

SYNTHESIS, CHARACTERIZATION, ELECTRICAL AND CATALYTIC STUDIES OF SOME COORDINATION COMPOUNDS DERIVED FROM UNSYMMETRICAL SCHIFF BASE LIGAND

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ABSTRACT. New unsymmetrical tetradentate Schiff base ligand derived from 5-chloro-2-hydroxyacetophenone, 2-hydroxy-5-methyl-3-nitro acetophenone and carbohydrazide and its complexes with VO(IV), Cr(III), Mn(III), Fe(III), MoO₂(VI), WO₂(VI), Zr(IV) and UO₂(VI) have been prepared. They were characterized by elemental analysis, IR and electronic spectra, magnetic susceptibility measurements and thermal analyses. The Schiff base ligand has also been characterised by ¹H-NMR spectroscopy. The thermal behaviour of metal complexes shows that the hydrated complexes lose water molecules of hydration in the first and then is immediately followed by decomposition of ligand molecule in the subsequent steps. The IR spectra suggest that ligand acts as dibasic tetradentate nature and coordination takes place through azomethine nitrogen and phenolate oxygen. The crystalline nature of the VO(IV) complex was conformed through the powder XRD analysis. The catalytic activity of the VO(IV) and Mn(III) complexes have been tested in the epoxidation reaction of styrene and conversion of styrene were 11.14-24.35% and 9.64-23.42%, respectively. The solid state electrical conductivity of ligand and its complexes were measured, which could obeyed the relation $\sigma = \sigma^0 \exp(E_a/KT)$ over the temperature range 313-413 K.

KEY WORDS: Schiff base, Metal complexes, TGA, Electrical conductivity, XRD, Oxidation of styrene

INTRODUCTION

The Schiff base ligands are an important class of organic ligands in coordination chemistry, which increase the chemical and biological aspects of the compounds because they act as antibacterial, antiviral, antifungal agents, as homogeneous or heterogeneous catalysts and display magnetic properties [1-4]. Schiff bases offer a versatile and flexible series of ligands due to easily preparation, diversity of structures, and providing the effects of steric interactions on coordination geometries and many applications [5]. Multidentate Schiff bases generate stable complexes with most metallic ions and especially with transition ones and have ability to stabilize them in various oxidation states. During the past decades, considerable attention has been paid to the chemistry of the metal complexes of with symmetrical Schiff base ligands containing N and other donors atoms. However, very little information is available for metal complexes of unsymmetrical Schiff base ligands [6-9]. Unsymmetrical Schiff base ligands derived from substituted carbohydrazide have played an important part in revealing the preferred coordination geometries of metal complexes and have valuable importance in the coordination chemistry due to their preparative accessibility and structural variability. The preparation of the metal complexes of unsymmetrical Schiff base of carbohydrazide and substituted hydroxyl acetophenone has come from the desire to form simple unsymmetrical complexes for their physicochemical characterization and structural elucidation. Here in we describe the synthesis and characterization of the unsymmetrical Schiff base ligand derived from 5-chloro-2-hydroxy acetophenone, 2-hydroxy-5-methyl-3-nitro acetophenone and carbohydrazide and its metal complexes involving tri-, tetra-, and hexavalent metal ions.

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EXPERIMENTAL

All the chemicals and solvents were of analytical grade and used as received without further purifications. Vanadyl sulfate pentahydrate, chromium chloride hexahydrate, anhydrous ferric chloride, dioxotungsten, tetrathiocyanate, zirconium acetate, uranyl nitrate hexahydrate and carbonylhydrazide were obtained from Rankem and SD fine chemicals (Mumbai, India). $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ was prepared by the oxidation of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ using Christensen's method [10] and bis(acetyl acetonato) dioxomolybdenum(VI) was synthesized according to literature method [11].

Preparation of Ligand (H_2L)

The ligand N -[1-(5-chloro-2-hydroxyphenyl)ethylidene]- N' -[1-(2-hydroxy-5-methyl-3-nitrophenyl)ethylidene] carbonylhydrazide was prepared by dropwise addition of equimolar amounts of 5-chloro-2-hydroxy acetophenone (2.4 g, 0.016 mol) to 2-hydroxy-5-methyl-3-nitroacetophenone (3.12 g, 0.016 mol) with stirring at room temperature. This resulting reaction mixture was reacted with a hot ethanol-DMF solution (60:40 v/v; 25 mL) of carbonylhydrazide (1.44 g, 0.016 mol) and mixture was refluxed on sand bath for about 9 h at 225 °C. The solvent was then partially evaporated in air and faint yellow coloured compound obtained was filtered and washed it with ethanol, petroleum ether and dried in vacuum over anhydrous CaCl_2 . The synthesized ligand was crystallized and conformed through its melting point 313 °C (yield: 72%) and its NMR analysis as follows: 12.68 (s, 1H, OH, phenolic), 14.30 (s, 1H, OH, phenolic), 10.19 (s, 1H, imino, NH), 10.23 (s, 1H, imino, NH), 2.12 (s, 3H, Ar- CH_3), 2.31 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 6.91-7.95 (m, 5H, aryl-H). The schematic representation of the synthesis of ligand H_2L is shown in Figure 1.

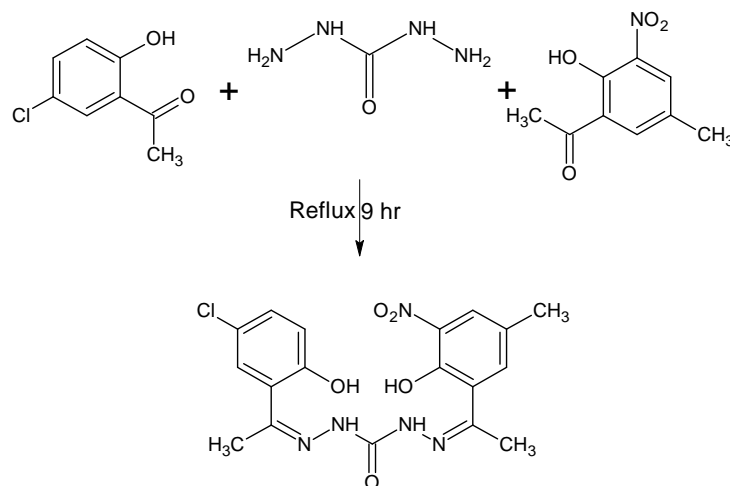


Figure 1. Scheme for the synthesis of ligand.

Synthesis of $\text{VO}(\text{IV})$, $\text{Cr}(\text{III})$, $\text{Mn}(\text{III})$, $\text{Fe}(\text{III})$, $\text{MoO}_2(\text{VI})$, $\text{Zr}(\text{IV})$ and $\text{UO}_2(\text{VI})$ complex

The complexes were prepared by refluxing equimolar solution of hot DMF (25 mL) of the organic ligand (0.016 mol) with a hot ethanol solution of the appropriate metal salt (0.016 mol) on sand bath for 6-7 h at 270-300 °C depending on the metal salt used. On cooling to room

temperature, complexes obtained were filtered, washed thoroughly with ethanol, DMF and petroleum ether to remove unreacted ligand and metal salt. Finally all complexes dried under vacuum at room temperature (yield: 65-70%).

Synthesis of $WO_2(VI)$ complex

Sodium tungstate dihydrate (1.2 g, 0.00363 mol) and ammonium thiocyanate (2.9 g, 0.038 mol) were dissolved in water (30 mL) at room temperature and 7.5 mL of 11 M HCl was added to it. The resulting yellow solution was cooled in an ice bath and to this a hot DMF solution (10 mL) of ligand (0.00363 mol) was added with continuous stirring. The precipitate so formed was filtered under suction, washed 3-4 times with water containing few drops of HCl and dried in vacuo.

Physical measurements

Elemental analysis carbon, hydrogen and nitrogen were obtained using Carlo Erba 1108 analyser in microanalytical laboratory, SAIF, CDRI, Lucknow. IR spectra were recorded on a Perkin-Elmer 597 spectrophotometer using KBr pellets at SAIF Punjab University, Chandigarh. 1H -NMR spectrum of ligand was obtained using a Bruker Avance-II 400 NMR spectrophotometer in DMSO solvent at SAIF Punjab University, Chandigarh. The reflectance spectra of the complexes were recorded on Varian SE UV-NIR spectrophotometer at SAIF, IIT, Chennai using MgO as reference. Magnetic susceptibility was measured at room temperature by Gouy's method using $Hg[Co(NCS)_4]$ as a calibrant and the diamagnetic corrections were made using Pascal's constants. The solid state electrical conductivity of compounds was measured by Zentech Electrometer in their compressed pellet form over 313-403 K temperature range. Thermogravimetric analysis of the complexes was carried out on Perkin Elmer TG-2 thermobalance in ambient air with a heating rate of 10 °C/min. Metal contents of the complexes were analysed gravimetrically after decomposing the complexes with a mixture of $HClO_4$, H_2SO_4 and HNO_3 and then igniting to metal oxide. The XRD measurement of the complexes was recorded on a Bruker AXS, D8-ADVANCE (GmbH, Karlsruhe, Germany) equipped with θ/θ goniometer and a Lynx Eye detector. Qualitative and quantitative analysis of products and reactant were measured on GC (Shimadzu 14B Gas chromatography equipped with SE-30 column and FID detector).

Oxidation of styrene

The oxidation of styrene was tested with VO(IV) and Mn(III) complexes as representative cases. The catalytic reactions were carried out in 250 mL reaction flask fitted with water condenser and a similar procedure was used in both the reactions. In a typical experiment, styrene (1.04 g, 10 mmol) and aqueous 30% H_2O_2 (2.27 g, 20 mmol) were mixed in 10 mL of MeCN and the reaction mixture was heated with continuous stirring 8 h in an oil bath at 80 °C. An appropriate amount of catalyst (0.020 g) was added to the reaction mixture and reaction was considered to begin. The reaction was monitored at various time periods and checked by the gas chromatography. The effect of catalyst concentration with styrene was also studied to obtain suitable reaction conditions for oxidation of styrene.

RESULTS AND DISCUSSION

The reaction of 5-chloro-2-hydroxyacetophenone and 2-hydroxy-5-methyl-3-nitro acetophenone with carbonylhydrazide in hot DMF-ethanol yields the Schiff base (H_2L). The reaction of H_2L in DMF and appropriate metal salts in ethanol gives the complexes. The analytical data of the

ligand and its complexes are given in Table 1. All the complexes are coloured solids, non-hygroscopic, air stable and insoluble in water and common organic solvents but sparingly soluble in DMSO. The elemental analysis shows 1:1 metal to ligand stoichiometry for all the complexes.

IR spectra

The IR spectra of the complexes are compared with those of the free ligand in order to determine the coordination sites that may be involved in chelation. The FT-IR spectrum of the free ligand shows characteristic band at 2998 cm^{-1} , assignable to $\nu(\text{OH})$ intramolecular hydrogen bonding between phenolic hydrogen and azomethine nitrogen atoms, which disappears in the spectra of metal complexes, indicating deprotonation of the OH group upon binding with metal ions. This is further supporting by shifting of the $\nu(\text{CO})$ (phenolic) band at 1263 cm^{-1} , to a higher frequency in complexes, suggesting the coordination of ligand through phenolic oxygen via deprotonation [12, 13]. The band at 1654 cm^{-1} (azomethine $\text{C}=\text{N}$) shifted position on complexation [14-16]. The $\nu(\text{N-H})$ and $\nu(\text{C}=\text{O})$ bands of the ligand at 3288 and 1717 cm^{-1} do not change their position after complexation, indicating that ligand exist in keto form in free state as well as in all the complexes [17]. The coordination of the acetate group is confirmed due to the difference between the two bands ($\Delta\nu > 181\text{ cm}^{-1}$) in Mn(III) complex, appeared at 1621 and 1440 cm^{-1} which are assignable to $\nu_{\text{sym}}(\text{OCO})$ and $\nu_{\text{asym}}(\text{OCO})$ mode [18, 19]. A broad and strong band centred in the region $3300\text{-}3500\text{ cm}^{-1}$ and another sharp shoulder in the region $1650\text{-}1500\text{ cm}^{-1}$ may be assigned to $\nu(\text{OH})$ and $\nu(\text{HOH})$ vibrations of water molecules, respectively [20]. The additional strong and sharp band at $870\text{-}818\text{ cm}^{-1}$ arising due to OH rocking vibrations in the spectra of complexes further confirms the presence of coordinated water molecules [20]. The coordination of water in VO(IV), Cr(III), Fe(III) and Zr(IV) complexes is indicated by the appearance of bands at $3429\text{-}3357$, $1656\text{-}1581$, $878\text{-}840$ and $781\text{-}765\text{ cm}^{-1}$ assignable to $\gamma(\text{O-H})$, $\delta(\text{O-H})$, $\rho_r(\text{H}_2\text{O})$ and $\rho_w(\text{H}_2\text{O})$ mode, respectively [20]. The spectra of VO(IV) and Zr(IV) complexes show new bands at around 973 and 1129 cm^{-1} , respectively, due to $\nu(\text{V}=\text{O})$ and $\nu(\text{ZrOH})$ vibration. Also, the absence of a new band at $850\text{-}950\text{ cm}^{-1}$ in Zr(IV) complex due to $\nu(\text{Zr}=\text{O})$ stretch. The $\text{MoO}_2(\text{VI})$, $\text{UO}_2(\text{VI})$, $\text{WO}_2(\text{VI})$ complexes show new bands around 956 , 960 , 943 cm^{-1} due to $\nu_{\text{asym}}(\text{O}=\text{Mo}=\text{O})$, $\nu_{\text{asym}}(\text{O}=\text{U}=\text{O})$ and $\nu_{\text{asym}}(\text{O}=\text{W}=\text{O})$ vibrations [21]. The $\text{WO}_2(\text{VI})$ complex shows bands around 2063 (CN), 776 (CS) and 468 cm^{-1} (NCS) suggesting that the thiocyanate group act as ligand in which bonding through nitrogen takes place [22]. The IR spectra of complexes show new bands in the region $584\text{-}558$ and $487\text{-}451\text{ cm}^{-1}$ due to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ vibrations respectively indicating the coordination of ligand through phenolic oxygen and azomethine nitrogen atoms.

Electronic spectra

The electronic spectrum of VO(IV) complex shows three bands at 10965 , 18904 and 25974 cm^{-1} due to $d_{xy}(b_2) \rightarrow d_{xy}d_{yz}(e^*)$, $d_{xy}(b_2) \rightarrow d_{x^2-y^2}(b_1^*)$ and $d_{xy}(b_2) \rightarrow d_{z^2}(a_1^*)$, transitions, respectively, towards square pyramidal geometry of complex. The Cr(III) complex shows absorption bands at 16366 , 21367 and 36496 cm^{-1} due to ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$, transitions, respectively, indicating an octahedral geometry around the Cr(III) ion [23, 24]. The ligand field parameters, Dq, Racahinter electronic repulsion parameter (B'), nephelauxetic ratio (β) and % covalency of metal-ligand bond have been calculated for Cr(III) complex and the values of Dq, B' , β , ν_2/ν_1 and % covalency are found to be 1636.6 cm^{-1} , 584 cm^{-1} , 0.636 , 1.30 and 36.4 . The Racahinter electronic repulsion parameter (B') for complex is found to be lower than the free ion values (918 cm^{-1}) suggesting delocalization of electron on metal into molecular orbital covering both the metal and the ligand, i.e. the appreciable covalent

character in the metal-ligand bond. The ν_2/ν_1 is found to be 1.30 which is very close to the value (1.42) reported for octahedral Cr(III) complex. The Mn(III) complex shows absorption bands at 13605, 17212, 19646 and 28902 cm^{-1} , corresponds to ${}^5B_1 \rightarrow {}^5B_2$, ${}^5B_1 \rightarrow {}^5A_1$ and ${}^5B_1 \rightarrow {}^5E$ and LMCT transitions respectively towards square pyramidal geometry around metal ion [25]. The Fe(III) complex shows absorption bands at 13369, 16000 and 22883 cm^{-1} corresponding to ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4E_g$ transitions, respectively, towards an octahedral geometry.

Magnetic properties

The magnetic susceptibility of the VO(IV), Cr(III), Mn(III) and Fe(III) complexes was measured at room temperature. The observed magnetic moment for VO(IV), Cr(III), Mn(III) and Fe(III) complexes at room temperature is 1.63, 3.88, 4.69 and 5.88 B.M., respectively. A magnetic moment value of complexes which is close to the spin only values suggests their high spin nature. These value supports to the literature value of these complexes. The MoO₂(VI), WO₂(VI), Zr(IV) and UO₂(VI) complexes are found to be diamagnetic as expected from their electronic configurations.

Table 1. Analytical and electrical conductivity data of H₂L complex.

S. No.	Proposed composition of the complexes	σ ($\Omega^{-1}\text{cm}^{-1}$)	E_a (eV)	Colour	Elemental analysis % found (calculated)			
					M	C	H	N
1	H ₂ L	3.31×10^{-12}	0.160	Lemmon lime	--	50.23 (51.50)	4.04 (4.32)	15.70 (16.68)
2	{[VOL]H ₂ O}	6.98×10^{-12}	0.089	Dark evergreen	9.71 (10.13)	42.12 (43.00)	3.20 (3.61)	12.27 (13.93)
3	{[CrL·H ₂ O·Cl]·H ₂ O}	9.77×10^{-10}	0.214	Umber	8.87 (9.61)	38.67 (39.94)	3.19 (3.72)	11.82 (12.94)
4	[MnL·OAc]	1.58×10^{-09}	0.249	Dark orange	9.64 (10.33)	44.33 (45.17)	2.92 (3.60)	12.22 (13.17)
5	{[FeL·H ₂ O·Cl]·H ₂ O}	8.13×10^{-12}	0.162	Maroon	9.37 (10.24)	38.42 (39.66)	2.81 (3.70)	11.09 (12.85)
6	{[ZrL(OH) ₂ H ₂ O]·H ₂ O}	3.02×10^{-10}	0.222	Safari	14.94 (15.75)	35.97 (37.33)	3.09 (3.83)	11.48 (12.09)
7	[MoO ₂ L]	2.34×10^{-09}	0.270	Orange	16.88 (17.58)	38.41 (39.61)	2.38 (2.96)	11.68 (12.83)
8	[WO ₂ L·NCS]	1.26×10^{-07}	0.226	Light yellow	25.49 (26.58)	31.79 (32.99)	1.95 (2.33)	11.54 (12.15)
9	[UO ₂ L]	1.26×10^{-09}	0.260	Dark red gray	33.77 (34.61)	30.90 (31.43)	1.98 (2.34)	9.81 (10.18)

Electrical conductivity measurements

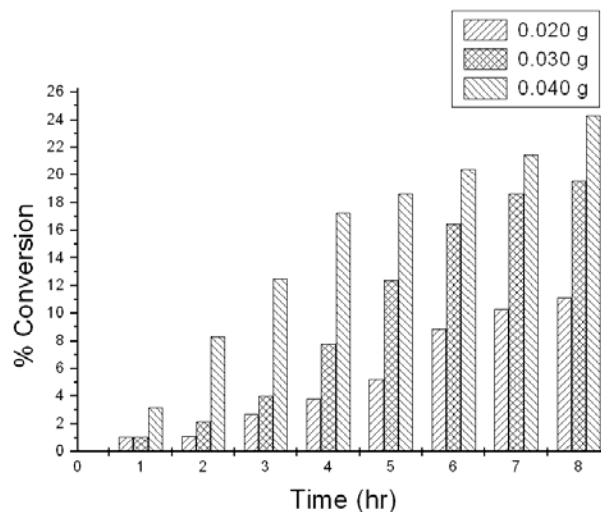
The solid state d.c. electrical conductivity was measured in a compressed pellet form over a temperature range 313-413 K and values reported in Table 1. The electrical conductivity (σ) varies experimentally with the absolute temperature according to the relation $\sigma = \sigma^0 \exp(-E_a/KT)$ where σ^0 is constant, E_a is the activation energy of electrical conduction, T is the absolute temperature and K is Boltzman constant. The plots of $\log \sigma$ vs. $1/T$ are found to be linear over studied temperature range and conductivity increases with increasing temperature. This suggests that the compounds behave as a semiconducting material [26, 27]. The solid state d.c. electrical conductivity lies in the ranges 3.31×10^{-12} to $1.26 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ and the decreasing in the order WO₂ > MoO₂ > Mn > UO₂ > Cr > Zr > Fe > VO > H₂L.

Oxidation of styrene

The catalytic oxidation of styrene gives the products styrene oxide, benzaldehyde, benzoic acid, phenyl acetic acid and 1-phenyl ethane-1,2-diol and other side products [28]. In the present study oxidation of styrene catalysed by the VO(IV) and Mn(III) complexes was carried out. The catalytic activity of these complexes was checked as a function of the amount of catalyst and H₂O₂ used as oxidant. The amount of catalyst is used like 0.020, 0.030 and 0.040 g, respectively, amount of styrene and H₂O₂ (1:2) was fixed in presence of acetonitrile at 80 °C. The conversion of styrene in VO(IV) and Mn(III) complexes was 11.14-24.35% and 9.64-23.42%, respectively (Table 2, Figures 2 and 3), which show 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 H₂O₂, 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. The conversion of styrene increases with increase in amount of catalyst in presence of fixed amount of H₂O₂ and styrene in case of VO(IV) complex catalyst while in Mn(III) complex with increase in catalyst decrease in conversion of styrene. This may be due to the electron rich metal centre of complex and it may have access and hence the formation of metal oxo species is easy than electron deficient metal centre complex and hence

Table 2. Catalytic activity of H₂L complexes.

S. No.	Complexes	Amount of catalyst (g)	% Conversion
1	{[VOL]H ₂ O}	0.020	11.14
		0.030	19.60
		0.040	24.35
2	[MnL'OAc]	0.020	9.64
		0.030	16.8
		0.040	23.42

Figure 2. Effect of {[VOL]H₂O} complex catalyst on % styrene conversion.

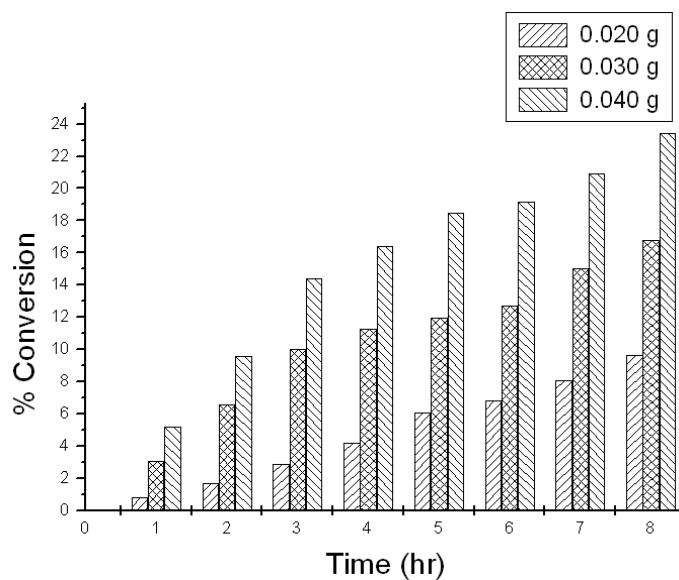


Figure 3. Effect of $[\text{MnL.OAc}]$ complex catalyst on % styrene conversion.

conversion is vary in VO(IV) and Mn(III) complexes [29]. The percentage conversion of styrene was decreases significantly this may be due degradation of the catalyst. The proposed mechanism for oxidation of styrene by H_2O_2 with VO(IV) complex is shown in Figure 4. A blank experiment was performed in each case, where in the absence of catalyst no epoxide was formed under the same reaction condition.

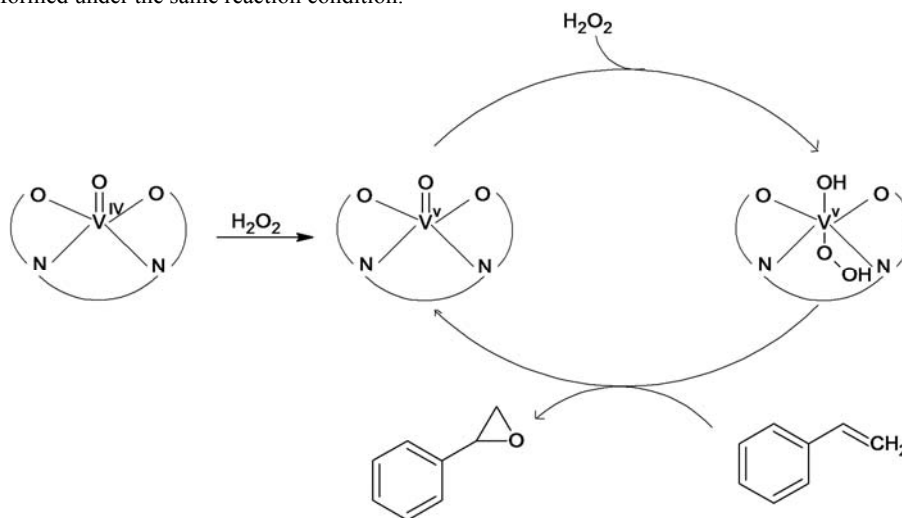


Figure 4. The proposed mechanism of the epoxidation of styrene by VO(IV) complex in the presence of H_2O_2 .

Thermogravimetric study

Thermal studies of ligand and its complexes were carried out at a heating rate of 10 °C/min to observe their thermal behaviour and thermograms indicate the presence of lattice/coordinated water in complexes. The thermograms of Cr(III), Fe(III) and Zr(IV) complexes indicate three stage decomposition pattern, whereas VO(IV), Mn(III), MoO₂(VI), WO₂(VI) and UO₂(VI) complexes show two stage decomposition. The TG analysis of VO(IV), Cr(III), Fe(III) and Zr(IV) complexes shows elimination of a water molecule takes place at 70-110 °C indicating the presence of lattice water molecule whereas Cr(III), Fe(III) and Zr(IV) complexes shows water elimination at 130-225 °C indicating the presence of an coordinated water molecule in the complexes [% wt. loss, obs./calcd. VO(IV): 3.92/3.58; Cr(III): 3.76/3.32; Fe(III): 3.72/3.30 and Zr(IV): 3.53/3.10 for lattice water and Cr(III): 3.66/3.32; Fe(III): 3.68/3.30 and Zr(IV): 3.57/3.10 for coordinated water]. The thermogram of Mn(III) complexes is almost stable up to 245 °C and thereafter it shows gradual loss upto ~310 °C corresponding to one mole of acetate group. MoO₂(VI), WO₂(VI) and UO₂(VI) complexes are almost stable up to 190 °C indicating that absence of any lattice or coordinated water molecule in their complexes. The WO₂(VI) complex shows loss in range the 185-234 °C which corresponds to loss of one thiocyanato group. In all complexes, a rapid weight-loss between 275-420 °C due to quantitative elimination of ligand followed by a gradual weight loss up to 690 °C due to complete decomposition of coordinated ligand. The thermal degradation of the ligand molecule is observed in complexes by gradual weight-loss in the range 310-690 °C. Above 690 °C, nature of the curve is almost horizontal indicating the formation of corresponding metallic oxides. The half decomposition temperature and the kinetic parameters calculated for the compounds are given in Table 3. The relative thermal stability on the basis of half composition temperature is found to be: VO(IV) > Fe(III) > Cr(III) > Mn(III) > Zr(IV) > UO₂(VI) > WO₂(VI) > MoO₂(VI) > H₂L. From the thermal decomposition data various kinetic and thermodynamic parameters such as energy of activation (E_a), frequency factor (Z) and entropy change ($-\Delta S$) have been evaluated by employing Horowitz-Metzger method and values are summarized in Table 3. The activation energies of decomposition are found in the range 34.91-74.55 KJmol⁻¹. The obtained high values of the activation energy of complexes may be due to the stability of chelation due to their coordinated bond and it suggested predicting the bond strength of ligand towards the metal ions and also revealed that the decrease in their atomic radii [30]. The positive sign of ΔG for the complexes reveals that the free energy of the final products is higher than that of the initial compound, and all the decomposition steps are non-spontaneous process. Also the values of ΔG increase significantly for subsequent decomposition steps of the complexes. This is due to the increasing the values of ΔS significantly from one step to another in the complexes. The negative values of ΔS indicate a more ordered activated state that may be possible through the chemisorptions of oxygen and other decomposition products. The more ordered nature may be due to the polarization of bonds in activated state which might happen through charge transfer of electronic transitions.

Powder XRD study

The {[VOL]H₂O} complex was subjected to powder X-ray diffraction analysis (Figure 5). The presence of sharp reflections in XRD pattern of {[VOL]H₂O} indicates the crystalline nature of compound. The XRD spectrum has been recorded with Cu K α X ray tube in the range $2\theta = 4-35^\circ$ with $\lambda = 1.5406 \text{ \AA}$. All the main peaks have been indexed by using appropriate methodology and use of computer program (PowdMult, Version 2.3). The indexing is confirmed on the basis of correction obtained between observed and calculated values. The 2θ values and relative intensities corresponding to the prominent peaks have been listed in Table 4. The 2θ values and relative intensities corresponding to the prominent peaks have been listed in Table 4. The unit

cell lattice parameter of {[VOL]H₂O} complex are $a = 16.2604 \text{ \AA}$, $b = 10.0403 \text{ \AA}$, $c = 6.7669 \text{ \AA}$, $\alpha = 98.342^\circ$, $\beta = 108.203^\circ$, $\gamma = 91.858^\circ$, volume (V) = 1034.80 \AA^3 belongs to triclinic system.

Table 3. Thermal decomposition data of H₂L and its complexes.

S. No.	Compound	MP ^o /half decomp. temp. (°C)	Activation energy 'E _a ' (K J mol ⁻¹)	Frequency factor 'Z' (s ⁻¹)	Entropy change 'ΔS' (J mol ⁻¹ K ⁻¹)	Free Energy Change 'ΔG' (K J mol ⁻¹)
1.	H ₂ L	313	34.91	37.14	-26.52	50.45
2.	{[VOL]H ₂ O}	412	46.01	31.67	-26.83	64.39
3.	{[Cr L:H ₂ OCl]H ₂ O}	394	56.21	44.42	-26.47	73.87
4.	[MnL·OAc]	365	23.70	11.97	-27.74	41.39
5.	{[FeL:H ₂ OCl]H ₂ O}	411	41.17	43.88	-26.51	59.30
6.	{[ZrL(OH) ₂ H ₂ O]H ₂ O}	356	74.55	123.52	-25.39	90.52
7.	[MoO ₂ L]	329	39.37	55.46	-26.14	55.11
8.	[WO ₂ L·NCS]	351	21.15	14.32	-27.53	38.34
9.	[UO ₂ L]	355	58.06	29.91	-26.80	74.89

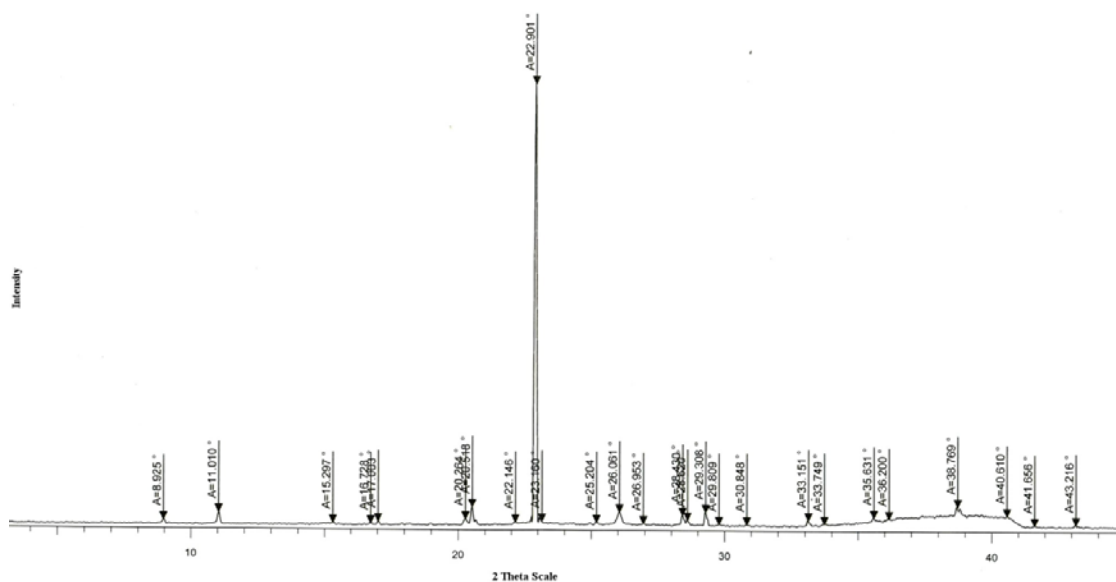


Figure 5. X-ray diffraction spectrum of {[VOL]H₂O} complex.

Table 4. The parameters of unit cell and observed and calculated X-ray diffraction data of {[VOL]H₂O} complex.

System: triclinic, a = 16.2604 Å, b = 10.0403 Å, c = 6.7669 Å, $\alpha = 98.342^\circ$, $\beta = 108.203^\circ$, $\gamma = 91.858^\circ$, V = 1034.80 Å ³						
Peak no.	d (Obs.)	d (Cal.)	2 θ (Obs.)	2 θ (Cal.)	$\Delta 2\theta$	(h k l)
1	9.9000	9.9000	8.93	8.93	0.00	0 1 0
2	8.0300	8.0300	11.01	11.01	0.00	1 1 0
3	5.7870	5.7870	15.30	15.30	0.00	0 -1 1
4	5.2960	5.2960	16.73	16.73	0.00	1 0 1
5	5.2100	5.2100	17.00	17.00	0.00	-1 1 1
6	4.3790	4.3790	20.26	20.26	0.00	1 1 1
7	4.3250	4.3294	20.52	20.50	0.02	-2 2 0
8	4.0110	4.0150	22.14	22.12	0.02	2 2 0
9	3.8800	3.8893	22.90	22.85	0.05	-4 0 1
10	3.8370	3.8484	23.16	23.09	0.07	4 0 0
11	3.5310	3.5345	25.20	25.18	0.02	-3 -2 1
12	3.4160	3.4238	26.06	26.00	0.06	3 2 0
13	3.3050	3.3075	26.96	26.94	0.02	-1 -1 2
14	3.1370	3.1315	28.43	28.48	-0.05	-1 -3 1
15	3.1170	3.1281	28.62	28.51	0.11	-2 3 0
16	3.0450	3.0437	29.31	29.32	-0.01	5 -1 1
17	2.9950	2.9971	29.81	29.79	0.02	-2 -3 1
18	2.8960	2.8950	30.85	30.86	-0.01	4 -1 1
19	2.7000	2.6981	33.15	33.18	-0.03	-6 0 1
20	2.6540	2.6480	33.74	33.82	-0.08	2 0 2
21	2.5180	2.5137	35.63	35.69	-0.06	2 -2 2
22	2.4790	2.4786	36.21	36.21	0.00	5 -1 1
23	2.3210	2.3208	38.77	38.77	0.00	-7 0 1
24	2.2200	2.2236	40.61	40.54	0.07	-1 4 1
25	2.1660	2.1647	41.66	41.69	-0.03	-4 4 0
26	2.0920	2.0958	43.21	43.13	0.09	3 -3 2

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