

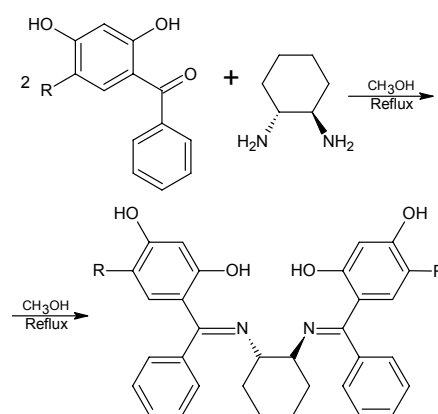
SYNTHESIS, CHARACTERIZATION AND CATALYTIC STUDIES OF SOME OXOVANADIUM(IV) COMPLEXES OF TETRADENTATE SCHIFF BASE LIGANDS

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Oxovanadium(IV) complexes of the type $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ and $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ [where $\text{L}^1 = N,N'$ -(\pm)-*trans*-bis(2,4-dihydroxybenzophenone)-1,2-cyclohexanediamine and $\text{L}^2 = N,N'$ -(\pm)-*trans*-bis(2,4-dihydroxy-5-nitrobenzophenone)-1,2-cyclohexanediamine respectively] have synthesized and characterized by elemental analyses, magnetic susceptibility measurements, electronic, IR, ESR spectra and X-ray diffraction studies. The thermal behavior of ligands and their complexes have been studied using TG-DTG technique. The IR spectral data reveal that the ligands behave as dibasic tetradentate nature coordinating through azomethine nitrogen and phenolic oxygen atoms. The magnetic susceptibility measurements, electronic and ESR spectral data of complexes indicate a mononuclear square pyramidal geometry around VO(IV) ion. The solid state electrical conductivity of these complexes was measured by two probe method and compounds showed semiconducting behavior as their conductivity increases with increase in temperature. Both the complexes $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ and $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ were also tested for their catalytic epoxidation of styrene utilizing hydrogen peroxide as an oxidant.



INTRODUCTION

Schiff bases and their vanadium complexes have expanded enormously and include a vast area of organometallic compounds and various aspects of bioinorganic chemistry. Salen or salen type ligands bind vanadium ions through two nitrogens and two oxygens. This tetradentate binding resembles the porphyrin framework in the heme base deoxidative enzyme.¹⁻⁴ Salen derivatives are more easily synthesized than porphyrins and their structures are more easily manipulated to create an asymmetric environment around the active vanadium ion. Similarly, salen compounds are very important molecules and have attracted main attention in both academic and applied research.

The industrial importance of vanadium compounds in different oxidation states is multifaceted.⁵⁻⁹ Vanadium complexes are considered as multifunctional molecules because of their interesting catalytic,⁹⁻¹³ spectroscopic,¹⁴ biological,^{15,16} mechanochemical¹⁷ and many other activities and characteristics.¹⁸⁻²³ One of the most widely studied characteristics of these complexes is their ability to catalyze the epoxidation reaction of olefins. The epoxidation products are among the most widely used and important intermediates in the laboratory syntheses and chemical industries. The vanadium complexes of Schiff bases are considered to be the most important stereochemical models in transition metal coordination chemistry due to their preparative accessibility and structural variety.

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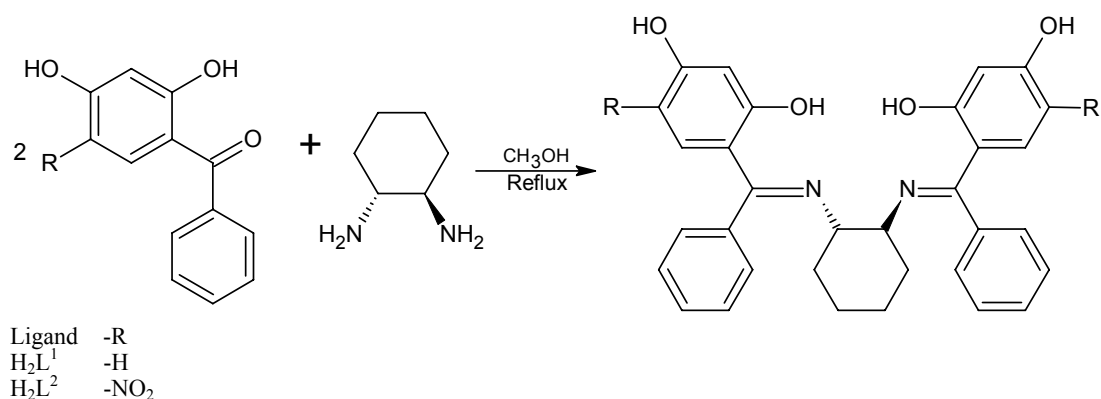


Fig. 1 – Structure of Schiff bases.

In view of importance associated with vanadium compounds, we report here the synthesis and characterization of vanadium complexes with tetradentate Schiff base ligands derived from the condensation of 2,4-dihydroxybenzophenone or 2,4-dihydroxy-5-nitrobenzophenone with (±)-*trans*-1,2-cyclohexanediamine (Fig. 1) and their catalytic activity.

RESULTS AND DISCUSSION

Vanadium complexes were found to be air stable at room temperature and insoluble in common solvents such as EtOH, CHCl₃, MeOH and water but found soluble in DMF and DMSO respectively. The elemental analyses of ligands and their vanadium complexes are in good consistent with theoretical expectations. Elemental analyses data suggest 1:1 metal-ligand stoichiometry for both the complexes (Table 1). The molar conductance of both the complexes was measured in DMSO using 10⁻³M solutions at room temperature and complexes show almost negligible conductivity indicating their non-electrolyte nature.

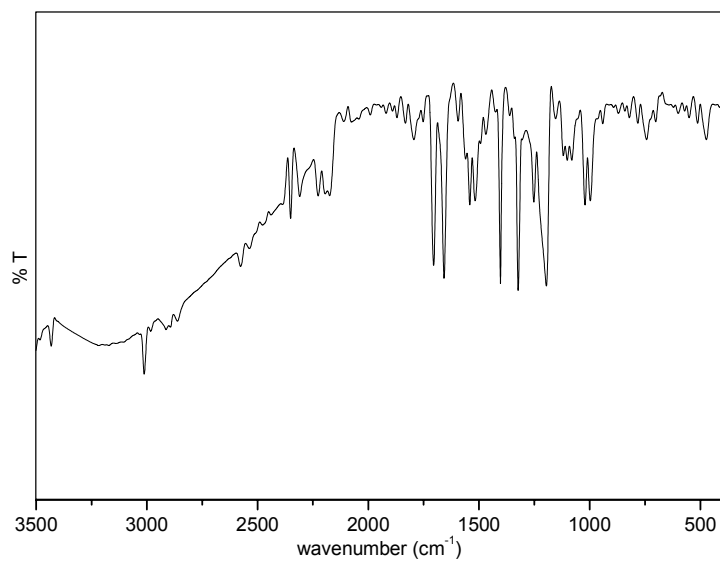
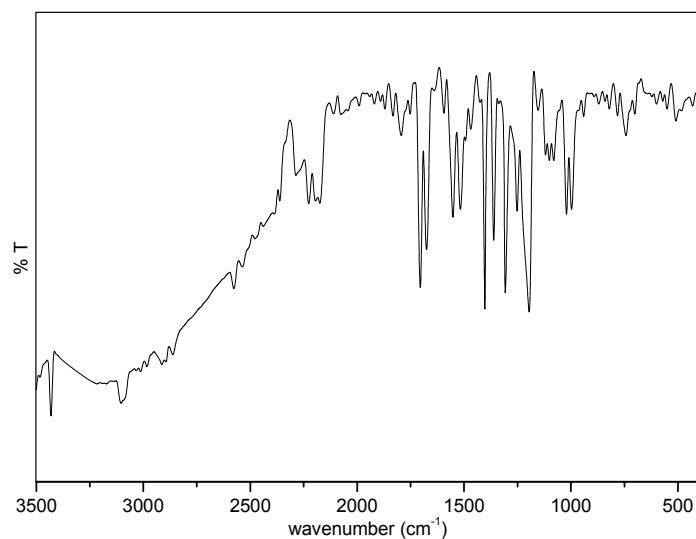
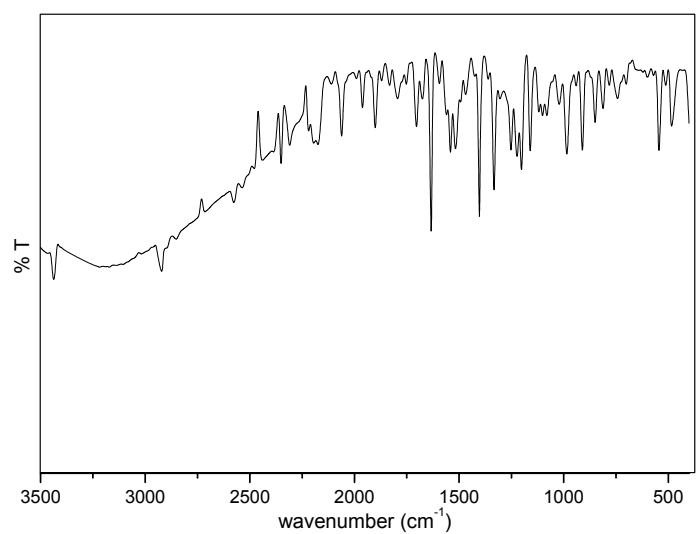
The IR spectra of ligands show a broad band in the 3012-3097 cm⁻¹ range, suggests the presence of extensive hydrogen bonding between phenolic

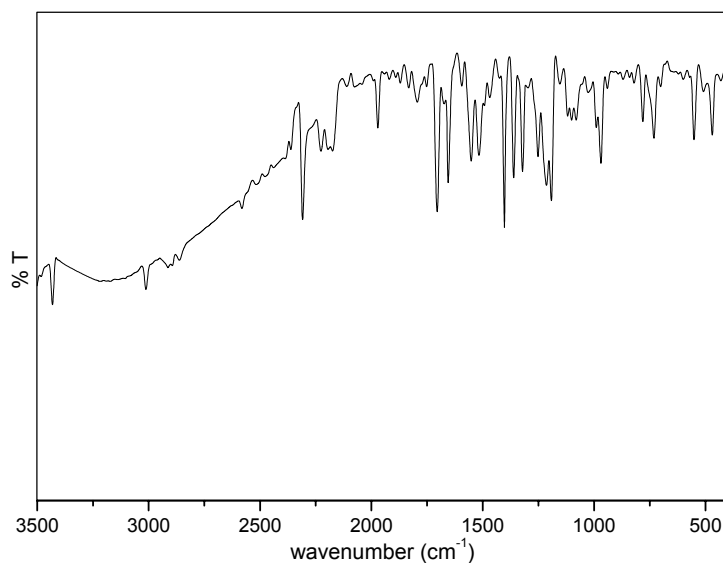
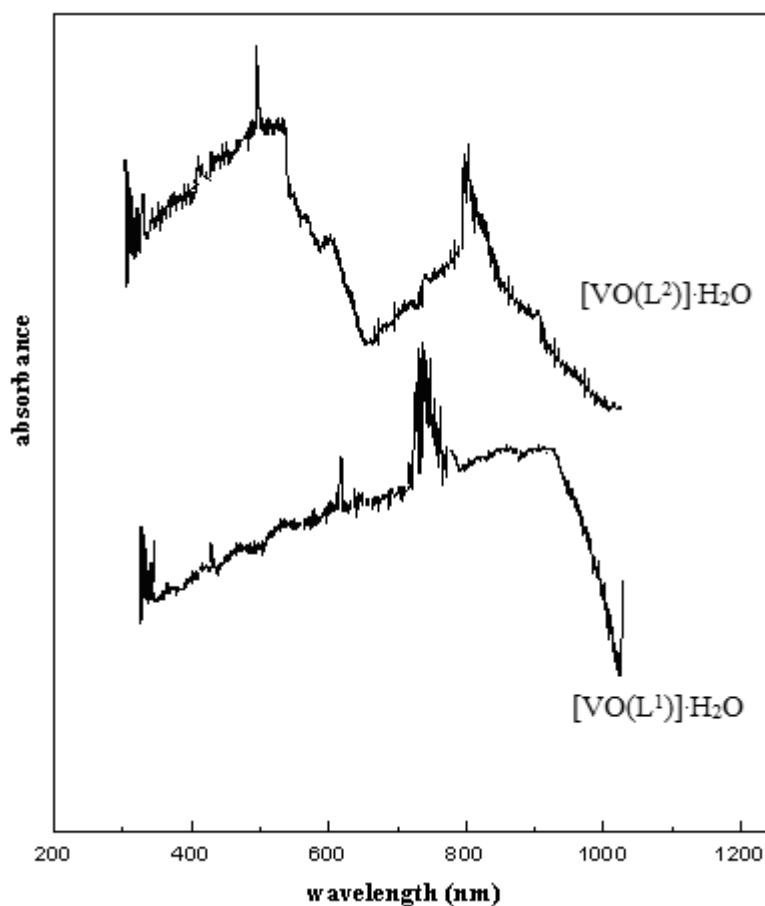
hydrogen and azomethine nitrogen atoms. Absence of these bands in spectra of complexes indicates the breaking of hydrogen bonding and coordination of phenolic oxygen to the vanadium ion after deprotonation (Figs. 2-5). This is further supported by the upward shift of the phenolic ν(C-O) mode to the extent 8-18 cm⁻¹ from ~1270 cm⁻¹. The strong band located at ~1655 cm⁻¹ corresponding to the C=N group in the spectra of ligands undergoes a modest decrease after complexation, inferring involvement of the azomethine nitrogen in coordination to the vanadium centre.²⁴ Coordination of azomethine nitrogen and phenolic oxygen are affirmed with presence of new bands in the range 517-552 cm⁻¹ and 459-472 cm⁻¹, assignable to ν(V-O) and ν(V-N) modes respectively.²⁵ The broad absorption band located in the 3417-3428 cm⁻¹ range represents a proof for water presence in the both complexes composition. In the spectra of complexes an additional band near ~980 cm⁻¹ is observed, suggests the presence of V=O bond in complexes.²⁶ Therefore, from the IR spectra, it is concluded that both the ligands behaves as dibasic tetradentate in nature, coordinating through azomethine nitrogen and deprotonated phenolic oxygen to the vanadium ion.

Table 1

Analytical and physical data for the ligands and their vanadium complexes

Compounds	Formula weight	Colour	Elemental analyses % found (calcd)				Electrical conductivity Ω ⁻¹ cm ⁻¹ at 373K
			C	H	N	V	
H ₂ L ¹	506.59	Yellow	74.93 (75.87)	6.36 (5.97)	5.01 (5.53)	--	--
H ₂ L ²	596.58	Yellow	65.72 (64.42)	5.13 (4.73)	10.28 (9.39)	--	--
VO(L ¹)]H ₂ O	589.53	Green	64.02 (65.19)	5.19 (5.13)	4.31 (4.75)	9.11 (8.64)	1.05×10 ⁻⁸
[VO(L ²)]H ₂ O	679.52	Gray	56.68 (56.56)	4.81 (4.15)	7.72 (8.24)	8.02 (7.50)	2.54×10 ⁻⁹

Fig. 2 – IR spectra of H₂L¹ ligand.Fig. 3 – IR spectra of H₂L² ligand.Fig. 4 – IR spectra of [VO(L¹)]H₂O complex.

Fig. 5 – IR spectra of $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ complex.Fig. 6 – Electronic spectra of $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ and $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ complexes.

The electronic spectra of $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ and $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ complexes show three bands, in the 13200-13569, 16432-16746 and 21632-22327 cm^{-1} range (Fig. 6). These bands are assigned to the ${}^2\text{B}_2 \rightarrow {}^2\text{E}$, ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ and ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$, transitions,

respectively towards square pyramidal geometry around vanadium ion, in which the ligand lie in the basal plane and oxygen at the apical position.²⁷ One more band is observed in the region 28747-29412 cm^{-1} which may be due to the ligand to metal

charge transfer transition. The measured values of magnetic moment for the VO(IV) complexes are 1.81 and 1.73 B.M. which correspond to one unpaired electron.

The X-band ESR spectrum of $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ complex was recorded in DMSO at 77K (Fig. 7) and data presented in Table 2. In solution at 77K (frozen state), the spectrum shows two type of resonance components, one set due to the parallel features and the other set due to perpendicular features which indicates axially symmetric anisotropy with well resolved sixteen line hyperfine splitting, characteristic of interaction between electron and vanadium nuclear spin. The various parameters, calculated from the spectra and values obtained are in accordance with that of a complex molecule which exists in square pyramidal geometry.^{28, 29} The observed order ($A_{\parallel} > A_{\perp}$ and $g_{\perp} > g_{\parallel}$) indicates that the

unpaired electron is localized in d_{xy} orbital. The smaller g_{\parallel} indicates increase in the delocalization of unpaired electrons away from the metal nucleus which has been interpreted in terms of increased covalency in the metal ligand bond.

The X-ray diffraction study of $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ and $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ complexes was carried out using $\text{CuK}\alpha$ radiation with $\lambda = 1.5418\text{\AA}$. The XRD patterns of both the complexes were recorded at 2θ value between 3° and 45° and are shown in Figs. 8 & 9. The diffraction patterns reveal the crystalline nature of the complexes. X-ray crystal system has been worked out by trial and error method for finding the best fit between observed and calculated values. The unit cell parameters for the complexes were determined and results of the analysis of both the complexes are given in Tables 3 & 4.

Table 2

ESR spectral data of $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ complex in DMSO solution at 77K

Complex	A_{\parallel}	A_{\perp}	A_{iso}	g_{\parallel}	g_{\perp}	g_{iso}
$[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$	172	76	108	1.90	1.98	1.95

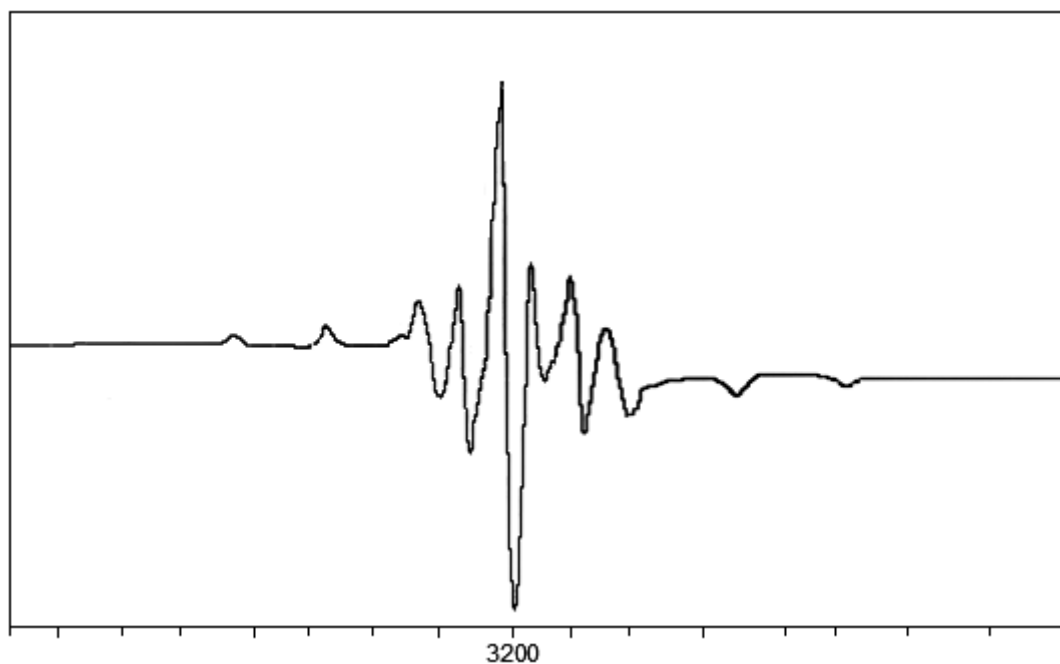


Fig. 7 – ESR spectra of $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ complex at 77K in DMSO.

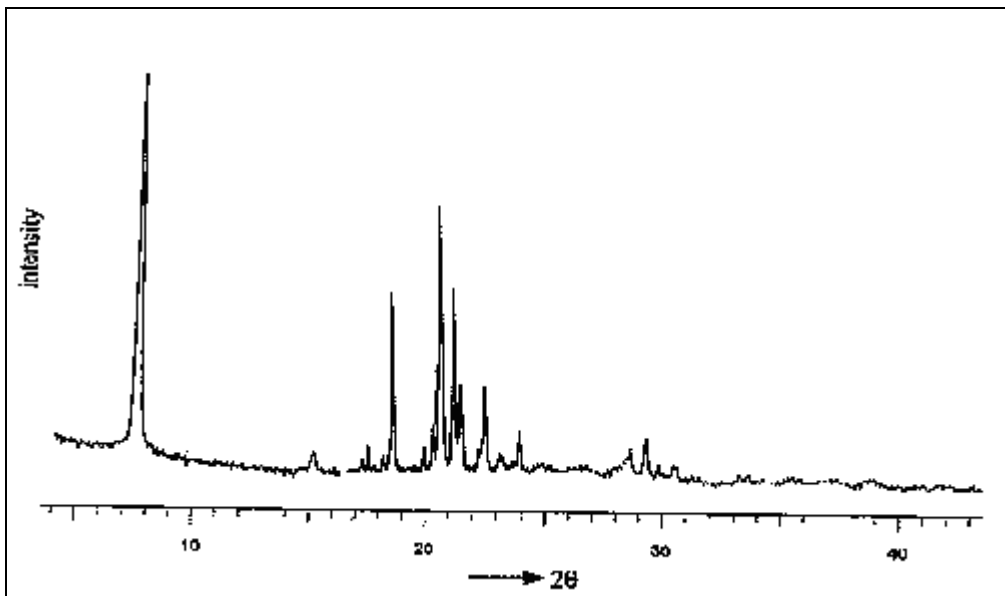
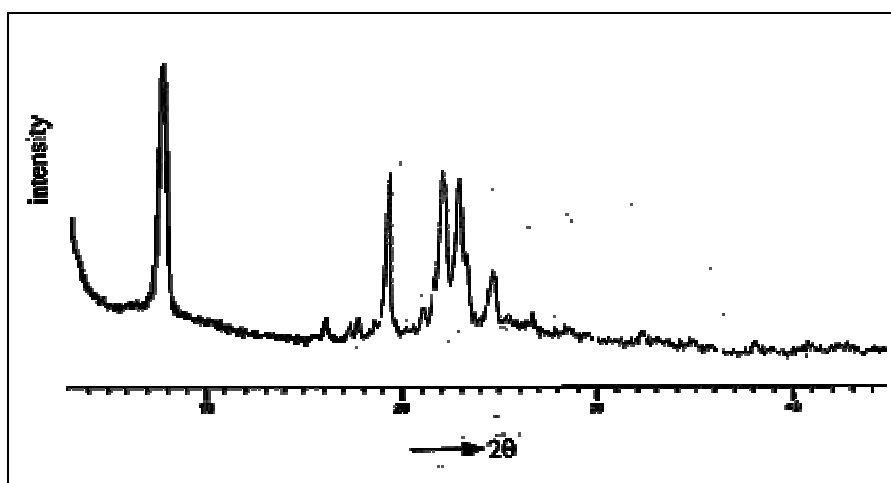
Fig. 8 – The pattern of X-ray diffraction for $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ complex.Fig. 9 – The pattern of X-ray diffraction for $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ complex.

Table 3

The parameters of units cell, and observed & calculated X-ray diffraction data of $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$

System: monoclinic $a = 14.5324 \text{ \AA}$, $b = 10.6713 \text{ \AA}$, $c = 12.4602 \text{ \AA}$ $\beta = 126.59^\circ$, $V = 1551.42 \text{ \AA}^3$						
Peak no.	d(Obs.)	d(Cal.)	2θ (Obs.)	2θ (Cal.)	$\Delta 2\theta$	(h k l)
1	11.8333	11.8487	7.46	7.46	0.00	-1 0 1
2	5.8212	5.8339	15.21	15.17	0.04	2 0 0
3	4.9978	5.0020	17.73	17.72	0.01	0 0 2
4	4.8509	4.8523	18.27	18.27	0.00	1 2 0
5	4.3243	4.3205	20.52	20.54	-0.02	-3 1 2
6	4.2869	4.2938	20.70	20.67	0.03	-3 1 1
7	4.1631	4.1515	21.33	21.39	-0.06	-2 0 3
8	4.0986	4.0892	21.67	21.72	-0.05	2 0 1
9	3.8895	3.8892	22.85	22.85	-0.00	3 0 0
10	3.6377	3.6415	24.45	24.42	0.03	-1 1 3
11	3.1201	3.1179	28.59	28.61	-0.02	1 2 2
12	3.0461	3.0494	29.30	29.26	0.04	-2 0 4

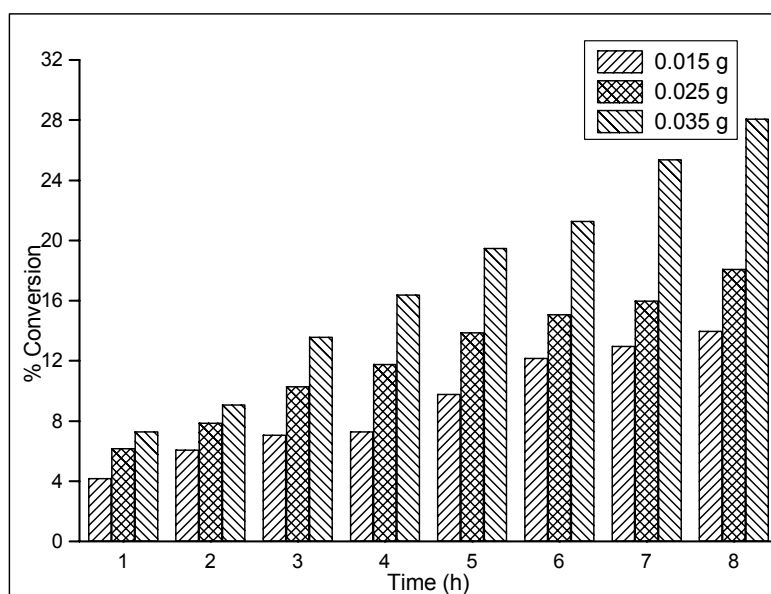
Table 4

The parameters of units cell, and observed & calculated X-ray diffraction data of $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ complex

System: monoclinic			$a=11.9366 \text{ \AA}$, $b=5.3938 \text{ \AA}$, $c=33.7662 \text{ \AA}$			$\beta=101.37^\circ$,	$V=2131.30 \text{ \AA}^3$
Peak no.	d(Obs.)	d(Cal.)	2θ (Obs.)	2θ (Cal.)	$\Delta 2\theta$	(h k l)	
1	11.8112	11.7877	7.48	7.49	-0.01	-1 0 1	
2	5.8430	5.8511	15.15	15.13	0.02	2 0 0	
3	5.3212	5.3236	16.65	16.64	0.01	0 1 1	
4	5.1252	5.1284	17.29	17.28	0.01	0 1 2	
5	4.8727	4.8887	18.19	18.13	0.06	-2 0 5	
6	4.4820	4.4791	19.79	19.81	-0.02	-2 0 6	
7	4.3915	4.3872	20.20	20.22	-0.02	2 0 4	
8	4.3307	4.3461	20.49	20.42	0.07	1 1 3	
9	4.1902	4.1817	21.19	21.23	-0.04	0 1 5	
10	4.1112	4.1119	21.60	21.59	0.01	1 0 7	
11	3.9121	3.9018	22.71	22.77	-0.06	-2 1 3	

Epoxidation of styrene was investigated using the $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ and $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ complexes as catalyst and H_2O_2 as an oxidant. The reactions were performed under previously optimized conditions, specially styrene/ H_2O_2 in CH_3CN . Three different amounts (viz. 0.015g, 0.025g and 0.035g) of catalyst under same condition in which 0.035g catalyst show maximum activity, as shown in Figs. 10 and 11. The conversion of styrene for $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ and $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ was found to be 28.1 and 35.2% respectively, shows extremely low product selectivity of styrene oxide (> 3%) in optimized condition within 8 h. But the product selectivity of benzaldehyde is greater (< 65%) this may due to the strong oxidizing nature of H_2O_2 , the

styrene oxide formed in the first step by epoxidation is mainly converted into benzaldehyde via hydroperoxystyrene as an intermediate. Further this may be by direct oxidative cleavage of the styrene side chain double bond via a radical mechanism.³⁰⁻³² The catalyst was reused under the same conditions, using same amounts of styrene and H_2O_2 . The proposed mechanism for epoxidation of styrene by H_2O_2 with $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ and $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ complexes is shown Fig. 12. $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ complex shows higher catalytic activity as compared to $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ complex which may due to the presence of electron withdrawing group on the ligand (H_2L^2).

Fig. 10 – Catalytic activity of $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ complex.

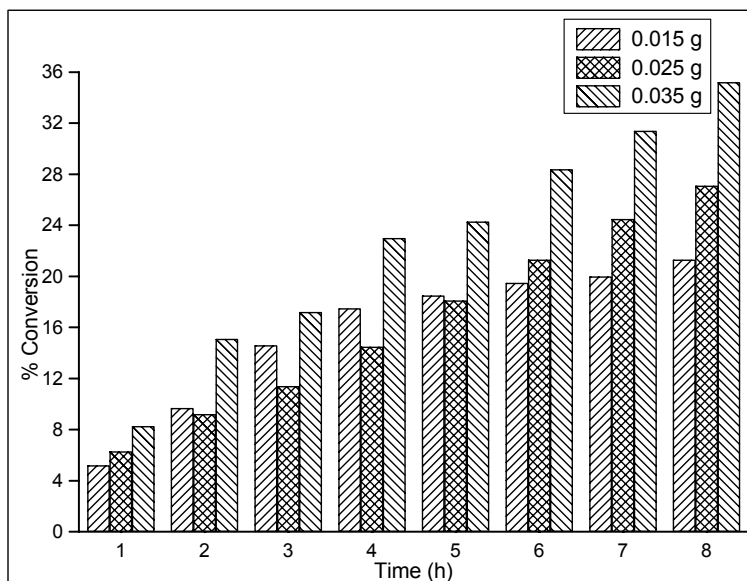


Fig. 11 – Catalytic activity of [VO(L²)]H₂O complex.

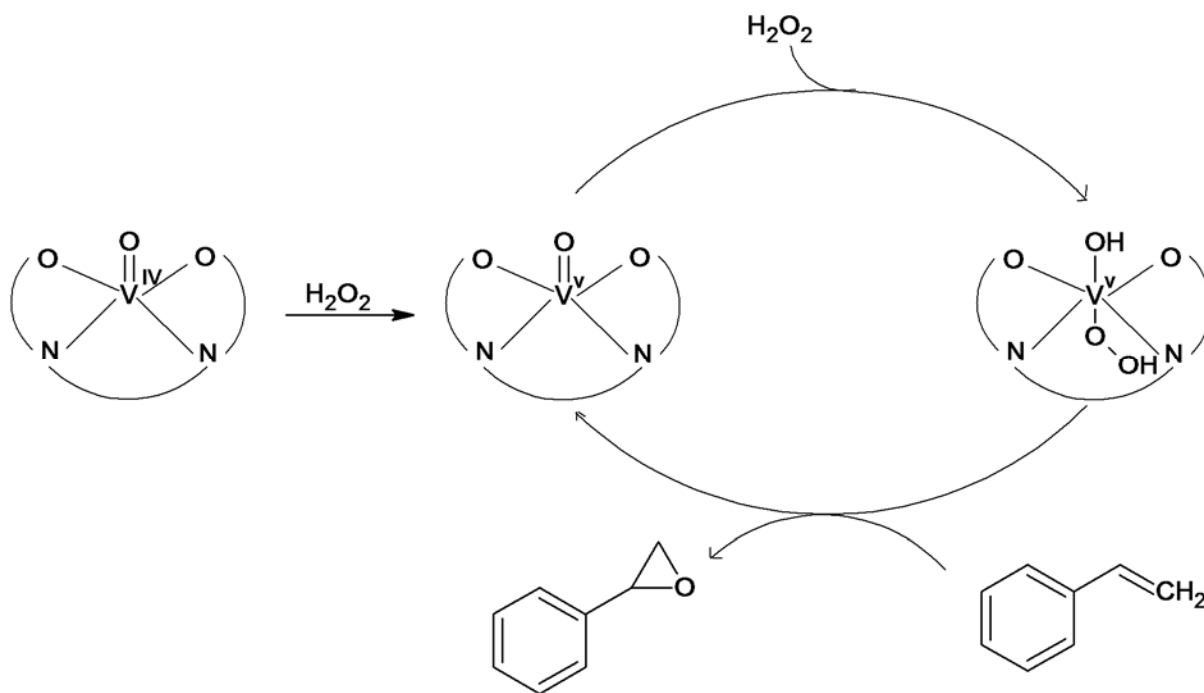


Fig. 12 – The proposed mechanism of the epoxidation of styrene by the $[VO(L^1)]H_2O$ and $[VO(L^2)]H_2O$ complexes in the presence of H_2O_2 .

The electrical conductivity (σ) of both the complexes was measured in the range of temperature 298-393K. The values of electrical conductivities (σ) are listed in Table 1. In both cases, conductivity increases with increase in temperature, indicating that these complexes lie in the range of semiconductors.³³ A plot of $\log \sigma$ vs $1/T$ of these complexes under investigation obeys the equation: $\sigma = \sigma_0 \exp(-E_a/kT)$.

The electrical conductivity of the complexes $[VO(L^1)]H_2O$ and $[VO(L^2)]H_2O$ are found to be 1.05×10^{-8} and $2.54 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$ at 373K respectively. In $[VO(L^2)]H_2O$ complex, the presence of $-NO_2$ group decrease the electron density on the conjugated ligand which may decrease its electrical conductivity as compared to $[VO(L^1)]H_2O$ complex.

The thermal behavior of both complexes was studied by TG/DTG analysis. The TG curves of ligands and their complexes have been shown in Figs. 13-16. Both ligands are decomposed in one step while $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ and $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ complexes decomposed in three steps in the temperature range 80-790°C. The first decomposition step with an estimated mass loss of 3.19% (calcd. 3.05%) and 3.01% (calcd. 2.64%) within the temperature range 83-138°C and 80-142°C for $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ and $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ complexes respectively, may be attributed to the

loss of hydrated water molecule.^{34,35} The second decomposition step is found within the temperature range 138-370°C with an estimated mass loss of 32.10% (calcd. 31.88%) and 40.89% (calcd. 41.20%), for $[\text{VO}(\text{L}^1)]\text{H}_2\text{O}$ and $[\text{VO}(\text{L}^2)]\text{H}_2\text{O}$ which are reasonably accounted by the partial removal of organic moiety from the complex. The remaining organic moiety from the complexes is removed in the temp range 345-790°C with estimated mass loss 51.46% (50.88%) and 44.23% (43.85%) respectively.

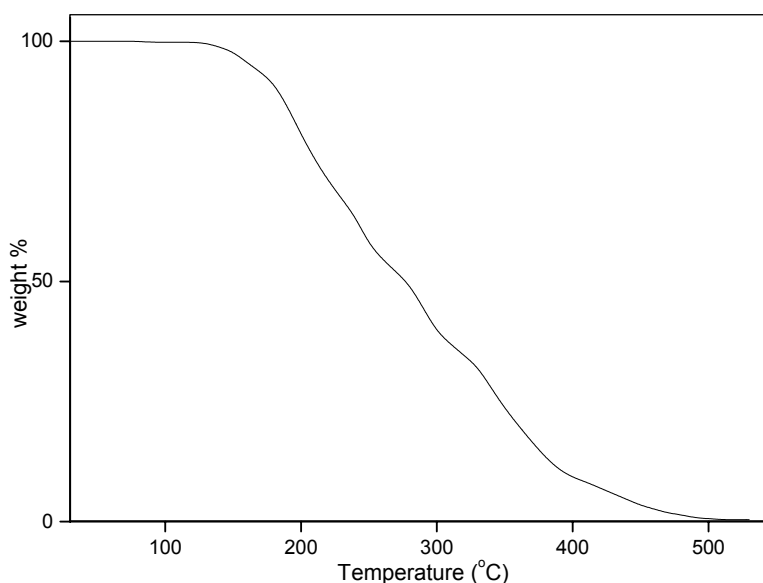


Fig. 13 – TG curve of H_2L^1 ligand.

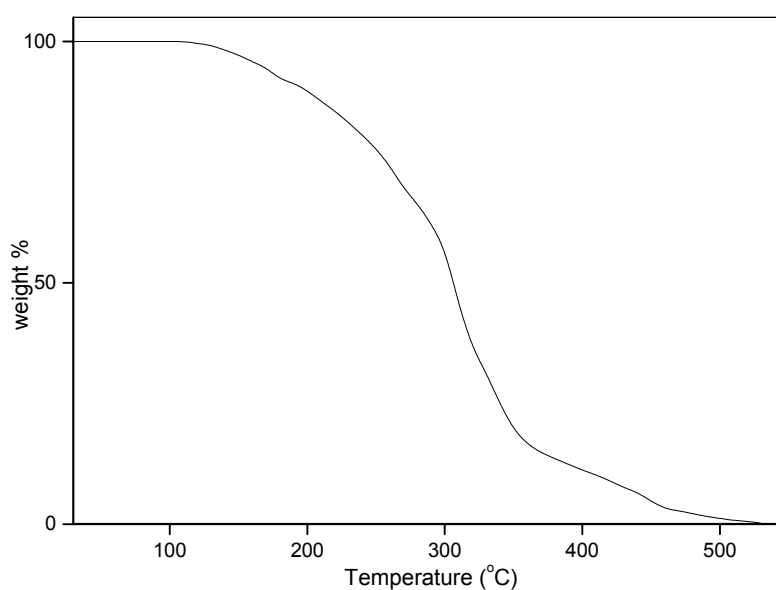
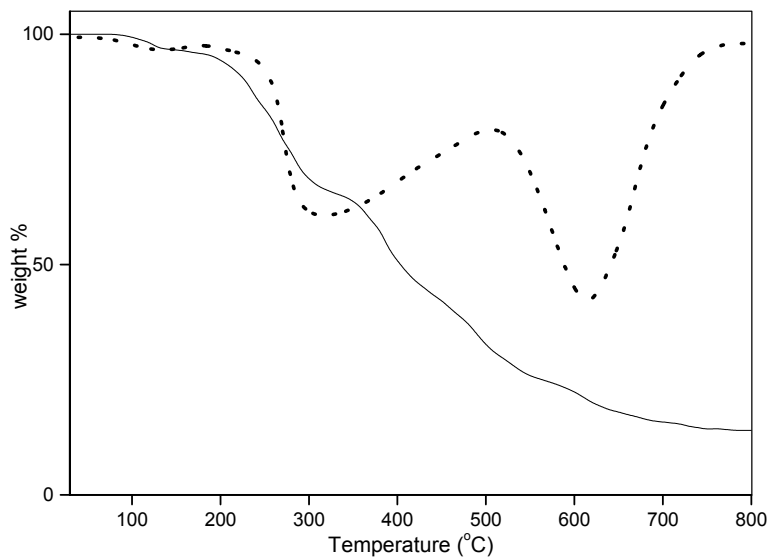
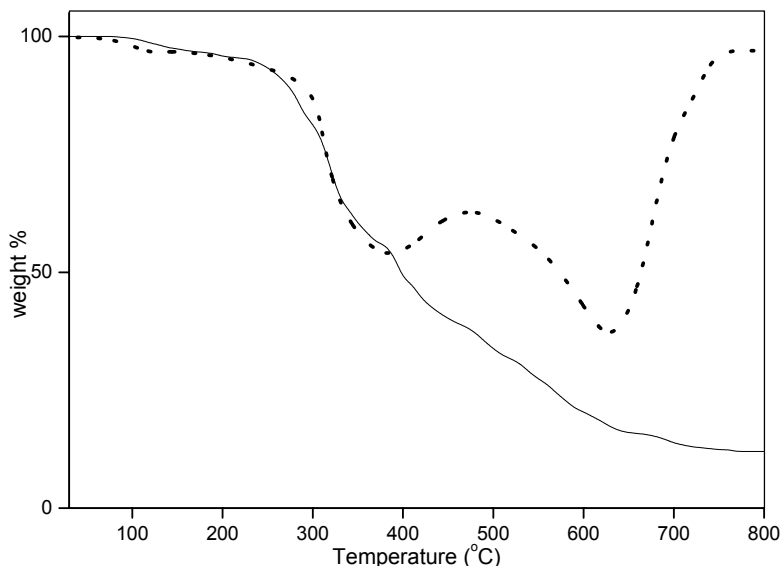


Fig. 14 – TG curve of H_2L^2 ligand.

Fig. 15 – TG/DTG curves of $[\text{VO}(\text{L}^1)]\cdot\text{H}_2\text{O}$ complex.Fig. 16 – TG/DTG curves of $[\text{VO}(\text{L}^2)]\cdot\text{H}_2\text{O}$ complex.

EXPERIMENTAL

Vanadyl sulphate ($\text{VOSO}_4\cdot 5\text{H}_2\text{O}$) was obtained from Qualigens Chemicals. The other chemicals used were of analytical grade and used as received. *trans*-1,2-diaminocyclohexane was obtained from Across Organics.

Synthesis of Schiff bases (H_2L^1) and (H_2L^2)

Both the Schiff bases (H_2L^1) and (H_2L^2) were prepared by a similar method: A solution of (\pm)-*trans*-1,2-diaminocyclohexane (10 mmol) in 10 ml of methanol was added drop wise to a hot methanolic solution of respective ketones (2,4-dihydroxybenzophenone or 2,4-dihydroxy-5-nitrobenzophenone) (20 mmol in 40 ml) with continuous stirring and the reaction mixture was heated under reflux on a

water bath for 2h. After cooling to room temperature, the coloured precipitate separated was filtered off, washed with methanol, and finally dried over anhydrous calcium chloride. The purity of the synthesized compounds was checked by TLC. Yield 59-63%, m.p. (H_2L^1): 247°C and (H_2L^2): 203°C.

$^1\text{H-NMR}$, δ_{H} (ppm):

(H_2L^1): 16.94 (s, 2H, OH C₂), 10.02 (s, 2H, OH C₄), 7.49-6.34 (m, 16H, Ar-H), 4.02 (m, 2H, CH), 1.89-1.34 (m, 8H, CH₂CH₂).

(H_2L^2): 17.56 (s, 2H, OH C₂), 10.78 (s, 2H, OH C₄), 8.85-6.94 (m, 14H, Ar-H), 4.13 (m, 2H, CH), 1.93-1.12 (m, 8H, CH₂CH₂).

Synthesis of $[\text{VO}(\text{L}^1)]\cdot\text{H}_2\text{O}$ and $[\text{VO}(\text{L}^2)]\cdot\text{H}_2\text{O}$ complexes

Equimolar quantities (5 mmol) of vanadyl sulphate ($\text{VOSO}_4\cdot 5\text{H}_2\text{O}$) and the ligands were dissolved separately in

minimum quantity of hot methanol (10 cm³). Both solutions were filtered and mixed in hot conditions. The resulting mixture was refluxed for 4–6 h in a water bath and a coloured solution was concentrated (*ca* 50%) and kept at room temperature for overnight and solid product was obtained. This was filtered, washed with diethyl ether and dried over fused calcium chloride.

Epoxidation of styrene

The catalytic epoxidation of styrene with [VO(L¹)]H₂O and [VO(L²)]H₂O complexes was studied. The catalytic reactions were carried out in 250 ml reaction flask fitted with water condenser. A general procedure was applied for all reactions. In a typical reaction, styrene (1.04 g; 10 mmol) and 30% H₂O₂ (2.27 g; 20 mmol) were mixed in 10 ml MeCN and the reaction mixture was heated in an oil bath with continuous stirring at 80°C for 1–8 h. The catalyst (0.015g, 0.025g and 0.035g) to be tested was added in to the reaction mixture. The reaction was monitored at various time periods and checked by the gas chromatography.

Physical measurements

IR spectra were recorded as KBr pellets using a Shimadzu 8201 spectrophotometer. Carbon, hydrogen and nitrogen contents were determined on a Carlo Erba 1108 elemental analyzer. Vanadium was estimated by gravimetric analysis, as V₂O₅. ¹H-NMR spectra of Schiff base ligands were recorded on Bruker DRX-300 NMR spectrophotometer in *d*₆-DMSO with TMS as an internal standard. Magnetic measurements were carried out by the Gouy's method using Hg[Co(CSN)₄] as calibrant. Diamagnetic corrections were made using Pascal's constants. The solid-state reflectance spectra of the complexes were recorded in the range 200–1000 nm (as MgO) on a Beckman DK-2A spectrophotometer. The X-band ESR spectra of representative vanadium (IV) complex was recorded on Varian E-112 spectrophotometer at IIT, Mumbai using TCNE (tetracyanoethylene) as the g-marker. Thermogravimetric analysis were performed on a TGA-2 Perkin Elmer thermal analyzer in the temperature range 40–800°C with a heating rate of 10°C min⁻¹. Gas chromatograph was obtained using a Shimadzu 14B gas chromatography with SE-30 column and FID. The electrical conductivity was measured as a function of temperature (298–393 K) using zentech electrometer. The samples were arranged between two copper electrodes. Both samples were compressed to pellets under a pressure of 3 toncm⁻². X-ray diffraction patterns were obtained with a BRUKER AXS, D8 ADVANCE (GmbH, Karlsruhe, West Germany) equipped with θ/θ goniometer and a Lynx Eye detector.

CONCLUSIONS

In the presence study two mononuclear oxovanadium (IV) Schiff base complexes have been synthesized. The IR spectral data suggest tetradentate behaviour of Schiff bases ligands coordinating through the azomethine nitrogen and phenolic oxygen atoms to vanadium ion. The ESR study of [VO(L¹)]H₂O complex suggest square pyramidal geometry around vanadium ion. The

catalytic activity of [VO(L¹)]H₂O and [VO(L²)]H₂O complexes was evaluated using H₂O₂ as an oxidant for styrene epoxidation. Although complexes does not have very much structural differences, but based on the trends observed in the catalytic activities, we can suggest complex with electron withdrawing group show good activity by stabilizing the charge on the central metal ion over the extended ring systems. Thermal decomposition of complexes allowed establishing the number and nature of water molecules, the composition of complexes and also intervals of thermal stability.

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