carried out by Vibrating Sample Magnetometer model 155, using nickel as standard.

### 2.2. Preparations

#### 2.2.1. Preparation of $[-\text{CH}_2(\text{H}_2\text{sal-dach})-]_n$ (I)

A solution of 1,2-diaminocyclohexane (1.44 g, 10 mmol) in 10 ml methanol was added drop wise to a hot methanolic solution of 5,5'-methylenebis(salicylaldehyde) (2.56 g, 10 mmol) and the reaction mixture was heated under reflux on a water bath for 2 h. After cooling to room temperature, the yellow precipitate of **I** was filtered off, washed with hot methanol and dried. Finally, the ligand was purified by refluxing the powdered sample in methanol (50 ml) for 1 h, filtering and drying at  $120^\circ\text{C}$  in an air oven.  $^1\text{H}$  NMR ( $\delta$  in ppm): 13.08 (s, 2H, OH),

8.36 (s, 2H,  $-\text{CH}=\text{N}-$ ), 6.69–7.08 (m, 6H, aromatic), 3.71 (s, 2H, bridging  $\text{CH}_2$ ), 3.2 (s, 2H,  $-\text{CH}-$  of cyclohexyl), 1.72, 1.49 (br, 8H,  $\text{CH}_2$  of cyclohexyl).

#### 2.2.2. Preparation of $[-\text{S}_2(\text{H}_2\text{sal-dach})-]_n$ (II)

This was prepared according to the procedure outlined for **I**.  $^1\text{H}$  NMR ( $\delta$  in ppm): 10.22 (s, 2H, OH), 8.46 (br, 2H,  $-\text{CH}=\text{N}-$ ), 6.72–7.53 (m, 6H, aromatic), 1.79, 1.47 (br, 8H,  $\text{CH}_2$  of cyclohexyl). Signal due to  $-\text{CH}-$  of cyclohexyl group could not be located due to appearance of a broad band of water at ca. 3.5 ppm.

#### 2.2.3. Preparation of $[-\text{CH}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}-]_n$ (I) and $[-\text{S}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}-]_n$ (2)

Both complexes were prepared by a general procedure: the ligand,  $[-\text{CH}_2(\text{H}_2\text{sal-dach})-]_n$  (1.67 g, equivalent to 5 mmol of repeating unit) or  $[-\text{S}_2(\text{H}_2\text{sal-dach})-]_n$  (1.76 g, equivalent to 5 mmol of repeating unit) was dissolved in 20 ml of DMF by heating on a water bath. A methanolic solution of  $[\text{VO}(\text{acac})_2]$  (1.33 g, 5 mmol in 10 ml) was added to the above solution and the reaction mixture was digested on a water bath for ca. 4 h. After cooling to room temperature, the green solid was filtered off, washed with methanol and dried at  $120^\circ\text{C}$  in an air oven.

#### 2.2.4. Preparation of $[\text{VO}(\text{sal-dach})]$ (3)

A solution of 1,2-diaminocyclohexane (0.720 g, 5 mmol) in 10 ml of methanol was mixed with salicylaldehyde (1.22 g, 10 mmol) dissolved in 10 ml of methanol and the reaction mixture was refluxed for 2 h where a dark yellow solution was obtained. A methanolic solution of  $[\text{VO}(\text{acac})_2]$  (1.33 g, 5 mmol in 10 ml) was added to the above solution and the reaction mixture was further refluxed for 2 h. During this period green solid of **3** slowly separated out. On cooling the flask to ca.  $2^\circ\text{C}$ , it was filtered, washed with methanol and dried in vacuum.

Analytical and physico-chemical data of the complexes are presented in Table 1.

### 2.3. Catalytic activity

#### 2.3.1. Oxidation of styrene

In a typical procedure, styrene (1.04 g, 10 mmol) and 70% (w/v) *tert*-butylhydroperoxide (TBHP) (3.84 g, 30 mmol) were taken in 20 ml of acetonitrile and the flask was maintained at the specified temperature ( $75^\circ\text{C}$ ) using an electrically heated oil bath. The catalyst (15 mg, equivalent to 0.032 mmol of repeating unit) to be examined was added and the reaction mixture was stirred for 6 h. The catalyst was separated with Whatman filter paper no. 1 and the liquid layer was analysed quantitatively by a Thermo trace gas chromatograph having HP-1 column (30 m  $\times$  0.25 mm) and FID detector. The products were identified by GC-MS (Perkin-Elmer Clarus 500 column; 30 m  $\times$  60 mm).

#### 2.3.2. Oxidation of cyclohexene

Cyclohexene (0.82 g, 10 mmol), 70% (w/v) *tert*-butylhydroperoxide (TBHP) (2.56 g, 20 mmol) and catalyst (15 mg, equivalent to 0.032 mmol of repeating unit) were transferred into 20 ml of acetonitrile and the reaction mixture

Table 1  
Physical and analytical data of ligands and complexes

Compounds	Colour	Yield (%)	$\mu_{\text{eff}}$ ( $\mu_{\text{B}}$ ) per metal	Found (calculated) (%)		
				C	H	N
$[-\text{CH}_2\{\text{H}_2\text{sal-dach}\}]_n$ ( <b>I</b> )	Yellow	82		75.1 (75.4)	6.6 (6.6)	8.2 (8.4)
$[-\text{CH}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}]_n$ ( <b>1</b> )	Green	68	1.74	60.6 (61.1)	6.1 (5.8)	8.6 (8.9)
$[-\text{S}_2\{\text{H}_2\text{sal-dach}\}]_n$ ( <b>II</b> )	Yellow	78		62.1 (62.5)	5.3 (5.2)	7.6 (7.3)
$[-\text{S}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}]_n$ ( <b>2</b> )	Green	72	1.78	52.6 (52.8)	5.0 (4.8)	7.7 (8.0)

was heated at 75 °C for 6 h with stirring in an oil bath. After removing the catalyst by filtration, the reaction products were analysed as mentioned above.

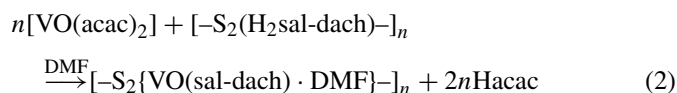
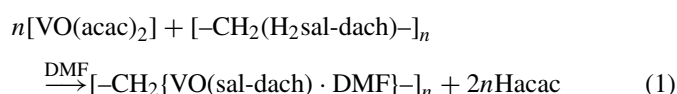
### 2.3.3. Oxidation of *trans*-stilbene

Same procedure as mentioned above was adopted for the oxidation of *trans*-stilbene. Catalyst (15 mg, equivalent to 0.032 mmol of repeating unit), *trans*-stilbene (1.82 g, 10 mmol) and 70% (w/v) *tert*-butylhydroperoxide (TBHP) (2.56 g, 20 mmol) were charged into 40 ml of acetonitrile and the reaction mixture was heated at 75 °C for 6 h with stirring in an oil bath. After removing the catalyst by filtration, the reaction products were analysed as mentioned above.

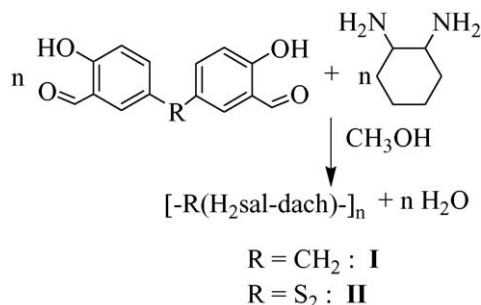
## 3. Result and discussion

Reaction between equimolar amounts of 5,5'-methylenebis(salicylaldehyde) or 5,5'-dithiobis(salicylaldehyde) and 1,2-diaminocyclohexane in refluxing methanol gave ligands  $[-\text{CH}_2(\text{H}_2\text{sal-dach})-]_n$  (**I**) and  $[-\text{S}_2(\text{H}_2\text{sal-dach})-]_n$  (**II**), respectively; Scheme 2. Spectroscopic (<sup>1</sup>H, IR and UV–vis) studies and elemental analyses of these ligands confirmed their structure.

These ligands react with  $[\text{VO}(\text{acac})_2]$  in  $\text{CH}_3\text{OH}/\text{DMF}$  to give coordination polymers **1** and **2**, respectively; Eqs. (1) and (2):



According to elemental analyses and thermogravimetric studies, these complexes have formula as mentioned above. These green



Scheme 2. Synthetic route to prepare ligands.

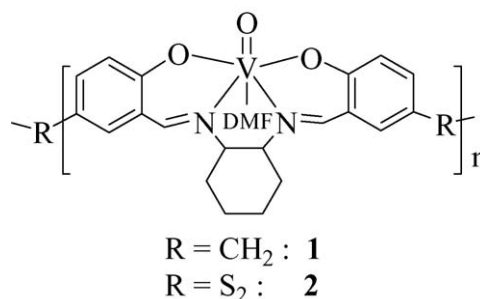
solids are insoluble in all coordinating and non-coordinating solvents and exhibit magnetic moment, at ambient temperature, of 1.74 and 1.78  $\mu_{\text{B}}$ , respectively, which is normally expected for  $d^1$  system. Structure of the prepared complexes is presented in Scheme 3 and is based on the elemental analyses, spectroscopic (IR and UV–vis) data and thermogravimetric studies.

### 3.1. Thermal studies

The results of the thermogravimetric analysis of the complexes are not very conclusive in terms of the loss of specific group(s) on increasing the temperature under dynamic air atmosphere. However, it is clear from the thermogravimetric profiles that these complexes are stable up to ca. 160 °C and the percentage of metal oxide formed at the end matches well with the expected value. For example, complex  $[-\text{CH}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}]_n$  (**1**) loses mass in three steps. A mass loss of 22.2% was observed in the 160–470 °C in the first two overlapping steps followed by a mass loss of 58.8% in a sharp and narrow temperature range of 470–520 °C. The total mass loss of 81.0% corresponds to the loss of all organic moieties including one mole of DMF minus 1.5{O}(calc. 80.7%). The remaining residue corresponds to the formation of  $\text{V}_2\text{O}_5$  (Obs. 19.0%, calc. 19.3%). Complex  $[-\text{S}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}]_n$  (**2**) loses a total mass of 83.2% in the first two overlapping steps (19.7% between 160 and 400 °C) followed by a sharp narrow step (63.5% between 400 and 485 °C). The remaining residue of 16.8% is close to the calculated value of 17.4% for  $\text{V}_2\text{O}_5$  formed.

### 3.2. IR spectral studies

IR spectra of both the ligands exhibit a broad band in the 2450–2850  $\text{cm}^{-1}$  region due to the presence of extensive hydro-



Scheme 3. Proposed structure of complexes.

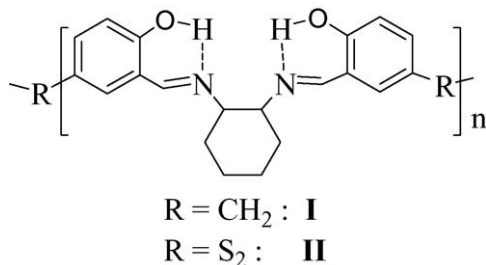
Table 2  
IR spectral data (in  $\text{cm}^{-1}$ ) of ligands and complexes

Compounds	$\nu(\text{OH} \cdots \text{N})$	$\nu(\text{C}=\text{O})$ (DMF)	$-\text{CH}_2-$	$\nu(\text{C}=\text{N})$	$\nu(\text{V}=\text{O})$
$[-\text{CH}_2(\text{H}_2\text{sal-dach})-]_n$ ( <b>I</b> )	2450–2750		2856–2930	1630	
$[-\text{CH}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}-]_n$ ( <b>1</b> )		1666	2858–2930	1619	982
$[-\text{S}_2(\text{H}_2\text{sal-dach})-]_n$ ( <b>II</b> )	2500–2850		2840–2930	1631	
$[-\text{S}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}-]_n$ ( <b>2</b> )		1665	2850–2930	1618	988
$[\text{VO}(\text{sal-dach})]$ ( <b>3</b> )			2860–2930	1618	983

gen bonding between phenolic hydrogen and azomethine nitrogen atoms as shown in Scheme 4. Absence of this band in complexes indicates the breaking of hydrogen bonding followed by coordination of phenolic oxygen to the metal ion after deprotonation. A sharp band at  $1630\text{--}1631\text{ cm}^{-1}$  due to azomethine  $\nu(\text{C}=\text{N})$  stretch of ligands shifts to lower wave number by  $11\text{--}13\text{ cm}^{-1}$  and this indicates the coordination of azomethine nitrogen to the metal ion. The presence of multiple bands at  $2840\text{--}2930\text{ cm}^{-1}$  in ligands and their complexes with only marginal shifting suggests the presence of  $\text{CH}_2$  group of cyclohexane and the repeating unit bridged by  $\text{CH}_2$  group in ligand **I** as well as its complex. Thus, each repeating unit of the polymeric ligands behaves as a dibasic tetradentate ONNO donor. In addition, both polymeric oxovanadium(IV) complexes exhibit a sharp band at  $982\text{ cm}^{-1}$  (in **1**) and at  $988\text{ cm}^{-1}$  (in **2**) due to the presence of  $\nu(\text{V}=\text{O})$  stretch. Monomeric complex  $[\text{VO}(\text{sal-dach})]$  exhibit this band at  $983\text{ cm}^{-1}$ . The coordinated DMF in complexes **1** and **2** exhibits a band at ca.  $1665\text{ cm}^{-1}$  due to the  $\nu(\text{C}=\text{O})$  stretch [42]. IR spectral data are listed in Table 2.

### 3.3. Electronic spectral studies

Table 3 provides electronic spectral data of ligands and complexes along with their probable assignments. The electronic spectra of both the ligands recorded in DMF exhibit two bands at ca. 270 and 326 nm. Based on their extinction coefficients these are assigned as due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively. Both bands shift to lower energy in complexes indicating the coordination of ligands to the metal ions. This is further supported by the appearance of a lower intensity band at 411 nm (in **1**) or at 406 nm (in **2**) due to ligand to metal charge transfer (LMCT) transition. In addition, both the complexes display a weak broad band covering the region  $590\text{--}700\text{ nm}$  due to expected d–d transition. The electronic spectra of both the complexes are reproduced in Fig. 1. Monomeric complex  $[\text{VO}(\text{sal-dach})]$  (**3**) exhibits very similar electronic spectrum.



Scheme 4.

Table 3  
UV–vis data for ligands and complexes

Compounds/solvent	$\lambda_{\text{max}}$ (nm) ( $\epsilon$ ( $\text{M}^{-1}\text{cm}^{-1}$ ))	Assignment
$[-\text{CH}_2(\text{H}_2\text{sal-dach})-]_n$ (DMF)	268 (21243)	$\pi \rightarrow \pi^*$
	328 (12976)	$n \rightarrow \pi^*$
$[-\text{CH}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}-]_n$ (Nujol)	228	$\pi \rightarrow \pi^*$
	297	$n \rightarrow \pi^*$
	411	LMCT
	591	d–d
$[-\text{S}_2(\text{H}_2\text{sal-dach})-]_n$ (DMF)	272 (23824)	$\pi \rightarrow \pi^*$
	326 (12041)	$n \rightarrow \pi^*$
$[-\text{S}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}-]_n$ (Nujol)	218	$\pi \rightarrow \pi^*$
	292	$n \rightarrow \pi^*$
	406	LMCT
	699	d–d
$[\text{VO}(\text{sal-dach})]$ (Methanol)	236 (24658)	$\pi \rightarrow \pi^*$
	278 (13123)	$n \rightarrow \pi^*$
	360 (4741)	LMCT
	568 (52)	d–d

### 3.4. Catalytic activity studies

#### 3.4.1. Oxidation of styrene

Oxidation of styrene has been investigated by several workers using homogeneous as well as heterogeneous catalysts and major oxidation products generally obtained are styreneoxide, benzaldehyde, benzoic acid, phenyl acetaldehyde and 1-

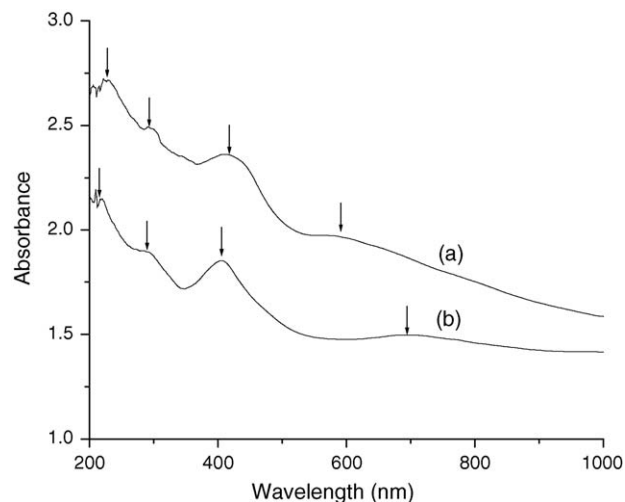
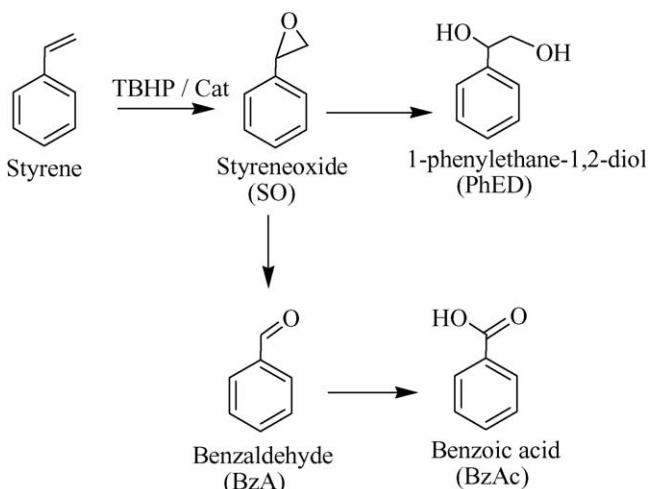


Fig. 1. Electronic spectra of  $[-\text{CH}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}-]_n$  (a) and  $[-\text{S}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}-]_n$  (b).



Scheme 5. Various oxidation products of styrene.

phenylethane-1,2-diol [20–25]. We have found that coordination polymers **1** and **2** satisfactorily catalyse the oxidation of styrene using TBHP as oxidant and gives styreneoxide, benzaldehyde, 1-phenylethane-1,2-diol and benzoic acid along with some unidentified products; Scheme 5.

In order to optimise the reaction conditions for the maximum oxidation of styrene, following parameters have been studied in detail considering  $[-CH_2\{VO(\text{sal-dach})\cdot\text{DMF}\}]_n$  as a representative catalyst:

- effect of temperature;
- effect of TBHP concentration (moles of TBHP per moles of styrene).

In search of suitable reaction temperature, reaction mixture having styrene (1.04 g, 10 mmol), catalyst (15 mg, equivalent to 0.032 mmol of repeating unit) and 70% TBHP (3.84 g, 30 mmol) in 20 ml of acetonitrile were stirred at four different temperatures (viz. 50, 65, 75 and 80 °C) and the obtained results are presented in Fig. 2. It is clear from the plot that increment of temperature increases the conversion and at 75 °C a maximum of 76% con-

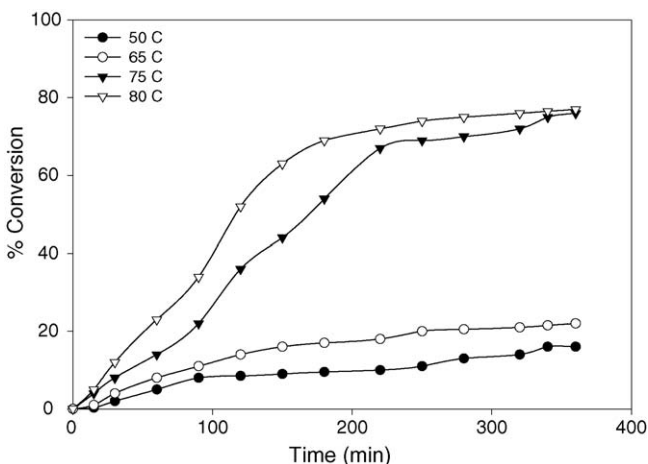


Fig. 2. Effect of temperature on total conversion.

Table 4  
Effect of TBHP on the oxidation of styrene and the product selectivity

Substrate:oxidant ratio	Conversion (%) <sup>a</sup>	Product selectivity (%)				
		SO <sup>b</sup>	BzA <sup>c</sup>	BzAA <sup>d</sup>	PhED <sup>e</sup>	Others
1:0.5	12	60	30	3	3	4
1:1	30	28	53	4	12	3
1:2	68.5	23	54	5	11	7
1:3	76	15	65	6	8	6
1:4	47	18	48	15	12	7

<sup>a</sup> Reaction conditions: styrene (1.04 g, 10 mmol), catalyst (15 mg, equivalent to 0.032 mmol of repeating unit), temperature (75 °C) and acetonitrile (20 ml).

<sup>b</sup> Styrene oxide.

<sup>c</sup> Benzaldehyde.

<sup>d</sup> Benzoic acid.

<sup>e</sup> 1-Phenylethane-1,2-diol.

version of styrene was obtained in 6 h of reaction time. No further improvement in the oxidation was observed on carrying out the reaction at 80 °C except slight reduction in time to acquire the steady state. However, this temperature caused the formation of colloidal solution, which makes the recovery of the catalyst difficult from the reaction mixture. Thus, 75 °C was considered to be the best suited reaction temperature to carry out the reaction. The IR spectrum of the recovered catalyst is also identical to that of fresh catalyst under this condition.

The effect of amount of TBHP on the oxidation of styrene was also studied as a function of time and the results are presented in Table 4. Five different molar ratios of styrene to 70% TBHP (e.g. 1:0.5, 1:1, 1:2, 1:3 and 1:4) were used for which 10 mmol of styrene (1.04 g) and 15 mg of catalyst were taken in 20 ml of acetonitrile and the reaction was carried out at 75 °C. It is clear from the table that percentage oxidation of styrene improved from 12 to 76% on increasing styrene to oxidant ratio from 1:0.5 to 1:3 (styrene to TBHP). However, this change causes the reduction of the selectivity of styreneoxide from 60 to 15%, while increment of the selectivity of benzaldehyde from 30 to 65%. The total conversion of styrene went down from 76 to 47% on further increasing the substrate:oxidant ratio to 1:4, though reaction reached to the steady state within 4 h. The suppression in conversion due to the presence of excess water supplied by TBHP it self may be the possible reason [43].

Carrying out this reaction with 30% aqueous H<sub>2</sub>O<sub>2</sub> under above optimised reaction conditions (i.e. 1:3, substrate to oxidant ratio) gave 80% conversion but the recovery of the catalyst from the reaction mixture became very difficult due to partial decomposition as well as blending of the complexes with solvent.

Thus, under the optimised reaction conditions (i.e. styrene (1.04 g, 10 mmol), catalyst (15 mg) and 70% TBHP (3.84 g, 30 mmol), acetonitrile (10 ml), temperature (75 °C) and time (6 h)), catalytic activity of both the complexes  $[-CH_2\{VO(\text{sal-dach})\cdot\text{DMF}\}]_n$  and  $[-S_2\{VO(\text{sal-dach})\cdot\text{DMF}\}]_n$  was compared. Fig. 3 presents percent conversion of styrene along with the selectivity of various reaction products as a bar diagram. The percent conversion of styrene follows the order: 85% ( $[-S_2\{VO(\text{sal-dach})\cdot\text{DMF}\}]_n$ ) > 76% ( $[-CH_2\{VO(\text{sal-dach})\cdot\text{DMF}\}]_n$ ), where formations of styreneoxide are 15

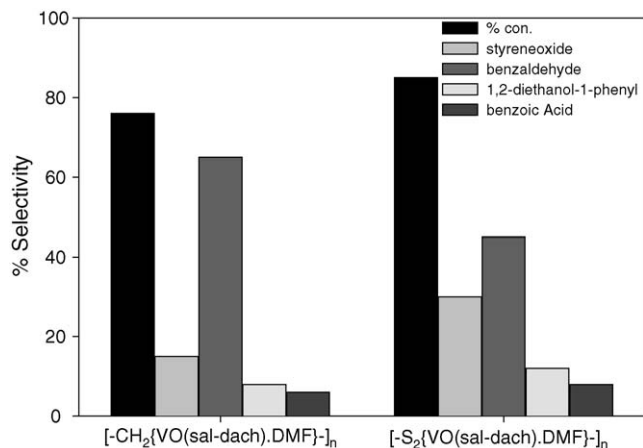


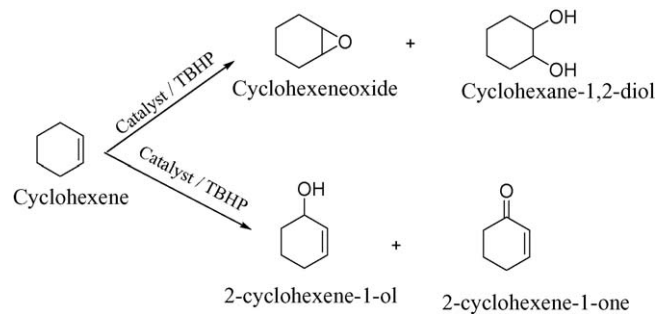
Fig. 3. Bar diagram showing total conversion of styrene and selectivity of various products.

and 30%, respectively. Further,  $[-S_2\{VO(sal-dach).DMF\}-]_n$  requires ca. 4 h to complete the reaction while  $[-CH_2\{VO(sal-dach).DMF\}-]_n$  takes little longer time of 6 h to do so. Thus, turns over frequency (TOF: moles of substrate converted per mole of metal in the solid catalyst per hour) of the two catalysts are 39.6 (for **1**) and 73.3 (for **2**). However, in both cases, the selectivity of various products follows the order: benzaldehyde > styreneoxide > 1-phenylethane-1,2-diol > benzoic acid. The highest formation of benzaldehyde is probably due to a nucleophilic attack of TBHP to styreneoxide. Benzaldehyde formation may also be facilitated by direct oxidative cleavage of the styrene side chain double bond via radical mechanism. Other products, e.g. benzoic acid formation through benzaldehyde is rather slow in both reactions. Water present in TBHP as well as formed during the reaction if any, is probably responsible for partial hydrolysis of styreneoxide to 1-phenylethane-1,2-diol.

### 3.4.2. Oxidation of cyclohexene

Oxidation of cyclohexene catalysed by complexes **1** and **2** gave cyclohexeneoxide, 2-cyclohexene-1-ol, cyclohexane-1,2-diol and 2-cyclohexene-1-one as presented in Scheme 6.

As 75 °C was found an ideal temperature to run the catalytic reaction (vide supra), we have studied the effect of amount of oxidant (moles of TBHP per mole of substrate) for the fixed amount of cyclohexene (0.82 g, 10 mmol), catalyst (15 mg), ace-



Scheme 6. Various oxidation products of cyclohexene.




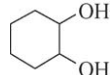
tonitrile (20 ml) and temperature (75 °C) to achieve maximum oxidation of cyclohexene using  $[-CH_2\{VO(sal-dach).DMF\}-]_n$  as a representative catalyst. The effect of TBHP concentration on the oxidation of cyclohexene after 6 h of the reaction time is illustrated in Table 5. Using four different oxidant: cyclohexene ratios (viz. 0.5:1, 1:1, 2:1 and 3:1) under above reaction conditions, the conversion is 51% with the lowest TBHP concentration. However, it reached to 98% with 1:2 (cyclohexene to TBHP) ratio. This conversion goes down with higher substrate to TBHP ratios, which is possibly due to excess water as noted earlier. Thus, a large concentration of oxidant is not an essential condition to maximize cyclohexene oxidation.

Under the optimised reaction conditions, both the catalysts performed oxidation of cyclohexene efficiently with high turn over rates of 51 ( $[-CH_2\{VO(sal-dach).DMF\}-]_n$ ) and 85 ( $[-S_2\{VO(sal-dach).DMF\}-]_n$ ) but gave nearly similar percent conversion of about 98%. The only difference in two catalysts are, reaction reaches to the steady state within 4 h in case of  $[-S_2\{VO(sal-dach).DMF\}-]_n$  while  $[-CH_2\{VO(sal-dach).DMF\}-]_n$  takes about 6 h. In terms of the selectivity of cyclohexeneoxide,  $[-S_2\{VO(sal-dach).DMF\}-]_n$  is more selective than  $[-CH_2\{VO(sal-dach).DMF\}-]_n$  (62% versus 45%). Other obtained products are in poor yield and their orders of selectivity differ in both catalysts. The percent conversion and selectivity of different products are represented as bar diagram in Fig. 4.

### 3.4.3. Oxidation of trans-stilbene

Both the complexes were also tested for the oxidation of *trans*-stilbene where stilbeneoxide, benzaldehyde and 1,2-

Table 5  
Effect of oxidants on the oxidation of cyclohexene and product selectivity<sup>a</sup>

Substrate:TBHP ratio	Conversion (%)	Product selectivity (%)				Others
						
1:0.5	51	58	11	20	6	5
1:1	84	52	15	24	6	3
1:2	98	45	8	26	13	8
1:3	94	42	20	14	12	12

<sup>a</sup> Reaction conditions: cyclohexene (0.82 g, 10 mmol), catalyst (15 mg, equivalent to 0.032 mmol of repeating unit), temperature (75 °C) and acetonitrile (20 ml).

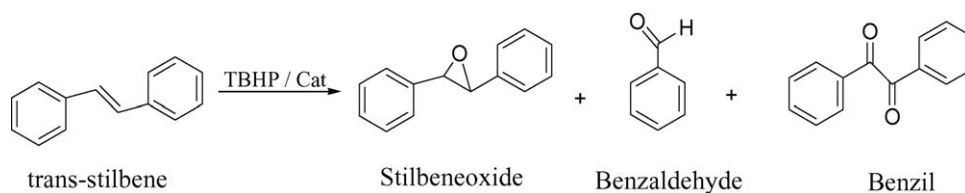
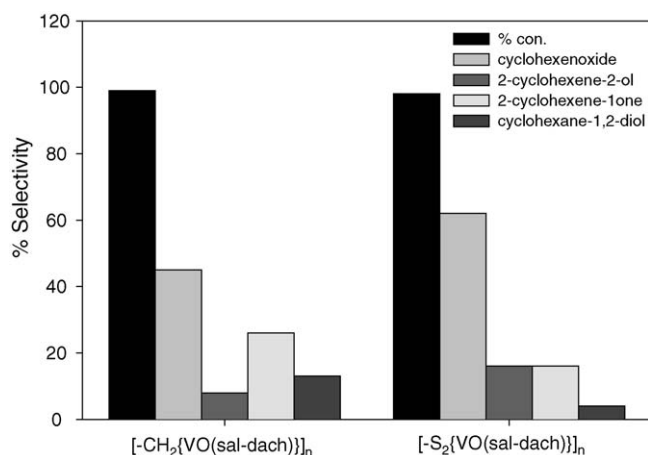
Scheme 7. Various oxidation products of *trans*-stilbene.

Fig. 4. Bar diagram showing conversion of cyclohexene and selectivity of various products.

diphenylethanedione (benzil) were obtained as major oxidation products as shown in Scheme 7.

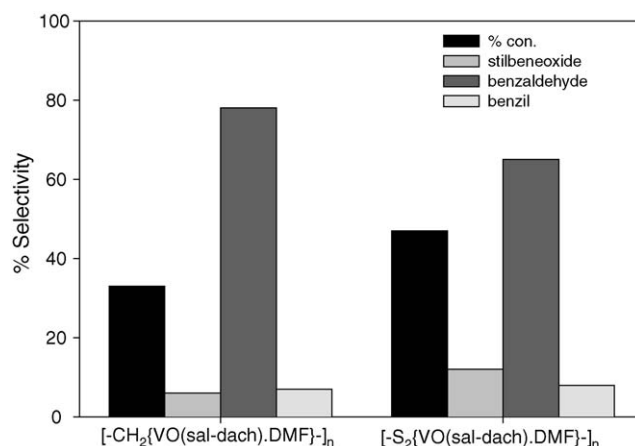
All reactions were carried out in 20 ml of acetonitrile at 75 °C using TBHP as oxidant. Complex  $[-\text{CH}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}]_n$  (15 mg) was used as a representative catalyst and amount of TBHP was varied for the fix amount of *trans*-stilbene. Results presented in Table 6 shows that amount of oxidant plays an important role in that increasing the amount of TBHP from 2.5 to 20 mmol (i.e. *trans*-stilbene to TBHP ratio from 1:0.5 to 1:4) increases the percent conversion of *trans*-stilbene considerably from 8 to 33% in 6 h of reaction time. However, the selectivity of epoxide goes down from 20 to 6%.

Catalytic activity of  $[-\text{S}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}]_n$  was also tested considering TBHP to *trans*-stilbene ratio of 1:4 under above reaction condition. The percentage conversion of both the catalysts along with the selectivity of oxidation products are presented as bar diagrams in Fig. 5. With the conversion of 33%, the selectivity of oxidation products catalysed by  $[-\text{CH}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}]_n$  follows the order:

Table 6  
Effect of oxidant on the conversion of *trans*-stilbene in 6 h of reaction time<sup>a</sup>

Substrate:TBHP ratio	Conversion (%)	Selectivity (%)			
		Stilbeneoxide	Benzaldehyde	Benzil	Others
1:0.5	8	20	50	17	13
1:1	16	14	55	18	13
1:2	23	8	60	22	10
1:3	27	9	65	20	6
1:4	33	6	78	7	9

<sup>a</sup> Reaction conditions: *trans*-stilbene (0.91 g, 5 mmol), catalyst (15 mg, equivalent to 0.032 mmol of repeating unit), temperature (75 °C) and acetonitrile (20 ml).

Fig. 5. Bar diagram showing total conversion of *trans*-stilbene and selectivity of various products.

benzaldehyde (78%) > unidentified (9%) > benzil (7%) > *trans*-stilbeneoxide (6%). Catalyst  $[-\text{S}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}]_n$  exhibits 47% conversion and follows different trend of order: benzaldehyde (65%) > unidentified (13%) > *trans*-stilbeneoxide (12%) > benzil (8%). Unidentified products are further oxidation products of benzil as indicated by GCMS, but these are only in trace amounts and in the frame of the present study, no efforts were undertaken to separate them. A considerably lower formation of *trans*-stilbeneoxide is probably due to further reaction of *trans*-stilbeneoxide with TBHP to give benzil which in turn converted into benzaldehyde due to hydrolysis. The TOF values found for this catalytic reaction are 8.6 ( $[-\text{CH}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}]_n$ ) and 13.5 ( $[-\text{S}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}]_n$ ).

#### 3.4.4. Possible reaction pathway of the catalysts, their stability, heterogeneity and reusability

In order to establish possible reaction pathway, a methanolic solution of the monomeric complex  $[\text{VO}(\text{sal-dach})]$  (prepared by reacting  $\text{N,N}'$ -bis(salicylidene)cyclohexane-1,2-diamine) with

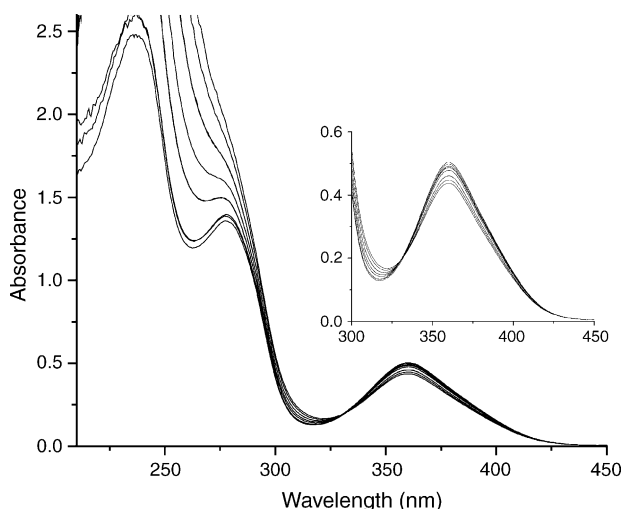


Fig. 6. Titration of [VO(sal-dach)] with TBHP; the spectra were recorded after the successive addition of one drop portions of TBHP to 10 ml of ca.  $10^{-4}$  M solution of [VO(sal-dach)] in methanol.

[VO(acac)<sub>2</sub>] in methanol) was treated with TBHP and the reaction was monitored by electronic absorption spectroscopy. As shown in Fig. 6, the intensity of the 360 nm band decreases on drop wise addition of TBHP to ca.  $10^{-4}$  M methanolic solution of [VO(sal-dach)]. At the same time the band at 278 nm marginally shifts towards higher wavelength along with broadening and increasing in band maximum while the band at 236 nm only gains intensity. The weak broad band appearing at 568 nm due to d–d transition (not shown here), slowly disappears. The observed result is similar to that noted earlier for [VO(sal-ophen)] ( $H_2$ sal-ophen = ligand derived from salicylaldehyde and *o*-phenylenediamine) and is due to the generation of oxomonoperoxovanadium(V) species [24]. The peroxo complex, thus, transfer one of its oxygen atoms to the substrates. However, no change in the electronic spectral patterns of the regenerated polymeric complexes after first cycle suggest that they convert back to oxovanadium(IV) species after transferring oxygen atom to the substrate and are reusable.

In order to check leaching of the metal ion from polymeric complexes into the reaction medium, a blank reaction was carried out using catalyst (15 mg), 70% TBHP (2.56 g, 20 mmol), acetonitrile (20 ml) and temperature 75 °C, and the reaction was stirred under the similar reaction conditions for 6 h. The absence of vanadium (estimated using inductive coupled plasma mass spectrometry (ICPMS)) in the filtrate suggests no leaching during catalytic reaction. The filtrate collected after first cycle of styrene oxidation was placed in a reaction flask and the reaction was continued for next 3 h after adding fresh oxidant. The gas chromatograph analysis showed no further increase in the oxidation of styrene. This observation suggests that the reaction is heterogeneous in nature. As observed earlier both the catalysts can safely be used at 75 °C without decomposition.

#### 4. Conclusions

We have prepared polymeric oxovanadium(IV) complexes with the polymeric Schiff bases derived from

5,5'-methylenebis(salicylaldehyde) or 5,5'-dithiobis(salicylaldehyde) and 1,2-diaminocyclohexane. Each monomer unit behaves as dibasic tetradentate ONNO donor ligand. The catalytic oxidation of styrene is 76–85% where major oxidation products follows the order: benzaldehyde > styreneoxide > 1-phenylethane-1,2-diol > benzoic acid. The formation of styreneoxide is relatively low due to its further conversion into other oxidation products. The catalytic potentials of these complexes towards the oxidation of cyclohexene are high (98%) but the selectivity of cyclohexeneoxide formation is 62% (with  $[-CH_2\{VO(sal-dach)\cdot DMF\}_n]$ ) or 45% (with  $[-S_2\{VO(sal-dach)\cdot DMF\}_n]$ ). The conversion of *trans*-stilbene was 33% (with **1**) or 47% (with **2**) where 6–12% selectivity of *trans*-stilbeneoxide and 65–78% of benzaldehyde were obtained.

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