

# Synthesis of Newer Schiff base Metal Complexes of V(V), Mo(VI), and Co(II) by Grinding Method and Their Application in the Oxidation of Alcohol and Thioethers by Using Green Oxidant

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## ABSTRACT

Two newer Schiff base and their metal complexes of V(V), Mo(VI), and Co(II) were synthesized by Grinding method. A mortar and pestle were used to achieve the synthesis. The Grinding method showed many fold reduction of reaction time over conventional method. All the compounds were well characterized by different analytical techniques such as elemental analysis, melting point determination, FTIR and <sup>1</sup>H NMR studies. The catalytic activities of each of the metal complexes were studied towards oxidation of benzyl alcohol, methylphenylsulfide and thiophene. Aqueous 30% H<sub>2</sub>O<sub>2</sub>, a green oxidant, was used as an oxidant. The oxidation under Grinding method showed superior activity over conventional method. The oxidations were selective and the products were isolated in pure form. Based on the observation, a reaction mechanism was proposed for the catalytic oxidation reactions.

**Keywords:** Metal Complexes, oxidation, Schiff base, grinding method

## 1. Introduction

Green Chemistry was introduced by Paul Anastas and John C. Warner in 1998. The purpose is to develop environmental techniques for human health and environment. Now-a-days, Green Chemistry has emerged as a cohesive area of study.[1] Possible identify the various trends to where some research has an intense and significant role has been made by green chemistry One of the main focuses of Green Chemistry research has been the development of environmentally friendly solvents.[2] For the past 15 years, Green chemistry has been a successful research field in a nascent stage of understanding and recognition Green chemistry has the potential and power in research to find out the innovations to understand the green catalytic properties.[3] Some of the challenges for chemists include the discovery and development of new synthetic pathways using alternative feedstocks or more selective chemistry, identifying alternative reaction conditions and solvents for improved selectivity and energy minimization, and designing less toxic and safer chemicals inherently.[4] In chemical synthesis, the ideal will be a combination a number of environmental, and economic targets and health and safety.

There are many methods towards green synthesis like microwave irradiation, ultrasound activation, etc.[5] The grinding method is related to mechanochemistry which is induced by external mechanical energy in the mortar and pestle in the grinding method mechanical force in the mortar and pestle shock and friction between two surfaces to perform synthesis this type of reaction is related to liquid-assisted grinding in which small amount of solvent is used for doing reaction.[6]

The concept of a Schiff base was introduced by "Hugo Schiff in 1888 It has the general formula  $R_2C=NR$ . Catalysis plays a pivotal role in modern chemical synthesis, enabling the development of efficient and sustainable routes to complex molecules.[7] In recent years, Schiff base catalysts with metal complexes have garnered significant attention due to their unique properties and wide-ranging applications.[8] The coordination of metal ions to Schiff base ligands imparts these catalysts with enhanced reactivity, selectivity, and stability, making them promising candidates for various chemical transformations.[9] Schiff bases, derived from the condensation reaction between a primary amine and an aldehyde or ketone, possess a versatile imine ( $-C=N-$ ) functional group.[10][11] When combined with metal ions, Schiff bases form metal complexes that exhibit distinct catalytic behavior compared to their free ligand counterparts.[12] The coordination of the metal ion to the Schiff base ligand creates a well-defined coordination sphere, influencing the overall geometry and electronic properties of the complex.[13] This, in turn, affects the catalytic activity and selectivity, making Schiff base catalysts with metal complexes highly tunable and versatile.[14] We synthesize and characterize Mo, Co, and V complexes using two Schiff base ligands and characterize it through grinding as well as conventional methods. And check their catalytic activity.

Vanadium metal has atomic number 23 and electronic configuration  $[Ar]4s^23d^3$ , and it has the ability to form a compound oxidation state with +5 to -3 it is the most abundant transition metal in seawater. It gained attention to its biological properties it is the 21st most abundant element in Earth's crust. Molybdenum metal has atomic no 42 and electronic configuration  $[Kr]4d^55s^1$ , and it has the ability to form a compound oxidation state with -2 to +6.

This work describes the synthesis and characterization of Schiff base complexes containing vanadium V(V), Mo(VI), and Co(II) using a grinding method. We compare the efficiency of this method with the conventional approach. The synthesized complexes were thoroughly analyzed using various techniques. Furthermore, the catalytic activity of these complexes was investigated for the oxidation of benzyl alcohol, thiophene, and methylphenylsulfide. We also compared the catalytic performance of complexes prepared to explain the catalytic of the complexes.

## 2. Experimental section

### Materials and methods

The materials used in the experimental work were purchased from commercial sources. Glutaraldehyde (25% pure) and 2-aminophenol were obtained from Qualikems Laboratory Reagents. Glyoxal (40% pure), ethanol amine, and all metal salts were purchased from Loba Chemie PVT. LTD. All the solvents were purchased from SD Fine Chemicals Ltd. The Mortar and pestle was purchased from a local market.

The method of thin layer chromatography (TLC) was used to determine the purity of the Schiff base ligands and their metal complexes as well as their reactivity study. An elemental analyzer from Thermo Scientific was used to perform the elemental analyses (C, H, and N) of the compounds. The FTIR spectra of the compounds were captured using an ATR-moded PerkinElmer (Spectrum-II) instrument. The samples were well-dried in order to eliminate any volatile contaminants before FTIR analysis. In DMSO-d<sub>6</sub> or CDCl<sub>3</sub>, the <sup>1</sup>H NMR spectra of the compounds were acquired using a Bruker AVANCE 400 MHz spectrometer.

## Synthesis

### Preparation of Ligands: L1 and L2

#### Conventional method

For the preparation of both the ligands L1 and L2, by the conventional method, was achieved by mixing the reactants at room temperature in a round bottom flask at 60°C. In the synthesis of ligand L2, glyoxal (40% pure solution) (0.5 ml) and ethanol amine (0.66 ml) were added into a round bottom flask containing 10 ml ethanol which was heated at 60°C. The ethanol amine was added dropwise to the reaction mixture. Same as L2, glutaraldehyde (25% aqueous solution) (0.38 ml, 0.96 mmol) and 2-aminophenol (0.182 g, 1.82 mmol) were reacted for L1. Reaction mixture was stirred magnetically at 60°C. The reaction progress was examine by taking TLC after 30 min intervals. After completion, the solvents from the reaction mixture were removed by heating it at 80°C on a water. Following the solvents' total elimination, a sticky dark brown product was obtained for L2, while L1 produced a solid dark brownish product. For later usage, the ligands were kept at room temperature in a desiccator.

#### Grinding method

For the preparation of both the ligands L1 and L2 by Grinding method, a mortar and pastel was used at room temperature. For L2, glyoxal (40% pure solution) (0.5 ml) and ethanol amine (0.66 ml) were added in a clean and dry mortar at room temperature. Same as L2, glutaraldehyde (25% aqueous solution) (0.38 ml, 0.96 mmol) and 2-aminophenol (0.200 g, 1.183 mmol) were added for L1. The mixture was ground with the help of a pastel after addition of 0.5 mL of ethanol. Examine the reaction in mortar and pistol by taking TLC after 5 min intervals. After completion, washed the mixture with petroleum ether (3 x 5 ml). The solvent was removed from the reaction by drying the mixture in a water bath at 80°C.

### Synthesis of metal complexes

#### Grinding method

The metal complexes of L1 and L2 were synthesized by a grinding method using motar pastel at room temperature. The usual procedure involved adding ligand L2 (0.66 g, 1.0 mmol) or L1 (0.282 g, 1.0 mmol) to a combination of ethanol (0.5 mL) and NaOH (0.112 g, 0.7 mmol for L1Mo & L2Mo or ( 0.028 g, 0.35 mmol for L1V, L2V, or 0.048 g, 0.3 mmol for L1Co, L2Co) in a mortar at room temperature. The grinding was then carried out with the addition of H<sub>2</sub>MoO<sub>4</sub> (0.113 g, 0.018 mmol), V<sub>2</sub>O<sub>5</sub> ( 0.0636 g, 0.0115 mmol), or CoCl<sub>2</sub>.6H<sub>2</sub>O (0.083 g, 0.019 mmol) to the pasty material. The mixture was ground well to pasty mass at room temperature and the progress was examine by taking TLC after 5 min interval until completion of the reaction. The product was washed with petroleum ether (3 x 5 ml), dry the mixture in a water bath at 80°C.

### **Conventional method**

Additionally, each of the metal complexes were synthesized using conventional method. The ligand, L1 or L2, NaOH, and metal precursors are used in the conventional procedure as mentioned above. But here with 10 ml ethanol were added to the reaction mixture and stirred magnetically at 65°C in a round bottom flask. The reaction process was monitored by using TLC. Heating at 80°C on a water bath to remove the solvents, after completion of the reaction. Later on, the solid products were washed with petroleum ether (3 x 5 ml), dried at 80°C, and stored the product under dessicator.

### **Catalytic activity**

#### **Oxidation of Benzyl alcohol**

As mentioned below both grinding and conventional methods were used to oxidation of benzyl alcohol.

#### **Conventional method**

This approach included the oxidation of benzyl alcohol in a round-bottom flask with a reflux condenser under the influence of a magnetic stirrer. In the typical procedure, a combination of 30% H<sub>2</sub>O<sub>2</sub> (0.17 ml, 0.051g, 1.5 mmol), acetonitrile (5 ml), and metal complex (10 mg) were pre-loaded into a round bottom flask. To this mixture, benzyl alcohol (0.108 g, 1.0 mmol) was added. The reaction was maintained at the temperature mentioned in the results and discussion section by magnetic stirring. The reaction proceeded at the temperature specified in the results and discussion section with TLC monitoring its progress. Upon completion, the solvents were evaporated under reduced pressure. The products were then extracted using an ethylacetate-water system, and their yield was calculated. Identification of the products was achieved by comparing their R<sub>f</sub> values to those of authentic samples.

#### **Grinding method**

In the procedure, the oxidation of benzyl alcohol was performed using a mortar and pestle. Specifically, benzyl alcohol, 30% H<sub>2</sub>O<sub>2</sub>, acetonitrile (approximately 0.3-0.5 ml), and the metal complex (quantities specified earlier, except for acetonitrile) were ground together in the mortar at room temperature. The reaction progress was monitored using TLC. Upon completion, the products were extracted from the reaction mixture and the yield was calculated using the previously described method.

#### **Oxidation of thiophene**

As was previously mentioned for the oxidation of benzyl alcohol, conventional as well as grinding procedures were used to oxidize thiophene. However, the amount of catalyst, solvent, oxidant, and substrate were altered in this instance. Thiophene (0.84 g, 1.0 mmol), 30% H<sub>2</sub>O<sub>2</sub> (0.041 g, 1.2 mmol), solvent ( 5 ml), and catalyst (10 mg ) were utilized in the typical conventional manner. In contrast, the grinding method involved thiophene (0.84 g, 1.0 mmol), 30% H<sub>2</sub>O<sub>2</sub> (0.068 g, 2.0 mmol), acetonitrile (approximately 0.3-0.5 ml), and catalyst (10 mg), without any solvent.

#### **Oxidation of methylphenylsulfide**

As was previously mentioned for the oxidation of benzyl alcohol, conventional as well as grinding procedures were used to oxidize thiophene. However, the amount of catalyst, solvent, oxidant, and substrate were altered in this instance. Methylphenylsulfide (0.124 g, 1.0 mmol),

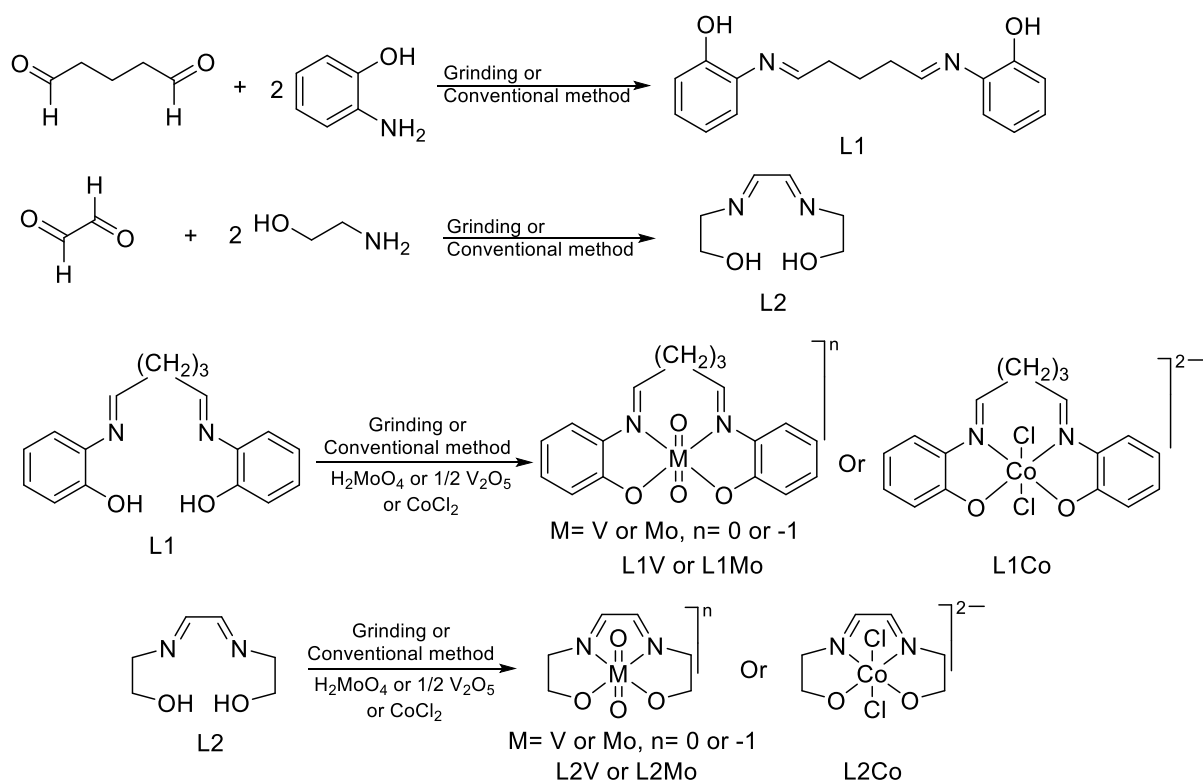
30% H<sub>2</sub>O<sub>2</sub> (0.041 g, 1.2 mmol), solvent ( 5 ml), and catalyst (10 mg ) were utilized in the typical conventional manner. In contrast, the grinding method involved thioanisole (0.124 g,1.0 mmol), 30% H<sub>2</sub>O<sub>2</sub> (0.068 g, 2.0 mmol), acetonitrile (approximately 0.3-0.5 ml), and catalyst (10 mg), without any solvent.

## 4. Results and Discussion

### Synthesis

As indicated in schemes 1 we created a ligand by a grinding or mechanochemical process that was not previously reported. The procedure is easy, solvent-free, requires no additives, and is environmentally friendly. Moreover, the process of Schiff base synthesis was found to be acid-free in grinding method. Using a mortar and pestle at room temperature for 30 min, the mixture of glutaraldehyde and 2-amino phenol and the other ligand is glyoxal and ethanol amine was grind in motar-pistel (1:1) to achieve a 99% isolated yield. In different analytical techniques, the product is confirmed pure. Glutaraldehyde and 2-amino phenol react in ethanol under reflux conditions using a conventional technique, yielding an 80% yield after 12 to 14 hours. Also, the second ligand Glyoxal and ethanol amine in ethanol under reflux conditions uses conventional techniques, yielding a 70% yield after 8 hours. This proved the grinding process's superiority over the conventional method.

The complex was synthesized by the method by reacting L1 with vanadium pentoxide in 0.25 ml of the ethanol as solvent (Scheme 1), it is required to make a pasty mixture. NaOH is required in the reaction mixture because it deprotonate the ligand and it also provides the counteraction in the complexes. After grinding for the required reaction time, the products were isolated with 97-98% yield. The detail results are shown in Table-1. Therefore, compared to the conventional technique, the LAG synthesis of metal complex is substantially more successful.



**Scheme-1.** Synthetic scheme of ligand L1, L2, and their metal complexes.

**Table-1:** Comparison between conventional method and grinding method for the formation of ligands and their metal complexes.

Compounds	Color	Conventional method		Grinding method	
		Reaction time	Yield%	Reaction time	Yield%
L1	light brown	18 h	99	35 min	97
L2	brown	36 h	97	30 min	96
L1-Mo	brown	16 h	97	35 min	98
L1-V	brown	15 h	98	30 min	97
L1-Co	red	18 h	96	35 min	98
L2-Mo	brown	22 h	<1	40 min	98
L2-V	green	24 h	<1	45 min	98
L2-Co	red	30 h	<1	45 min	97

### Characterization

Each of the synthesized compounds were characterized by elemental analysis, FTIR, <sup>1</sup>H NMR, and melting point determination. The elemental analysis data for the ligand and their metal complexes are presented in Table-2. From the data it is evident that the the theoretical and experimental composition of the elements were within  $\pm 0.5\%$ . This confirms the possibility of formation of the compounds as assigned in their formula. Further, the melting point of the ligands showed the thermal stability upto 250°C as the metal complexes did not melt below 250°C. Unfortunately, we could not get crystals suitable for single crystal XRD for any of the compounds so far.

**Table-2:** Elemental analysis data for the synthesized compounds.

Compound	Molecular Formula	Element (Expt./Theo.)			
		C%	H%	N%	Metal%
<b>L1</b>	C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	71.93/72.32	6.28/6.43	9.75/9.92	---
<b>L2</b>	C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	49.72/49.99	8.05/8.39	19.23/19.43	---
<b>L1V</b>	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> VNa	52.58/52.86	3.87/4.18	7.11/7.25	12.85/13.19
<b>L1Mo</b>	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> Mo	49.63/50.01	3.66/3.95	6.58/6.86	23.17/23.50
<b>L1Co</b>	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub> CoNa <sub>2</sub>	44.53/44.76	3.37/3.54	5.89/6.14	12.77/12.92
<b>L2V</b>	C <sub>6</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> VNa	28.76/29.05	4.23/4.06	11.16/11.29	20.35/20.53
<b>L2Mo</b>	C <sub>6</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> Mo	26.25/26.68	3.49/3.73	10.04/10.37	35.24/35.53
<b>L2Co</b>	C <sub>6</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub> CoNa <sub>2</sub>	22.38/22.66	2.99/3.17	8.55/8.81	18.37/18.53

### FTIR analysis

The FTIR spectra of L2 and L2V are shown below in Figure-1. The characteristic peak assignments for all the compounds are given in Table-3. It was evident from the FTIR analysis that the spectrum of free ligand and their metal complexes were distinctly different. In particular the stretching imine (-CH=N-) peak appeared in L2 at 1648 cm<sup>-1</sup>, while in the L2V the same peak shifted to 1648 cm<sup>-1</sup>.

Further strong stretching peak of hydroxyl (-OH) present in the L2 disappeared or intensity decreased substantially in L2V. These observation clearly indicated the coordination of L2 with vanadium centre via nitrogen and oxygen atom of the L2. Additionally, in the spectrum of L2V, two characteristic peaks appeared at 832 and 873  $\text{cm}^{-1}$ , responsible for  $\nu(\text{O}=\text{V}=\text{O})_{\text{symmetric}}$  and  $\nu(\text{O}=\text{V}=\text{O})_{\text{asymmetric}}$  vibration of  $\text{VO}_2^+$  moiety. Thus, FTIR spectral analysis confirmed the formation of compounds as proposed in Scheme-1.

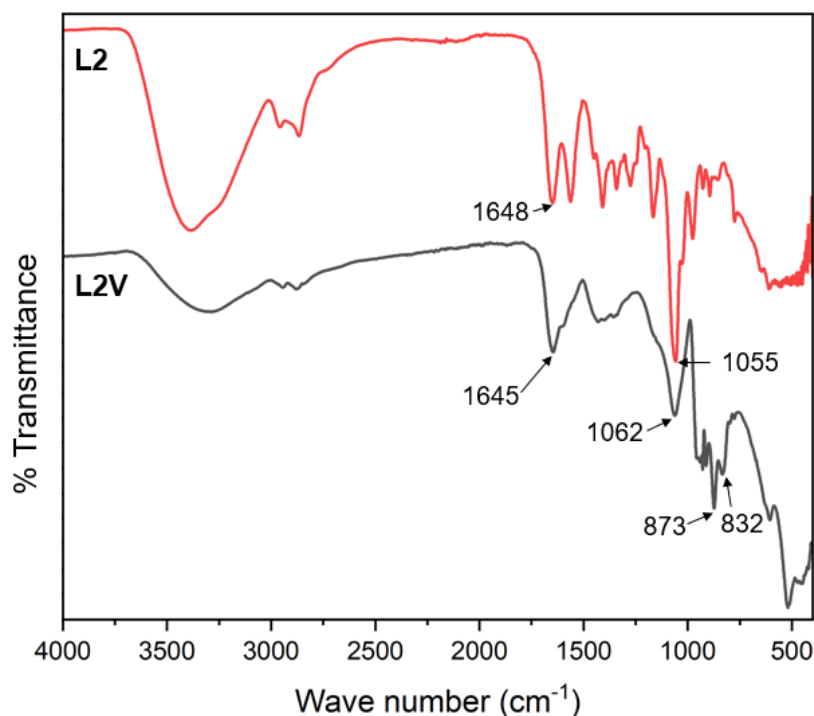


Figure-1: FTIR spectra of L2 and L2V.

Table-3: FTIR spectral data for all the synthesized compounds.

Compound	$\nu(\text{O-H})$	$\nu(\text{C=N})$	$\nu(\text{MO}_2)_{\text{sym}}$	$\nu(\text{MO}_2)_{\text{asym}}$	$\nu(\text{C-O})$
<b>L1</b>	3270 (br, vs)	1632	---	---	1098
<b>L2</b>	3291 (br, vs)	1648	---	---	1058
<b>L1V</b>	3289 (br, vw)	1624 (sh, m)	939	839	1062
<b>L1Mo</b>	3299 (br, vw)	1622 (sh, m)	855	819	1089
<b>L1Co</b>	3286 (br, vw)	1620 (sh, m)	---	---	1067
<b>L2V</b>	3301 (br, vw)	1645	873	834	1062
<b>L2Mo</b>	3295 (br, vw)	1641	853	816	1063
<b>L2Co</b>	3263 (br, vw)	1640	---	---	1056

M = Mo or Cr, br = broad peak, vs = very strong, vw = very weak

## $^1\text{H}$ NMR

Crucial information can be derived from the  $^1\text{H}$  NMR study of the ligands and their complexes. The  $^1\text{H}$  NMR spectra for L2 and L2Mo are shown in Figure 2 & 3 and the peak assignments for all the compounds are presented in Table-4. By choosing the  $^1\text{H}$  NMR spectra of L2 and L2Mo as the representative compound, it was evident that the imine (-HC=N-) and hydroxyl (-OH) peaks for L2 appeared at 8.12 and 4.33  $\delta$ , respectively.

But after metal complex formation in L2Mo, the imine peak shifted to 7.68  $\delta$ . Interestingly, the disappearance of hydroxyl peaks in the L2Mo spectrum confirmed conversion of hydroxy into alkoxide group. These observation confirmed the coordination of the ligand with the metal centre as suggested by FTIR spectral analysis. Similar observation were found for the rest of the compounds and data are included in Table-4. But, for the complexes L1Co and L2Co, no characteristic peaks were appeared in their  $^1\text{H}$  NMR spectra within the normal range. This may be due to the paramagnetic effect of the cobalt(II) centre.

**Table-4.**  $^1\text{H}$ -NMR peak assignments for the compounds (recorded in DMSO- $d_6$ ).

Compound	-HC=N-	-OH	-CH <sub>2</sub> -	-C-H aromatic
<b>L1</b>	8.26 (2H)	2.63 (2H)	2.15 (4H), 2.04 (2H)	6.88-7.42 (8H)
<b>L2</b>	8.12 (2H)	4.33 (2H)	4.15 (4H), 3.58 (4H)	---
<b>L1V</b>	7.99 (2H)	---	2.10 (4H), 1.96 (2H)	6.88-7.44 (8H)
<b>L1Mo</b>	7.87 (2H)	---	2.03 (4H), 1.95 (2H)	6.82-7.41 (8H)
<b>L1Co</b>	---	---	---	---
<b>L2V</b>	7.75 (2H)	---	3.72 (4H), 3.61 (4H)	---
<b>L2Mo</b>	7.68 (2H)	---	3.71 (4H), 3.59 (4H)	---
<b>L2Co</b>	---	---	---	---

“---” indicates not present.

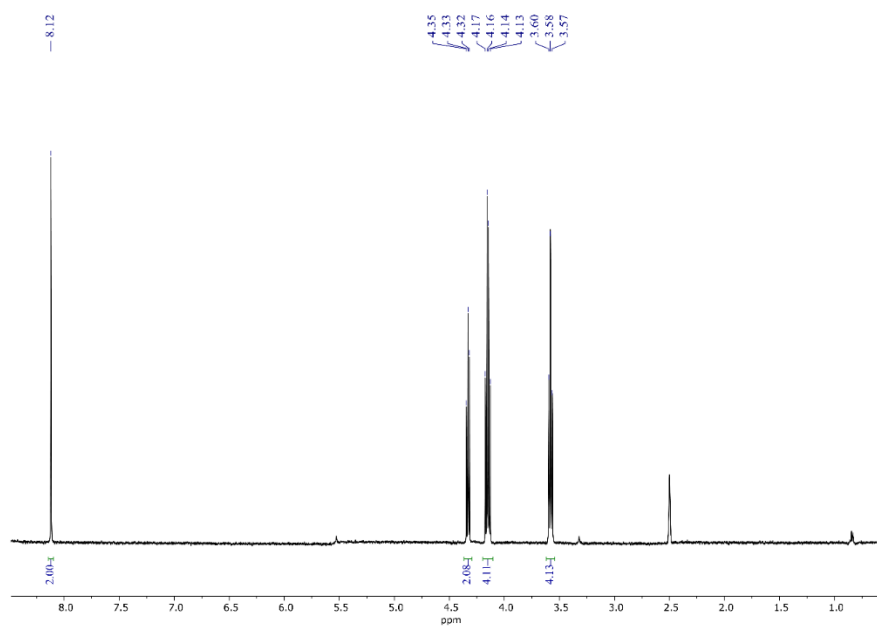


Figure-2.  $^1\text{H}$  NMR spectrum of L2 in DMSO- $d_6$ .



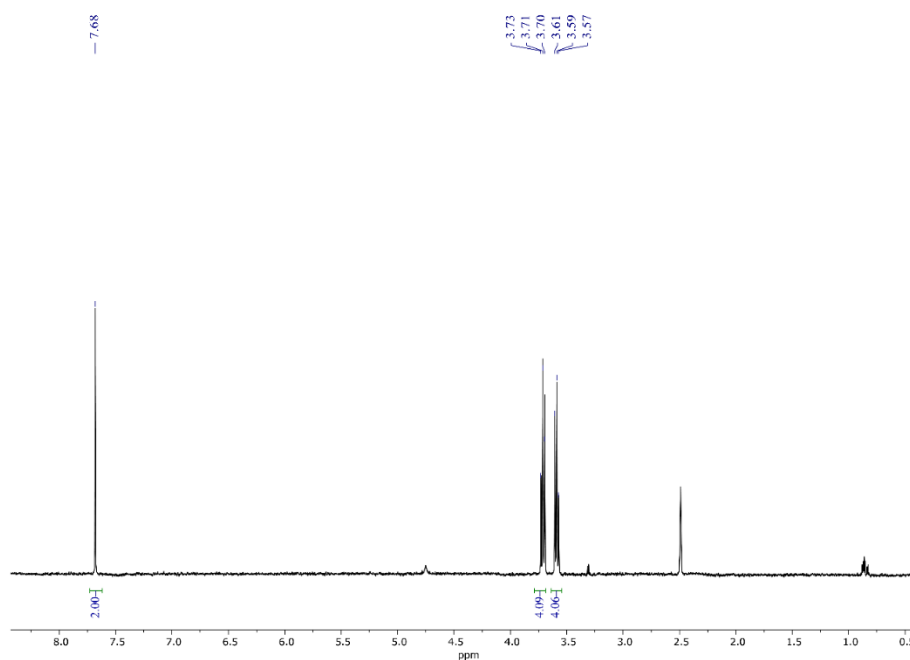


Figure-3.  $^1\text{H}$  NMR spectrum of L2Mo in DMSO- $d_6$ .

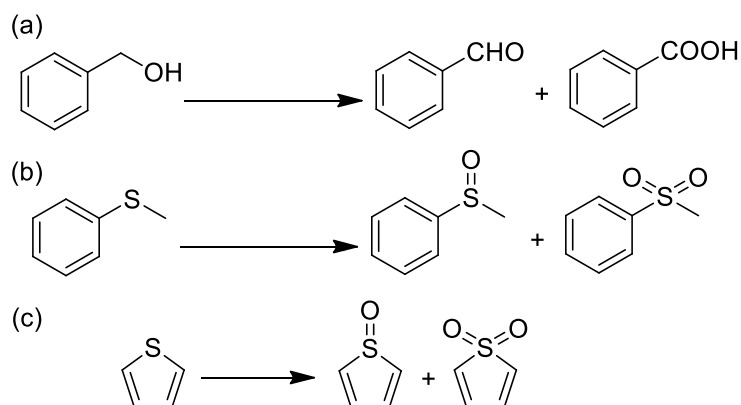
Thus, on the basis of above observation, the proposed structure for the synthesized compounds may be assigned as shown in Scheme-1. In all metal complexes, the ligand is coordinated with the metal centre via oxygen and nitrogen atoms.

### Catalytic activity of metal complexes

The catalytic activity was investigated with the Mo(VI), V(V), and Co(II) metal complexes of L1 and L2. The reaction parameters such as substrates, solvent, oxidant, temperature, and catalyst amount were studied to obtain the optimal conditions.

### Oxidation of benzyl alcohol

The selectivity of the resultant product is crucial in any chemical process. Benzaldehyde and benzoic acid are the products of benzyl alcohol oxidation (Scheme-2). Thus, it is desirable to obtain only one product on a selective basis. The above mentioned parameters were used to determine optimum reaction condition, in order to get high yield and product selectivity.



**Scheme-2.** Oxidation of (a) benzyl alcohol, (b) methylphenylsulfide, and (c) thiophene.

It has been shown that the solvent significantly affects the yield and selectivity of the product. We have used a typical approach to perform the reaction in ethanol methanol, chloroform, acetonitrile, dichloromethane, hexane, solventless, water, etc. 10 mg of catalyst (L1V) and a molar ratio of substrate:oxidant of 1:1.5 was used to perform the reactions at 75°C. The outcomes are compiled below in Table-5. The experiments clearly demonstrated that benzyl alcohol was selectively oxidized to benzaldehyde in all tested solvents and solventless conditions, without any over-oxidation to benzoic acid. Acetonitrile was identified as the most effective solvent, achieving a 98% yield in 8 hours, likely due to the increased stability of the intermediate in this solvent. While oxidation was also possible in ethanol and methanol, the yields were lower, around 50%, even after 24 hours, likely due to competing oxidation reactions involving the solvent. Oxidation in chloroform, dichloromethane, and hexane resulted in poor yields (4%, 8%, and 6%, respectively) after 24 hours, probably due to oxidant immiscibility with these solvents. Additionally, reactions conducted in water and under solventless conditions required longer times 17 and 12 hours, respectively, which were higher than the reaction time compared to acetonitrile as solvent.

**Table-5.** Screening of solvents in oxidation of benzyl alcohol.

Solvent	Time (h)	Yield (%)	Product selectivity, a:b
Acetonitrile	8.0	98	100:0
Ethanol	24.0	51	100:0
Methanol*	24.0	48	100:0
Chloroform*	24.0	4	100:0
Dichloromethane*	24.0	8	100:0
Hexane	24.0	6	100:0
Solventless	12.0	98	100:0
Water	17.0	98	100:0

<sup>a</sup>Reaction condition: benzyl alcohol= 0.108 g, 1.0 mmol, 30% $H_2O_2$ =0.17 ml, 0.051 g, 1.5 mmol, Solvent=5 ml, L1V= 10 mg, Temperature = 75°C. \*Reactions were conducted at the boiling point of the used solvent.

Upon identifying acetonitrile as the optimal solvent, we proceeded with the oxidation process to evaluate temperature impact while maintaining a substrate-to-oxidant molar ratio of 1:1.5 and utilizing 10 mg of the L1V as catalyst in acetonitrile. The experiments were carried out at various temperatures: room temperature (RT), 45, 60 and 75 °C. As depicted in the Figure-4, the time necessary to reach a complete 100% conversion of benzyl alcohol into benzaldehyde is shown. Notably, an increase in the reaction temperature resulted in a marked reduction in reaction time. Specifically, the reaction at 75°C exhibited a reaction time that was approximately half that required at room temperature.

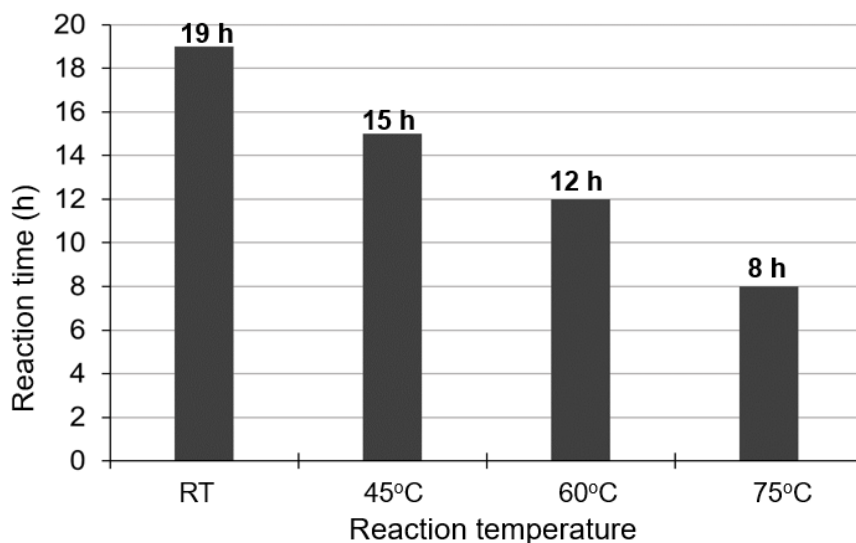


Figure-4. Effect of temperature on oxidation of benzyl alcohol.

To accelerate the oxidation reaction, the amounts of oxidant and catalyst were varied. Initially, the catalyst amount was adjusted, and reactions were conducted with 5, 10, 15, and 20 mg of L1V at a substrate-to-oxidant molar ratio of 1:1.5 in acetonitrile at 75°C. It was observed that reducing the L1V amount from 10 mg to 5 mg increased the reaction time while increasing it from 10 mg to 20 mg did not significantly affect the reaction time. Additionally, to further oxidize benzyl alcohol to benzoic acid, substrate-to-oxidant molar ratios of 1:1.5, 1:2, and 1:4 were tested. However, no over-oxidation to benzoic acid was observed, demonstrating the reaction's product selectivity.

To reduce the environmental impact of solvents, reactions were carried out using the grinding method with a mortar and pestle. Using only about 0.3-0.5 mL of acetonitrile, a reaction was performed at room temperature with a substrate-to-oxidant molar ratio of 1:1.5 and 10 mg of L1V. Notably, the reaction time decreased to 60 minutes to achieve 100% conversion without compromising product selectivity. The optimal reaction conditions for the selective oxidation of benzyl alcohol to benzaldehyde were found to be a substrate-to-oxidant molar ratio of 1:1.5 with 10 mg of catalyst at 75°C in acetonitrile (using the conventional method). However, with the grinding method, the same ratio of substrate, oxidant, and catalyst achieved successful oxidation using minimal acetonitrile at room temperature. The catalytic activities of each complex were explored using both conventional and grinding methods under optimized conditions, as shown in Table-6. The results indicate that the grinding method is faster than the conventional method, offering advantages such as room temperature operation and minimal solvent use. The catalyst L1V demonstrated the best catalytic activity, while L1Co and L2Co showed no activity even after 24 hours.

Table-6. Oxidation of benzyl alcohol under conventional and grinding methods using catalytic amount of Schiff base complexes of L1 and L2.

Compound	Conventional method <sup>a</sup>		Grinding method <sup>b</sup>	
	Time	Yield, %	Time	Yield, %
L1V	8.0 h	98	50 min	98
L1Mo	9.0 h	98	1.0 h	98
L1Co	24.0 h	No reaction	2.0 h	No reaction
L2V	12.0 h	97	45 min	97
L2Mo	9.0 h	98	30 min	98
L2Co	30.0 h	No reaction	2.0 h	No reaction

<sup>a</sup>Reaction condition: benzyl alcohol= 0.108 g, 1.0 mmol, 30% H<sub>2</sub>O<sub>2</sub>=0.17 ml, 0.051 g, 1.5 mmol, acetonitrile =5 ml, catalyst = 10 mg, Temperature= 75°C.

<sup>b</sup>Reaction conditions : Benzyl alcohol = 0.108 g, 1.0 mmol, 30% H<sub>2</sub>O<sub>2</sub> = 0.17 ml, 0.051 g, 1.5 mmol, acetonitrile = 0.3-0.5 ml, catalyst =10mg, Tempertaure = RT.

### Oxidation of methylphenylsulfide and thiophene

When we oxidize methylphenylsulfide (MPS) with an oxidant, it turns into methylphenylsulfoxide (MPSO) and eventually methylphenylsulfone (MPSOO). Similarly, oxidizing thiophene (TP) yields thiophene-1-oxide (TPO) and thiophene-di-oxide (TPOO). (the process are illustrated in Scheme 2). In our initial experiments to test the catalytic activities of complexes, we used L1V as catalyst and optimized the reaction conditions for MPS. To achieve selective oxidation (meaning purely MPSO), we examined various reaction parameters. The effect of different solvents is shown in Figure-5, with acetonitrile being the best choice for both product yield and favoring MPSO formation. Importantly, under the optimized conditions (1:1.2 ratio of MPS to hydrogen peroxide), no over-oxidation to MPSOO was observed.

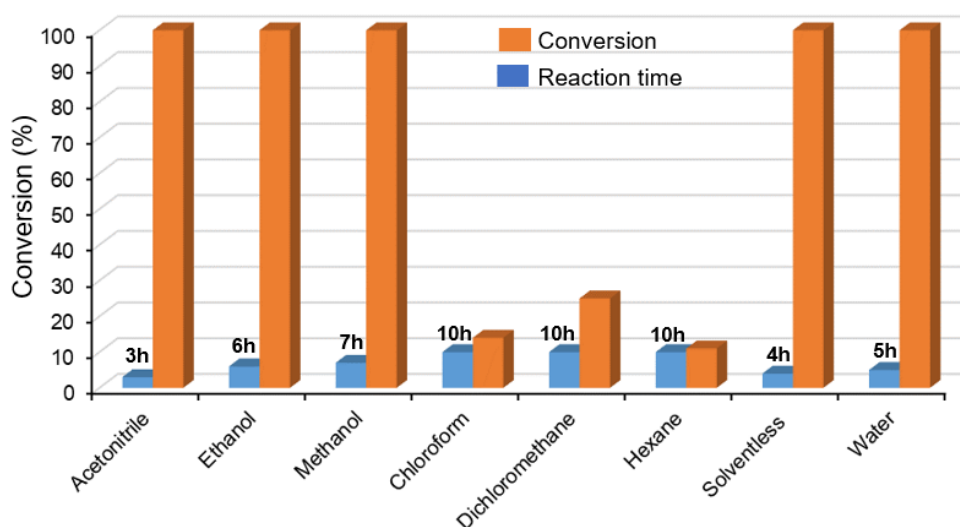


Figure-5. Solvent effect on oxidation of MPS with catalytic amounts of L1V.

In the catalytic oxidation of MPS, the molar ratio of MPS: H<sub>2</sub>O<sub>2</sub> had a significant role in the product selectivity. When maintaining a molar ratio of MPS to H<sub>2</sub>O<sub>2</sub> at 1:1.2 and 1:2.5 in acetonitrile as the solvent, MPSO and MPSOO were the sole products obtained, respectively. Additionally, we conducted the reaction at various temperatures including room temperature (RT), 60, and 75°C. The highest activity was observed at 75°C.

Following the successful selective oxidation of MPS with L1V using conventional methods, we experimented with the grinding method using a mortar and pestle. Interestingly, this method achieved selective oxidation with minimal solvent (approximately 0.3-0.5 mL of acetonitrile) at room temperature and also reduced the reaction time. The results, presented in Table-7, show that an identical molar ratio of MPS:H<sub>2</sub>O<sub>2</sub> was maintained at 1:1.2 for MPSO and 1:2.5 for MPSOO to ensure product selectivity.

For the oxidation of thiophene, the possible products are thiophene -1-oxide (TSO) or thiophene-di-oxide (TSOO) (Scheme-2). We performed oxidation reactions with thiophene molar ratios of 1:1.2 and 1:2.5, resulting in the formation of TSO and TSOO, respectively, as detailed in Table-8. However, these reactions required longer times than the oxidation of MPS, likely due to the lower nucleophilicity of the sulfur atom in thiophene compared to MPS. The grinding method yielded better results than the conventional heating, and the products were isolated in highly pure form. The compound L1V exhibited the best oxidation activity, whereas L1Co and L2Co did not facilitate thiophene oxidation.

Table-7. Oxidation of methylphenylsulfide by the metal complexes.

Compound	Conventional method <sup>a</sup>		Grinding method <sup>b</sup>	
	Time	Yield, %	Time	Yield, %
L1V	3.0 h	98	20 min	99
L1MO	4.0 h	97	25 min	98
L1CO	24.0 h	<6%	2.5 hr	<6%
L2V	4.5 h	99	25 min	98
L2MO	5.5 h	98	30 min	99
L2CO	24.0 h	<6%	2.5 hr	<6%

<sup>a</sup>Reaction condition: MPS: H<sub>2</sub>O<sub>2</sub> = 1:1.2 g, acetonitrile = 5 ml, Catalyst = 10 mg, Temperature = 75°.

<sup>b</sup>Reaction conditions: MPS: H<sub>2</sub>O<sub>2</sub> = 1:1.2 g, acetonitrile = ~0.3-0.5 ml, Catalyst = 10 mg, Temperature = RT

Table-8. Oxidation of thiophene -1-oxide catalyzed by synthesized complexes.

Compound	Conventional method <sup>a</sup>		Grinding method <sup>b</sup>	
	Time	Yield, %	Time	Yield, %
L1V	5.0 h	98	55 min	99
L1Mo	6.0 h	97	70 min	98
L1Co	24.0 h	No reaction	1.5 h	No reaction
L2V	5.5 h	99	40 min	97
L2Mo	7.0 h	98	45 min	99
L2Co	24.0 h	No reaction	2.0 h	No reaction

<sup>a</sup>Reaction condition: Thiophene: H<sub>2</sub>O<sub>2</sub> = 1:1.2 g, acetonitrile = 5 ml, Catalyst = 10 mg, Temperature of reaction = 75°.

<sup>b</sup>Reaction conditions Thiophene: H<sub>2</sub>O<sub>2</sub> = 1:1.2 g, acetonitrile = ~0.3-0.5 ml, Catalyst = 10mg, Temperature of reaction = RT

### Proposed mechanism of the catalytic reactions

A reaction mechanism has been suggested based on the reactivity of the complexes and existing literature.[15,16,17] Using L1V as the representative catalyst, the catalytic cycle for the oxidation reactions is depicted in Figure-6. Initially, the oxidant, H<sub>2</sub>O<sub>2</sub>, interacts with the VO<sub>2</sub><sup>+</sup> center, forming peroxovanadium species via path I. Subsequently, the peroxovanadium species react with alcohol or sulfides, converting them into products and regenerating the catalyst to its original form (path II). This cycle continues repetitively. After the reaction, hydrogen peroxide yield water as a by-product (path I).

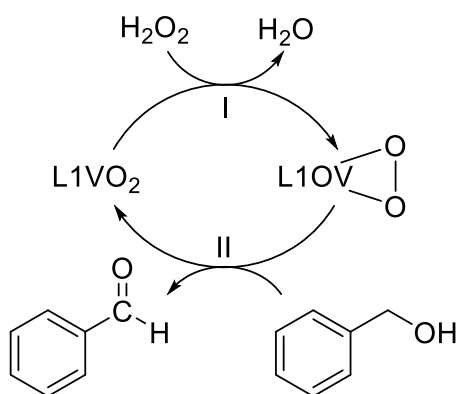


Figure-6. Proposed reaction mechanism.

### Conclusions

In conclusion, using the grinding approach, we have accomplished green synthesis of L1 and L2 and its metal complexes V(V), Mo(VI), and Co(II). Compared to the conventional heating procedure, the grinding protocol is simpler to follow and takes less reaction time to finish. Both L1 and L2 and their metal complexes were characterized by elemental and spectroscopic analysis. All metal complexes, except L1Co and L2Co, selectively and catalytically oxidize benzyl alcohol, thiophene, and methylphenylsulfide under the grinding method and conventional heating.

The oxidation reactions under the grinding method were found to be much faster than the conventional method. Also, we found that L1V shows a better catalytic activity for the oxidation of alcohol and sulfide. Under grinding method, a small amount of solvent was added in some of the reactions to facilitate the smooth mixing. Overall, these methods are simple, easy, convenient, high yield, save energy, and cost-effective, and environmentally friendly, this is the requirement of green chemistry.

## Acknowledgments

The authors are thankful to Center of Excellence, Department of Chemistry, UIS, Chandigarh University, Mohali, Punjab and Centre of Excellence, NFDD Centre, Saurashtra University, Rajkot, Gujarat for their help in analyzing the compounds.

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