

# Green Synthesis and Selective Catalytic Oxidation of Alcohol and Thioethers by Benzimidazole Based Metal Complexes of Mo(VI), V(V), and Co(II)

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## ABSTRACT

This work describes a green method for synthesizing benzimidazole-based metal complexes, viz., Mo(VI), V(V), and Co(II) complexes, through grinding method. This environmentally friendly technique minimizes its adverse impacts on the environment while providing benefits in terms of sustainability, simplicity, and efficiency by eschewing solvent-based conventional methods. The generated compounds were characterized using elemental analysis, FT-IR, <sup>1</sup>H NMR, and melting point determination techniques. Utilizing these compounds as selective catalysts in a range of processes, particularly the oxidation of benzyl alcohol, methyl phenyl sulfide, and thiophene, showed promising results in terms of both selectivity and catalytic activity. The green synthesis approach, in conjunction with the catalytic capabilities of these complexes, presents a significant step toward environmentally friendly and sustainable coordination chemistry and catalysis procedures.

**Keywords:** benzimidazole, metal complexes, oxidation catalyst, thiophene

## 1. Introduction

With a wide range of uses in agrochemicals, pharmaceuticals, and catalysis, benzimidazole and its derivatives have become an intriguing class of heterocyclic compounds [1], [2]. The synthesis and design of metal complexes based on benzimidazoles have attracted a lot of interest because of their special qualities and possible uses in catalytic processes. The development of "green" or ecologically friendly synthesis methods for these complexes, in line with sustainable chemistry concepts, has garnered increasing attention in recent years [3], [4]. The unique coordination behavior and catalytic potential of Mo(VI), V(V), and Co(II) metal centers have prompted substantial research into the synthesis of benzimidazole-based metal complexes of various metal centers. Complexes of molybdenum and vanadium have demonstrated encouraging catalytic activity in a range of oxidation processes [5], [6], and cobalt complexes have shown useful in a variety of catalytic processes, such as coupling reactions, oxidation, and reduction [7], [8].

The environmentally friendly production of these complexes involves the use of solvents like water or ionic liquids [9], [10], as well as the use of sustainable and renewable raw materials. In addition, research has been done on the use of alternative energy sources, like ultrasound or microwave irradiation, to improve the sustainability and efficiency of synthetic processes [11], [12]. These benzimidazole-based metal complexes have been thoroughly investigated for their selective catalytic uses in a variety of organic transformations. Complexes of molybdenum and vanadium have demonstrated exceptional catalytic activity in oxidation processes, such as the olefin epoxidation [13], alkane hydroxylation [14], and alcohols' oxidation [15] and sulfur-containing substances [16]. Additionally, these complexes have shown promise in the catalytic oxidation of sulfur compounds, which presents exciting possibilities for desulfurization procedures [17]. Conversely, the catalytic activity of cobalt complexes has been investigated in a variety of organic transformations, including oxidation processes (e.g., alcohol oxidation [18], olefin epoxidation [19]), reduction reactions (e.g., reduction of nitro compounds [20], hydrogenation of alkenes [21]), and coupling reactions (e.g., C-C and C-N bond formation [22], [23]). These benzimidazole-based metal complexes' distinct electronic and steric environments, which are adjustable by changing the ligand structure and metal coordination sphere, are responsible for their selective catalytic qualities [24], [25]. These complexes are appealing candidates for a variety of industrial applications because they frequently show better catalytic activity, selectivity, and stability than their traditional equivalents. Additionally, the synthesis and use of these complexes in line with green chemistry principles responds to the growing need in the chemical industry for sustainable and ecologically friendly methods [26], [27]. This area of study has a great deal of promise to advance sustainable chemical transformations and make a positive impact on the environment by addressing environmental issues and encouraging the creation of effective and selective catalytic systems. Surprisingly, the application of grinding method in the synthesis of benzimidazole based metal complexes is very limited.

We are reporting herein, the synthesis of benzimidazole-based metal complexes of Mo(VI), V(V), and Co(II) by grinding methodology. All the complexes were characterized by different analytical techniques. Further, the catalytic activities of the compounds were studied towards oxidation of benzyl alcohol, methyl phenyl sulfide and thiophene.

## 2. EXPERIMENTAL

### 2.1. Materials and methods

Without additional purification, molybdic acid ( $\text{H}_2\text{MoO}_4$ ), vanadium pentoxide ( $\text{V}_2\text{O}_5$ ), and cobalt(II)chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), benzyl alcohol, thiophene, acetonitrile, ethanol, methanol, dimethylsulfoxide (DMSO), dichloromethane (DCM) were purchased from Loba Chemie Pvt. Ltd., Mumbai, India and employed exactly as directed. Ethyl acetate and petroleum ether was also used as a solvent for thin layer chromatography (TLC). A PerkinElmer (Spectrum-II) instrument with ATR mode was used to record the FTIR spectra of compounds. NMR spectra of the compounds were recorded in deuterated solvents such as  $\text{DMSO-d}_6$  or  $\text{CDCl}_3$  by using a Bruker AVANCE 400 MHz spectrometer. The elemental analyses (C, H, and N) of the compounds were done by using a Thermo Scientific elemental analyser. Metal content in the complexes were estimated by adopting following procedure.

### Estimation of V

Vanadium was estimated volumetrically by titration with a standard potassium permanganate solution.[28] A near boiling solution of an accurately weighed amount of the vanadium(V) compound was treated with a stream of sulphur dioxide for ca.10 min, and then with a stream of carbon dioxide to expel any excess of sulphur dioxide. The vanadium (IV) solution thus obtained was cooled at ca. 80°C and finally titrated with a standard potassium permanganate solution.

### Estimation of Mo

Molybdenum was estimated by precipitation as molybdenum oxinate,  $\text{MoO}_2(\text{C}_9\text{H}_6\text{ON})_2$ . [29] In the typical method, an accurately weighed amount of the compounds was dissolved in 20 mL distilled water in a 250 mL beaker and then acidified with a few drops of dilute 1M sulfuric acid. To the mixture, 5 mL of 2M ammonium acetate was added and diluted it to 50-100 mL followed by heating upto boiling. The molybdenum was precipitated by the addition of 3% solution of oxine in dilute acetic acid until the supernatant liquid becomes perceptibly yellow. The mixture was then boiled gently and stirred for 3 minutes. The precipitate was then filtered through a constant-weighed sintered glass crucible and washed with hot water until free from the reagent. After washing, it was dried to constant weight at 130-140°C.

### Estimation of Co

The amount of cobalt was estimated spectrophotometrically by using 1-(2-thiazolylazo)-2-naphthol (TAN) in the presence of the surfactant cetyltrimethylammonium bromide (CTAB) aqueous micellar solution [30]. This method has been developed for the quick and simple detection of trace amounts of cobalt. The micellar system improves molar absorption efficiency, selectivity, and sensitivity. At a maximum wavelength ( $\lambda_{\text{max}}$ ) of 572.7 nm, the coefficient of molar absorption ( $\epsilon$ ) and Sandell's sensitivity were found to be  $\epsilon = 1.89 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $3.1 \text{ ng cm}^{-2}$ , respectively. The synthesis of the  $\text{Co}[\text{TAN}]_2$  complex was realized with a stoichiometric metal-ligand ratio of 1:2 and linear concentration calibration within the range of 0.02-9.0  $\mu\text{g mL}^{-1}$ .

#### 2.1. Synthesis of ligand, L

The ligand (L) was synthesized by the conventional method as well as grinding method.

##### By conventional method

The conventional method was adopted from a reported method and performed with slight modifications.[31] In the typical conventional method, o-phenylenediamine (9.45 g, 87.4 mmol) and thioglycolic acid (19.8 g, 215 mmol) were added into a round-bottom flask containing 4M HCl (100 mL) solution. The reaction mixture was refluxed under magnetic stirring for 24 h. The color of the reaction mixture changed to green. Subsequently, the reaction mixture was cooled at 0°C in an ice bath, and by maintaining the temperature below 5 °C, the pH of the reaction mixture was adjusted to 7.0 by the slow addition of concentrated ammonia solution. After the precipitation from the solution was completed, the separated gray-white solid was filtered and washed the residue with deionized water till the filtrate become colourless. The product was air dried and stored at room temperature. Isolated yield was 98%.

## By Grinding method

In the grinding method, the ligand (L) was synthesized by using a mortar and pestle. In the typical process, o-phenylenediamine (2.00 g, 18.5 mmol) and thioglycolic acid (4.25 g, 46.3 mmol) were added into a mortar pestle containing a 4M HCl (10 mL) solution. The reaction mixture was ground at room temperature for 1 h. The color of the reaction mixture changed to green. Subsequently, the reaction mixture was cooled at 0°C in an ice bath, and by maintaining the temperature below 5 °C, the pH of the reaction mixture was adjusted to 7.0 by the slow addition of concentrated ammonia solution. After the precipitation from the solution was completed, the separated gray-white solid was filtered and washed the residue with deionized water till the filtrate become colourless. The product was air dried and stored at room temperature. Isolated yield was 99%.

## 2.2. Synthesis of metal complexes L<sub>2</sub>Mo, L<sub>2</sub>Co and L<sub>2</sub>V

All the metal complex were synthesized by grinding method. In the representative method for the synthesis of L<sub>2</sub>Mo, ligand (0.1 g, 0.61 mmol) and 0.5 mL of ethanol were mixed in a mortar-pestle to make a pasty mass. Subsequently, H<sub>2</sub>MoO<sub>4</sub> (0.049 g, 0.305 mmol) and NaOH (0.048 g, 1.22 mmol) were added to the above mixture and ground at room temperature. The progress of the reaction was followed by the TLC. After 30 min of grinding, the reaction mixture was allowed to stand in the mortar pestle for additional 15 min with occasional grinding. After completion of the reaction, the products were washed with hexane (3 x 5 mL) and air dried well to get a powdery product. Similar procedure has been applied for the synthesis of L<sub>2</sub>Co and LV. Isolated yield 98% (L<sub>2</sub>Mo), 99% (L<sub>2</sub>Co) and 90% (L<sub>2</sub>V).

## 2.2 Catalytic activity of complexes

### 2.2.1. Oxidation of benzyl alcohol

The oxidation reaction of benzyl alcohol was done by conventional method as well as grinding methods as mention below.

#### 2.2.1.1 By conventional method

In the typical representative process, the reaction was started by using 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (0.218 ml, 0.0655 g, 1.926 mmol) to a round bottom flask which contained 5 mL of acetonitrile as solvent and the Mo(VI) catalyst (0.01 g). All the reagents were mixed well under magnetic stirring and waited for 2-3 min. Finally, the substrate benzyl alcohol (0.1 mL, 0.104 g, 0.962 mmol) was added into the mixture and heated. The reaction was continuing until completed. TLC was checked after 30 min, 1 h, 2 h, 3 h and so on to follow the progress of the reaction. The identity of the products was confirmed by comparing their R<sub>f</sub>-factor with authentic samples. For spotting on TLC, diluted benzyl alcohol and reaction mixture was used. After completion of the reaction, the products were separated by ether extraction and purified by column chromatography.

#### 2.2.2.2 By grinding method

In the typical representative process, the reaction was started by mixing the reaction mixture in a mortar and pestle. In this method, benzyl alcohol, 30% H<sub>2</sub>O<sub>2</sub>, acetonitrile (~0.3-0.5 mL) and metal complex were ground in the mortar pestle at room temperature. TLC was used to monitor the progress of the reaction. After the completion of the reaction, the products were extracted from the mixture and calculated the yield by the method as mentioned above.

### 2.2.2. Oxidation of methyl phenyl sulfide

In the typical representative process, the reaction was started by using 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (0.041 g, 1.2 mmol) to a round bottom flask which contained 5 mL of acetonitrile as solvent and the Mo(VI) catalyst (0.01 g). All the reagents were mixed well under magnetic stirring and waited for 2-3 min. Finally, the substrate methyl phenyl sulfide (0.124 g, 1.0 mmol) was added into the mixture and heated. The reaction was continuing until completed. The monitoring of progress of the reaction, isolation and purification of products and their identification were done as mentioned above for oxidation of benzyl alcohol. On the other hand, in grinding method, methyl phenyl sulfide (0.124 g, 1.0 mmol), 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (0.041 g, 1.2 mmol), acetonitrile (~0.3-0.5 mL) and catalyst (0.01 g) were used (no/minimum solvent).

### 2.2.3. Oxidation of Thiophene

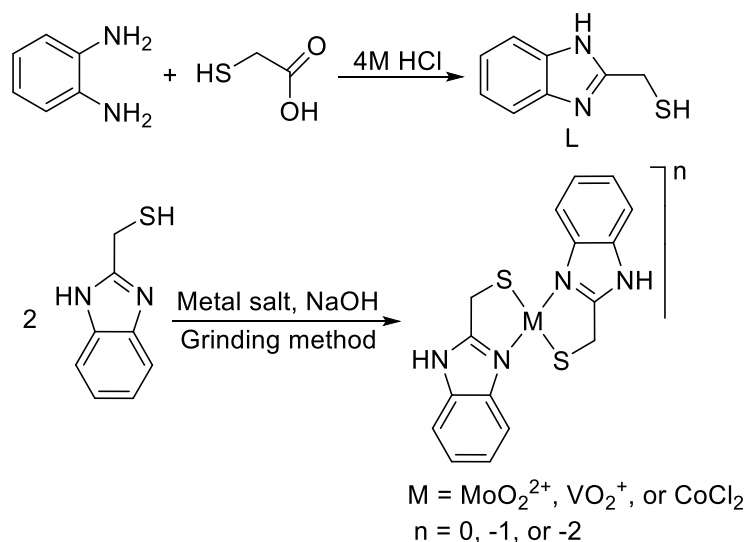
In the typical representative process, the reaction was started by using 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (0.041 g, 1.2 mmol) to a round bottom flask which contained 5 mL of acetonitrile as solvent and the Mo(VI) catalyst (0.01 g). All the reagents were mixed well under magnetic stirring and waited for 2-3 min. Finally, the substrate thiophene (0.84 g, 1.0 mmol) was added into the mixture and heated. The monitoring of progress of the reaction, isolation and purification of products and their identification were done as mentioned above for oxidation of benzyl alcohol. On the other hand, in grinding method, thiophene (0.84 g, 1.0 mmol), 30%  $\text{H}_2\text{O}_2$  (0.068 g, 2.0 mmol), acetonitrile (~0.3-0.5 mL) and catalyst (0.01 g) were used (no solvent).

## 3. Results and Discussion

### 3.1. Synthesis

The synthetic scheme for the synthesis of ligand and its metal complexes are shown in Scheme-1. The ligand (L) was synthesized by grinding method as well as conventional method. The synthesis by grinding method was not reported earlier but the conventional method was reported somewhere.[31] The advantages of the grinding method are outlined in the introduction. The synthesis was achieved by grinding the mixture of o-phenylenediamine and thioglycolic acid at a molar ratio of 1:2.5 in a mortar-pestle at room temperature. The reaction was completed in 1 h with an isolated yield of 99%. The product was pure, as confirmed by different analytical techniques. On the other hand, conventional method needed 24 h under reflux condition for its completion. This clearly demonstrated the advantages of the grinding method over the conventional method.

The metal complexes of L were synthesized by the LAG method by reacting the metal precursors with the ligand.  $\text{H}_2\text{MoO}_4$ ,  $\text{V}_2\text{O}_5$  and  $\text{CoCl}_2$  were used as metal precursors. The molar ratio of metal:ligand was kept at 1:2. We used very small amount of ethanol (~0.5 mL) as solvent to make the reaction mass pasty. The base, NaOH, was added to the reaction mixture to deprotonate the ligand and to provide the counter cation in the formation of complexes. The reactions were completed within 30 minutes of grinding, with very good isolated yield. We have also synthesized the metal complexes by refluxing the mixture of metal precursors, NaOH, and ligand in ethanol. But the process required over 20 h of reaction time to complete. Thus, the LAG method of synthesis is found to be much more effective than the conventional method. A comparison between these two methods and the color of metal complexes are given in Table-1.



**Scheme-1:** Synthetic scheme of ligand L and its metal complexes.

**Table-1:** Comparison of conventional and grinding method for the synthesis of ligands and its metal complexes.

Compounds	Colour	Conventional method		Grinding method	
		Reaction time	Yield (%)	Reaction time	Yield (%)
<b>L</b>	Colourless	26.5 h	95	30 min	98
<b>L<sub>2</sub>Mo</b>	White	20 h	98	30 min	99
<b>L<sub>2</sub>V</b>	Yellowish	26 h	95	30 min	97
<b>L<sub>2</sub>Co</b>	Brownish	30 h	92	30 min	94

### 3.2. Characterization

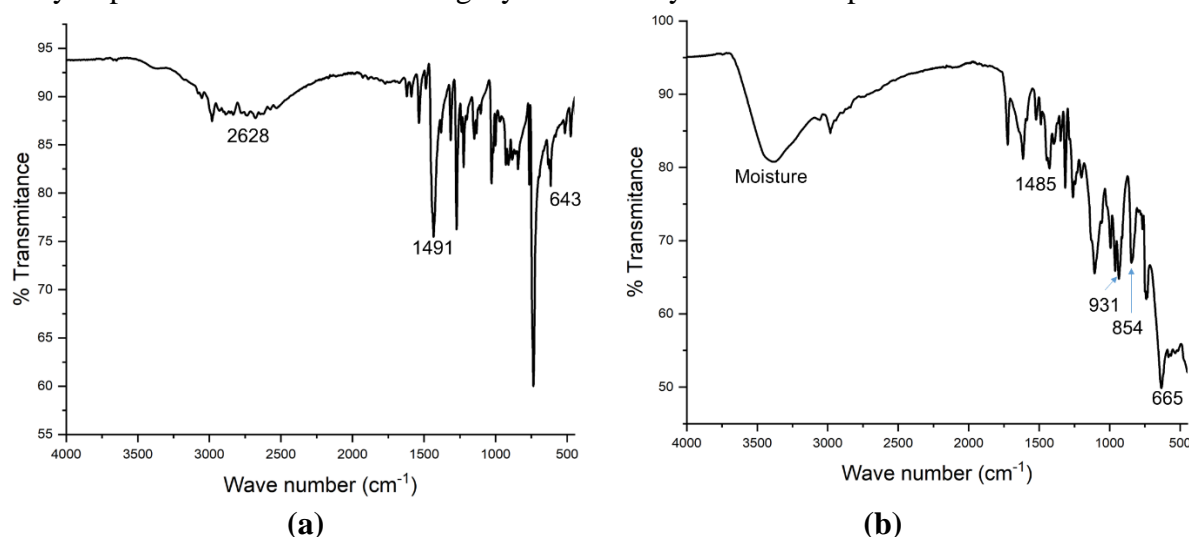
After the successfully synthesized the ligand, L and its metal complexes viz. L<sub>2</sub>Mo, L<sub>2</sub>V, and L<sub>2</sub>Co, all compounds were completely characterized by melting point determination, elementary analysis, FTIR, and <sup>1</sup>H NMR analysis. Table 2 shows the elemental analysis data for all the compounds. The elemental analysis data were found to be completely matched with the assigned molecular formulas. This shows the purity of the compound in solid form. Further calculation of metal-to-ligand molar ratio was found to be 1:2. This indicated the incorporation of one metal center with two ligands.

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

Compound	Molecular Formula	Element (Expt./Theo.)			
		C%	H%	N%	Metal%
<b>L</b>	C <sub>8</sub> H <sub>8</sub> N <sub>2</sub> S	58.23/58.51	4.78/4.91	17.29/17.06	---
<b>L<sub>2</sub>Mo</b>	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub> Mo	42.02/42.29	2.89/3.11	12.17/12.33	20.82/21.12
<b>L<sub>2</sub>V</b>	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub> VNa	44.14/44.45	2.95/3.26	12.67/12.96	11.61/11.78
<b>L<sub>2</sub>Co</b>	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> S <sub>2</sub> Cl <sub>2</sub> CoNa <sub>2</sub>	38.09/38.26	2.54/2.81	10.81/11.16	11.56/11.73

### 3.2.1 FTIR spectral analysis

The FTIR spectra for the ligand, L and L<sub>2</sub>Mo are shown in Figure-1, as representative of metal complexes, and the characteristic peaks for all the complexes are given in Table-3. In order to simplify the discussion, we are discussing herein by taking L<sub>2</sub>Mo as representative of complexes. The FTIR spectral analysis provided vital information about the structure of the complexes. It is evident that, the free ligand displayed peaks at 1491 and 2628 cm<sup>-1</sup> for the  $\nu(\text{C}=\text{N})$  and  $\nu(\text{S}-\text{H})$ , respectively. But after metal complex formation, with molybdenum in L<sub>2</sub>Mo, the peak responsible for S-H group was disappeared and the peak for  $\nu(\text{C}=\text{N})$  shifted to 1485 cm<sup>-1</sup>. This red shifting of  $\nu(\text{C}=\text{N})$  peak confirmed the coordination of benzimidazole moiety through N-atom. The disappearance of the  $\nu(\text{S}-\text{H})$  peak in L<sub>2</sub>Mo confirmed the coordination of thiolate group with the metal center. Interestingly, two new peaks appeared in the spectrum of L<sub>2</sub>Mo at 931 and 854 cm<sup>-1</sup> those are attributable to the  $\nu(\text{O}=\text{Mo}=\text{O})_{\text{asymmetric}}$  and  $\nu(\text{O}=\text{Mo}=\text{O})_{\text{symmetric}}$  mode of vibrations, respectively. Similar observations were found in L<sub>2</sub>V and L<sub>2</sub>Co. But in L<sub>2</sub>Co the peaks responsible for oxometal group was absent. Thus, FTIR analysis provided the structural integrity of the newly formed complexes.



**Figure 1:** FTIR spectra for (a) L and (b) L<sub>2</sub>Mo.

**Table-3:** FTIR peak assignments for L and complexes

Compound	$\nu(\text{S}-\text{H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{MO}_2)_{\text{sym}}$	$\nu(\text{MO}_2)_{\text{asym}}$	$\nu(\text{C}-\text{S})$
<b>L</b>	2628 (br, m)	1491 (s)	---	---	643
<b>L<sub>2</sub>Mo</b>	---	1485 (s)	854	931	665
<b>L<sub>2</sub>V</b>	---	1482 (s)	890	996	663
<b>L<sub>2</sub>Co</b>	---	1484 (s)	---	---	662

M = Mo or V, br = broad peak, s = strong, m = medium

### 3.2.2 <sup>1</sup>H NMR analysis

The <sup>1</sup>H NMR analysis of the ligand and its metal complexes provide important information regarding formation of the compounds. The important <sup>1</sup>H NMR peaks are presented in Table-4 and the representative spectra for L and L<sub>2</sub>Mo are shown in Figure-2. In the ligand, L, the peaks for -NH, -SH, -CH<sub>2</sub>- and -CH<sub>aromatic</sub> were appeared at 11.65, 2.12, 2.98,

and 7.05-7.61  $\delta$ , respectively. But, after metal complex formation, the peak for -SH disappeared which indicated the coordination of thiolate ion with the metal center. Besides, the -NH and -CH<sub>2</sub>- peaks were slightly shifter to down field after metal coordination. These shifting of peak positions confirmed the coordination of metal center with the ligand via N and S atom. This observation further confirmed the formation compounds as supported by FTIR spectral analysis. But, due to paramagnetic effect, the L<sub>2</sub>Co did not show characteristic <sup>1</sup>H NMR peaks.

**Table-4:** <sup>1</sup>H NMR peak assignments for the ligand and metal complexes.

Compound	-N-H	-SH	-CH <sub>2</sub> -	-C-H aromatic
<b>L</b>	11.65 (1H)	2.12 (1H)	2.98 (2H)	7.05-7.61 (4H)
<b>L<sub>2</sub>Mo</b>	11.75 (2H)	---	3.10 (4H)	7.11-7.72 (8H)
<b>L<sub>2</sub>V</b>	11.82	---	3.17 (4H)	7.15-7.69 (8H)
<b>L<sub>2</sub>Co</b>	---	---	---	---

“---” indicates not present.

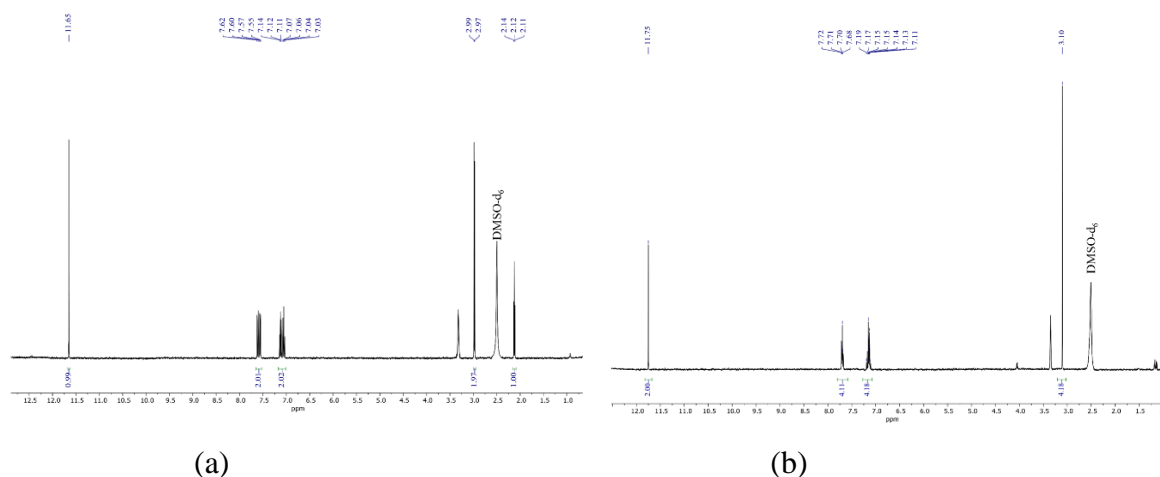


Figure-2: <sup>1</sup>H NMR spectra for (a) L and (b) L<sub>2</sub>Mo in DMSO-d<sub>6</sub>.

Thus, on the basis of above analysis, the structure of compounds may be proposed as given below in Figure-3.

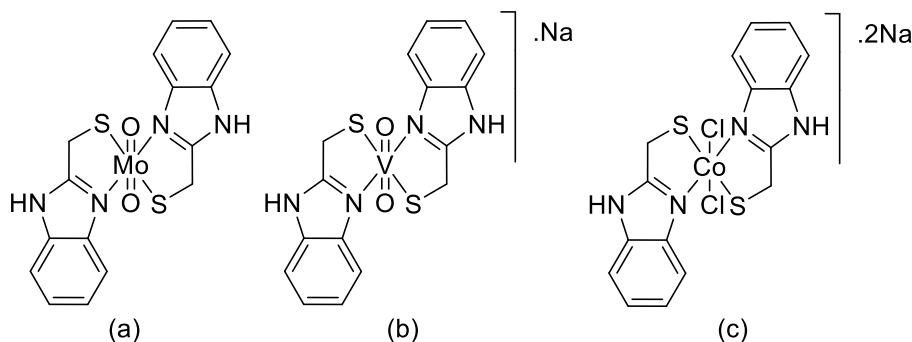


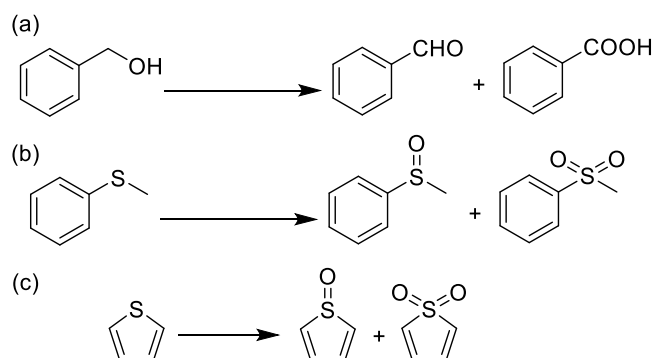
Figure-3: Proposed structure of complexes: (a) L<sub>2</sub>Mo, (b) L<sub>2</sub>V, and (c) L<sub>2</sub>Co.



### 3.3. Catalytic activity

#### 3.3.1 Selective oxidation of alcohol

The product selectivity of any chemical transformation is important. The oxidation of benzyl alcohol gives benzaldehyde and benzoic acid as products (Scheme-2). Thus, selectively getting only one product is a desirable condition. In order to achieve product selectivity and high yield, different reaction parameters, as mentioned above, were screened.



**Scheme 2.** Oxidation of (a) benzyl alcohol, (b) methyl phenyl sulfide, and (c) thiophene.

It was observed that solvent has great impact on product selectivity and yield. We have conducted the reaction in ethanol, methanol, acetonitrile, chloroform, dichloromethane, hexane, solventless, water, etc. in conventional method. The reactions were conducted by keeping the molar ratio of substrate:oxidant = 1:1.5 and 0.01 g of catalyst (LMO) at 75°C. The results are summarised below in Table-5. It is evident from the experiments that for all the solvents or solventless condition, benzyl alcohol was oxidized selectively into benzaldehyde. No over oxidation to benzoic acid was observed. The best solvent for this selective oxidation was found to be acetonitrile and achieved 98% yield in 9 h. It may be due to the higher stability of the intermediate in acetonitrile. Oxidation was possible in solvents ethanol and methanol as well. However, got lower yields viz. ~50% even though reactions were conducted for 24 h. This may be due to the possibility of competing oxidation reaction with the solvent and, thus, not suitable for this reaction. Oxidation in chloroform, dichloromethane, and hexane showed poor yield (viz. 5, 8 and 6%, respectively) in 24 h. This may be due to the immiscibility of oxidant with the solvents. We have also conducted the reactions in water as solvent and under solventless conditions. But the reaction times were found to be 16 h and 12 h for water and solventless condition, respectively, and those were higher than the reaction time in acetonitrile as solvent.

**Table 5.** Effect of solvent in the catalytic oxidation of benzyl alcohol by LMO.<sup>a</sup>

c	Time (h)	Yield (%)	Product selectivity, PhCHO:PhCOOH
<b>Acetonitrile</b>	<b>9.0</b>	<b>98</b>	<b>100:0</b>
Ethanol	24.0	54	100:0
Methanol*	24.0	47	100:0
Chloroform*	24.0	5	100:0
Dichloromethane*	24.0	8	100:0
Hexane*	24.0	6	100:0
Solventless	12.0	97	100:0
Water	16.0	98	100:0

<sup>a</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, Solvent = 5 mL, **L<sub>2</sub>Mo** = 0.01 g, Temperature = 75° C. \*Reactions were conducted at the boiling point of the used solvent.

After finding the best solvent, i.e., acetonitrile, we have conducted the oxidation reaction to screen the effect of temperature by keeping the molar ratio of substrate:oxidant = 1:1.5 and 0.01g of catalyst (**L<sub>2</sub>Mo**) in acetonitrile. The reactions were conducted at temperature of room temperature (RT), 45, 60, and 75°C. Figure 2 presents the required reaction time to achieve the 100% conversion of benzyl alcohol to benzaldehyde. It was seen that, with increase of reaction temperature, the reaction time decreases significantly. There was about 2-fold decrease of reaction time for the reaction at 75°C than RT.

In order to speed-up the oxidation reaction, amount of oxidant and catalyst were changed. In the preliminary stage, the amount of catalyst was changed and conducted the reactions with 5, 10, 15, and 20 mg of L<sub>2</sub>Mo at the molar ratio of Substrate:oxidant = 1:1.5 at 75°C in acetonitrile. It was found that lowering the amount of L<sub>2</sub>Mo from 0.01 g to 0.005 g increases the required reaction time. On the other hand, increasing the amount of L<sub>2</sub>Mo from 0.01g to 0.02g did not show a notable change in reaction time. In order to further oxidize benzyl alcohol to benzoic acid, the molar ratio of Substrate:oxidant was screened at 1:1.5, 1:2 and 1:4. However, no over oxidation to benzoic acid was observed. This showed the product selectivity of the reaction.

To minimize the impact of solvent on environment, reactions were conducted by grinding method by using a mortar and pestle. With minimum amount of acetonitrile (~0.3-0.5 mL), a reaction was done by maintaining molar ratio of Substrate:oxidant = 1:1.5 with 0.01 g L<sub>2</sub>Mo at RT.

Interestingly, the reaction time was decreased to 60 min to achieve the 100% conversion without compromising the product selectivity. Thus, the optimum reaction condition for the selective oxidation of benzyl alcohol to benzaldehyde was found to be molar ratio of Substrate:oxidant = 1:1.5 with 0.01g of catalyst at 75°C in acetonitrile as solvent (in conventional method). However, in grinding method, with the same ratio of substrate, oxidant and catalyst, the oxidation reaction can be successfully achieved with minimum amount of acetonitrile and RT. The catalytic activities for each of the complex was explored by conventional and grinding methods under optimized reaction condition and the results are shown in Table-6. It is evident from the results that the reaction by grinding method is faster than conventional method. Besides, it offered many advantages such as room temperature reaction and requirement of very small amount of solvent over conventional method. The catalyst L<sub>2</sub>Mo was found to offer best catalytic activity. On the other hand, LV(V) and LCo(II) did show low activity even after 24 h of reaction time.

**Table 6.** Oxidation of benzyl alcohol to benzaldehyde catalysed by synthesized complexes.

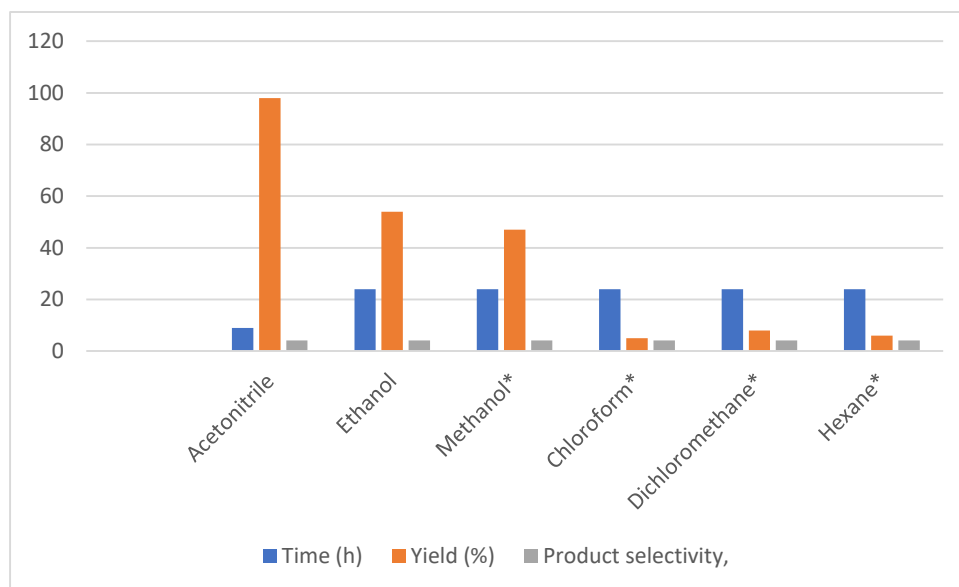
Compound	Conventional method <sup>a</sup>		Grinding method <sup>b</sup>	
	Time	Yield, %	Time	Yield, %
<b>L<sub>2</sub>Mo</b>	9.0 h	98	45 min	99
<b>L<sub>2</sub>V</b>	15.5 h	98	30 min	98
<b>L<sub>2</sub>Co</b>	24.0 h	95	1.0 h	93

<sup>a</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 = 5 mL, **L1W** = 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, **L1W** = 10 mg, Temperature = RT.

### 3.3.2 Selective oxidation of methyl phenyl sulfide and thiophene

The oxidation of methylphenylsulfide (MPS) leads to the formation of methylphenylsulfoxide (MPSO) and methylphenylsulfone (MPSOO) and the oxidation of thiophene (TP) leads to formation of thiophene-1-oxide (TPO) and thiophene-di-oxide (TPOO) (Scheme-2). In the preliminary catalytic study of the synthesized complexes, we had optimized the reaction conditions by choosing LMo as the representative catalyst. In order to obtain the selective oxidation, different reaction parameters, as mentioned above, were screened with MPS. The effect of solvents is shown in Figure-4 and acetonitrile was found to be best solvent in terms of reaction yield and sulfoxide selectivity. No over oxidation to MPSOO was observed at molar ratio of MPS:H<sub>2</sub>O<sub>2</sub> at 1:1.2.



**Figure 4.** Effect of solvent on the oxidation of MPS. Reaction condition: MPS (0.124 g, 1.0 mmol), z30% H<sub>2</sub>O<sub>2</sub> (0.041 g, 1.2 mmol), solvent (5 mL) and **LMo** (0.01 g).

The molar ratio of MPS:H<sub>2</sub>O<sub>2</sub> showed a significant role in the product selectivity in the catalytic oxidation of MPS. A molar ratio of MPS:H<sub>2</sub>O<sub>2</sub> maintained at 1:1.2 and 1:2.5 in acetonitrile as solvent showed sole product of MPSO and MPSOO, respectively. We have also conducted the reaction at different temperatures viz RT, 60 and 75°C. Highest activity was obtained at 75°C.

After successful selective oxidation of MPS with **LMo** under conventional method, we have conducted the reactions under grinding method by using a mortar and pastel. Interestingly, the selective oxidation was found with minimum amount of solvent (acetonitrile: ~0.3-0.5 mL) at room temperature. The reaction time was also decreased. The results are shown in Table-7. Identical molar ratio of MPS:H<sub>2</sub>O<sub>2</sub> was maintained at 1:1.2 and 1:2.5 for MPSO and MPSOO, respectively for product selectivity.

In case of oxidation of thiophene, the products may be thiophene-1-oxide (TSO) or thiophene-di-oxide (TSOO) (Scheme-2). We have conducted the oxidation reactions by choosing molar ratio of thiophene:H<sub>2</sub>O<sub>2</sub> at 1:1.2 and 1:2.5 and thiophene oxidised into TSO and TSOO, respectively. The results are shown in Table-8. However, the reaction needed little longer reaction time than oxidation of MPS. This may be due to the lower nucleophilicity of S-atom on thiophene than MPS. The results of grinding method were superior than conventional heating method. Besides, the products were isolated from the reaction mixture in highly pure form. The compound **LMo** showed the best oxidation activity and **LV(V)** and **LCo(II)** did not show oxidation of thiophene.

**Table 7.** Oxidation of MPS to MPSO catalysed by synthesized complexes.

Compound	Conventional method <sup>a</sup>		Grinding method <sup>b</sup>	
	Time	Yield, %	Time	Yield, %
<b>L<sub>2</sub>Mo</b>	2.5 h	99	25 min	98
<b>L<sub>2</sub>V</b>	3.5 h	97	30 min	98
<b>L<sub>2</sub>Co</b>	24.0 h	< 5%	2.0 h	< 5%

<sup>a</sup>Reaction conditions: MPS:H<sub>2</sub>O<sub>2</sub> = 1:1.2, catalyst = 0.01 g, acetonitrile = 5 mL, reaction temperature = 75°C.

<sup>b</sup>Reaction conditions: MPS:H<sub>2</sub>O<sub>2</sub> = 1:1.2, catalyst = 0.01 g, acetonitrile = ~0.3-0.5 mL, reaction temperature = RT.

**Table 8.** Oxidation of thiophene to thiophene-1-oxide catalysed by synthesized complexes.

Compound	Conventional method <sup>a</sup>		Grinding method <sup>b</sup>	
	Time	Yield, %	Time	Yield, %
<b>L<sub>2</sub>Mo</b>	4.0 h	98	45 min	99
<b>L<sub>2</sub>V</b>	5.0 h	99	65 min	97
<b>L<sub>2</sub>Co</b>	24.0 h	92	2.0 h	95

<sup>a</sup>Reaction conditions: thiophene:H<sub>2</sub>O<sub>2</sub> = 1:1.2, acetonitrile = 5 mL, catalyst = 0.01 g, reaction temperature = 75°C.

<sup>b</sup>Reaction conditions: thiophene:H<sub>2</sub>O<sub>2</sub> = 1:1.2, acetonitrile = ~0.3-0.5 mL, catalyst = 0.01 g, reaction temperature = RT.

### 3.3.3. Proposed reaction mechanism

Based on the available literature data and observations made herein, a proposed mechanism for catalytic oxidation of benzyl alcohol (as representative) is shown in Figure-5 by choosing  $L_2Mo$  as catalyst. In the preliminary step,  $L_2Mo$  reacted with  $H_2O_2$  to produce active peroxomolybdate species II (via path (a)). The active species II reacted with the substrate (benzyl alcohol) and oxidized it into benzaldehyde (via path (b)). After the oxidation, the species II is converted back into I, which is inactive, and again reacted with  $H_2O_2$ . In this way the cycle continues. After activating the species I, the  $H_2O_2$  is converted into water. The evidence of inactivity of species I came from the reaction of  $L_2Mo$  with benzyl alcohol in absence of  $H_2O_2$ , which was not proceed.

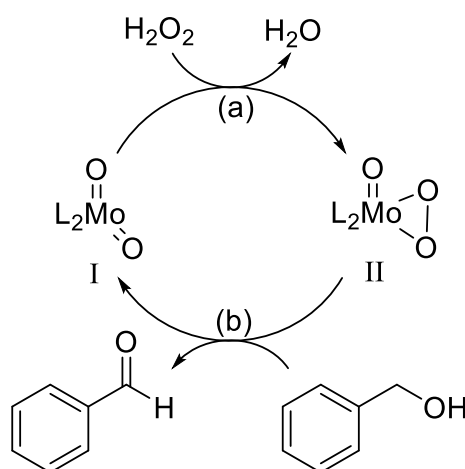


Figure-5: Proposed reaction mechanism.

## 4. Conclusions

The goal of this study was to synthesize catalytically active benzimidazole-metal complexes by applying green methodology. We have successfully achieved this by synthesizing L,  $L_2Mo$ ,  $L_2V$  and  $L_2Co$  by grinding method. The method offered several advantages over the conventional method such as shorter reaction time, improved reaction yield, requirement of minimum amount of solvents, etc. Each of the compounds were characterized fully with the help of different analytical methods such as melting point determination, FTIR,  $^1H$  NMR, etc. Further, we have successfully achieved good catalytic activities for each metal complexes towards oxidation of benzyl alcohol, methyl phenyl sulfide, and thiophene. The oxidation reactions were selective and products were isolated in pure form. Among them  $L_2Mo$  showed best activity.

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