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Journal of Sulfur Chemistry

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/gsrp20

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To cite this article: Hadi Kargar, Atefeh Moghimi, Mehdi Fallah-Mehrjardi, Reza Behjatmanesh-Ardakani, Hadi Amiri Rudbari & Khurram Shahzad Munawar (2021): New oxovanadium and dioxomolybdenum complexes as catalysts for sulfoxidation: experimental and theoretical investigations of E and Z isomers of ONO tridentate Schiff base ligand, Journal of Sulfur Chemistry, DOI: <u>10.1080/17415993.2021.1941020</u>

To link to this article: <u>https://doi.org/10.1080/17415993.2021.1941020</u>

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New oxovanadium and dioxomolybdenum complexes as catalysts for sulfoxidation: experimental and theoretical investigations of E and Z isomers of ONO tridentate Schiff base ligand

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ABSTRACT

A new ONO-tridentate Schiff base ligand (H₂L) derived by the condensation of nicotinic hydrazide with 5-chlorosalicylaldehyde has been prepared and characterized by combustion analysis (CHN), FT-IR and multinuclear (¹H and ¹³C) NMR spectroscopy. The crystalline nature and molecular structure of the ligand were confirmed by single-crystal X-ray diffraction analysis. Furthermore, the optimized structural parameters of the four possible configurations of the ligand including Z and E stereoisomers each containing two tautomeric forms (enol and keto) have also been investigated. The theoretical parameters were calculated by performing the DFT method using the B3LYP/Def2-TZVP level of theory. In addition to this, dioxomolybdenum(VI) (MoO₂L) and oxovanadium(V) (VOL) complexes with the entitled Schiff base ligand have also been prepared and characterized by different techniques. Then, the catalytic efficiencies of synthesized VOL and MoO₂L complexes were also explored for the oxidation of sulfides using 30% aqueous H_2O_2 as a source of oxygen. These homogeneous catalysts showed excellent catalytic activities in the oxidation of both aromatic and aliphatic sulfides.

ARTICLE HISTORY

Received 8 February 2021 Accepted 4 June 2021

KEYWORDS

Vanadium(V); molybdenum(VI); Schiff base; homogeneous catalyst; sulfoxidation

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Supplemental data for this article can be accessed here. https://doi.org/10.1080/17415993.2021.1941020



1. Introduction

Hydrazone, having -C(O)-NH-N = CH- moiety, constitutes a distinctive class of Schiff bases due to its particular modes of coordination and prodigious applications [1]. The aroylhydrazones possessing -OH group ortho to C = N group have the ability to manifest keto-enol tautomerism [2,3]. On the basis of this tautomeric interconversion, aroylhydrazones can behave like a neutral, monobasic, dibasic bidentate or tridentate ONO ligand and have the potential to bind with one or more than one metal centers. Usually, upon coordination with metal atoms, the deprotonation from OH to NH groups takes place [4–8].

The coordination chemistry of vanadium and molybdenum acquired considerable attention during the past few years due to their biochemical significance [9–12]. In spite of the key role of oxovanadium(V) [VO(V)] and dioxomolybdenum(VI) [MoO₂(VI)] complexes with aroylhydrazones in biological fields, their high catalytic activity made them more glamorous [13–16]. These vanadium and molybdenum based metal complexes have appreciable utilization in the field of organic chemistry, specifically for the oxidation of various organic species. These compounds have been extensively studied as oxidation catalysts for hydroxylation of benzene and phenols [17–19], epoxidation of olefins [20], oxidation of alcohols [19] and particularly sulfoxidation [21–24–25].

Sulfoxides are of prime importance due to their contribution in biological along with industrial asymmetric synthetic procedures. Sulfoxides are served as intermediates in formulations and processing of drugs, Swern oxidation [26,27] coupling reactions for the formation of C–C bond [28,29] and in the Diels–Alder reaction [30]. Numerous kinds of transition metals were employed in the literature for the sulfoxidation reactions such as iron, cobalt, titanium and manganese [31,32]. But oxovanadium complexes got an advantage over the rest of the metals because their cyclic voltammetry curves are capable of being reversed [33]. On the other hand, sulfoxidation by dioxomolybdenum complexes has the

advantages like excellent results under mild reaction conditions and the ability to interact with various kinds of substrates having diverse functional groups [34].

Many inorganic and organic species are employed for the oxidation processes and the most common oxygen-transfer reagents include hypochlorite (NaClO), peroxycarboxylic acids, periodic acid, dioxygen and hydrogen peroxide [35,36]. Among these oxidizing agents, H_2O_2 is considered an ideal oxidant because it is clean, non-toxic, cheap and environmentally friendly [37,38]. Moreover, it is frequently miscible with H_2O and many organic solvents, and produces only water as a by-product during the oxidation process. So, aqueous H_2O_2 along with a catalytic amount of various transition metals, specifically **VO(V)** and **MoO₂(VI)** complexes, are most frequently used [34,36,39–41].

In the current study, we are describing the synthesis of an ONO-donor aroylhydrazonebased azomethine compound by condensing nicotinic hydrazide and 5-chlorosalicylaldehyde and its vanadium and molybdenum complexes. On the basis of our interest in oxidation reactions [42–46] and keeping in mind the requirements of new effective catalytic systems, we have undertaken the exploration of new VO(V) and MoO₂(VI) complexes for the oxidation of sulfides by employing 30% aqueous H_2O_2 .

2. Results and discussion

2.1. Synthesis

An ONO donor Schiff base ligand (H_2L) has been synthesized in an alcoholic environment *via* condensation reaction by employing equimolar quantities of nicotinic hydrazide and 5-chlorosalicylaldehyde. The synthesized ligand was then treated separately with acety-acetonate salts of vanadium $[VO(acac)_2]$ and molybdenum $[MoO_2(acac)_2]$ in MeOH to generate the desired metal complexes, as given in Scheme 1. The synthesized metal



Scheme 1. Synthetic route of H₂L Schiff base ligand, VOL and MoO₂L complexes.



Scheme 2. Oxidation of sulfides with H₂O₂ carried out by homogeneous catalysts, VOL and MoO₂L.

complexes were then engaged in sulfoxidation to investigate their catalytic capabilities in the presence of aqueous hydrogen peroxide as presented in Scheme 2.

2.2. Structure description

A graphical representation of ligand (H_2L) is shown in the form of Figure 1. The exact molecular structure of the ligand is determined and investigated with the help of the DFT method by utilizing the B3LYP/Def2-TZVP level of theory both in gaseous and in solution forms. The geometrically optimized shapes of four possible configurations of the ligand including **Z** and **E** stereoisomers each containing two tautomeric forms, enol and keto, are shown in Figure S1. The summation of the electronic and the zero-point energy (E^{ZPE}), Gibbs free energy (G) and enthalpy (H) of four possible geometrical structures is given in Table S1. It was revealed from the data that the keto form of the stereoisomer **E** is more stable in its both gaseous and solution forms. The inferred results about the stability were further supported by the results obtained from single-crystal analysis. Table S2 gives a brief illustration of the prepared ligand (H_2L). The slight variation between the experimental and computational parameters may be ascribed on the basis of the fact that a solid crystalline sample is used for the collection of experimental data while computational details are collected by taking into account an isolated single gaseous molecule.

2.3. FT-IR study

Infrared spectral studies give a brief account of points of attachment of ligand with the metal atoms. Figure S2 shows a spectral representation of the ligand and its corresponding



Figure 1. ORTEP view of the asymmetric unit of H_2L ligand. Thermal ellipsoids are drawn at the 50% probability level, while the size of the hydrogen is shown arbitrarily.

metal complexes. The absorption spectra of the ligand show two prominent peaks *i.e.* 1676 and 3277 cm⁻¹, which are assigned to the ν (C = O) and ν (NH) moieties. The aforesaid peaks disappear in the FT-IR spectra of the oxovanadium and dioxomolybdenum complexes supporting the process of enolization of the amide group and a loss of proton to get attached with the metal atoms. The next point of attachment of ligand H_2L with the metal center is Schiff base linkage which is evident by transferring of its signal from $1616 \,\mathrm{cm}^{-1}$. The emergence of new peaks close to the fingerprint region at 1247 and 1292 cm^{-1} is assigned to the enolic ν (C–O) group in oxovanadium and dioxomolybdenum compounds, accordingly. Furthermore, the dioxomolybdenum moiety [cis-Mo(O)₂] shows its particular peaks at 916 and 933 cm⁻¹, which are strongly supported by the previously outlined analogous structures from the literature [47,48]. Likewise, V = O peak, which is the characteristic for the oxovanadium complexes observed at 952 cm^{-1} , is also comparable with the structurally equivalent compounds delineated earlier [49-51]. Coordination of ligand with metals is further assisted by the emergence of metal-oxygen and metal-nitrogen peaks at 572 and 478 cm⁻¹ for dioxomolybdenum compound and at 580 and 484 cm⁻¹ for oxovanadium compound, accordingly [49-52]. A comparative comprehensive analysis of the actual and theoretically calculated stretching vibrational peaks of the ligand is given in Table S3. It is revealed from the data that the results obtained from both kinds of parameters are closely related to each other.

2.4. ¹H and ¹³C NMR studies

The nuclear magnetic studies are further helpful in confirming the mode of attachment of ligand upon complexation. The prepared compounds were easily soluble in dimethyl sulfoxide; hence, its deuterated form (DMSO- d_6) was selected to measure the nuclear magnetic resonances (Figures S3–S8). The two very significant signals visible at $\delta = 11.37$ and 12.32 ppm in the ¹H NMR spectra of **H**₂**L** were allocated to the iminic (NH) and phenolic (OH) protons, correspondingly. The disappearance of these signals on reacting with metal centers is the confirmation of the fact that phenolic and enolic oxygens are involved in bonding with metal atoms. It also gives an indication of keto-imine tautomerism during complex formation. Furthermore, a downfield shifting of signal for azomethine proton was spotted from $\delta = 8.63$ ppm to $\delta = 8.75$ in **VOL** and $\delta = 8.98$ ppm in **MoO**₂**L**, which is due to the reduction of electronic density at this site due to the involvement azomethine nitrogen in the establishment of bond with the metal atom. The aromatic protons gave their peaks in the anticipated area ranging from $\delta = 6.96$ to 9.10 ppm. The influence of coordination on these aromatic protons is negligible as there is an insignificant change in chemical shift values upon complexation.

In ¹³C NMR spectra, the characteristic peaks for carbonyl (C=O), phenolic (C-OH) and methine (=C-) carbons in the oxovanadium(V) complex were detected at δ = 167.2, 158.7 and 155.4 ppm, accordingly. The same kinds of peaks in the dioxomolybdenum complex were also noticed in a nearly comparable range with the oxovanadium complex at δ = 167.7, 158.1 and 155.7 ppm, correspondingly. There is an appreciable change in the NMR signals of the carbon atoms, existing in the close territory of coordinated atoms *i.e.* C7, C1 and C8, which gives a confirmation of change in the electronic cloud due to the involvement of these moieties in complexation. The appearance of peaks for aromatic carbon atoms of all of the synthesized compounds in their corresponding portions confirms

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the earlier documented reports. All of the chemicals shift values whether experimental or calculated of the prepared compounds are listed in Table S4. It is revealed from the data that both kinds of investigations are supportive to each other and hence strengthens the concept of modes of coordination of ligand with metals.

2.5. Mulliken atomic charges

From Mulliken's charge analysis of H_2L (Table S5), it is evident that the negative charge densities in the ligand are mostly located on phenolic and carbonyl oxygens, and the carbon atoms connected with them (C1 and C8) have the highest charge densities.

2.6. Electronic properties studies

The elaboration of chemical reactivities of the molecules and their affiliations with physical and chemical properties can be investigated by using molecular electrostatic potential (MEP). The MEP studies are helpful for the location of electrophilic and nucleophilic sites of the molecules on the basis of their electrostatic potentials. These sites are denoted either by blue (electrophilic) or by red (nucleophilic) colors. The molecular electrostatic potential diagrams and the data of electrostatic potentials of four possible configurations of the ligand are presented in Figure S9. As it can be seen from the figure that in the keto form of **E** stereoisomer, the negative site with an electrostatic value of ~55 kcal mol⁻¹, present between the oxygen atoms of the carbonyl (C = O) and phenolic (–OH) groups, is marked by red color. Therefore, these atoms are the best candidates for nucleophilic attack on the metal atom to form a complex. The obtained data are completely compatible with Mulliken's atomic charges distribution and are given in Table S5.

To get the information about the electronic distribution of the frontier molecular orbitals, the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) energy levels of the H_2L were calculated by the B3LYP/Def2-TZVP level of theory. The HOMO and LUMO energies for four possible configurations of the ligand and their energy gaps (ΔE) are presented in Figure S10. In the keto form of E stereoisomer, the HOMO is localized mostly around the aryl ring, azomethine and carbonyl groups, while the LUMO is distributed over almost all of the atoms.

2.7. Catalytic activity studies

The catalytic efficiencies of the oxovanadium and dioxomolybdenum complexes were evaluated through the sulfoxidation reactions. The reaction conditions were optimized by selecting a model reaction involving the oxidation of 1 mmol of diphenyl sulfide $[(C_6H_5)_2]$ by using 2 mmol of H₂O₂.

2.7.1. Effect of solvent

Several different kinds of solvents, like C_2H_5OH , CH_3OH , CH_3CN , $(CH_3)_2CO$, 1,2dichloroethane, CH_3Cl , CCl_4 and dichloromethane (DCM) were examined by using H_2O_2 as an oxidant, and **VOL** and **MoO_2L** as catalysts, to sort out the most suitable solvent. Although it was revealed from the data that the reaction was carried out well in methanol and acetonitrile, the ecofriendly nature of ethanol persuaded us to choose it as the reaction solvent (Figure S11).

2.7.2. Effect of temperature

A series of experiments, performed in ethanol at different temperatures, indicated that the reaction was completed only under reflux conditions for both catalysts (Figure S12).

2.7.3. Effect of oxidant

The effect of various kinds of oxidants like NaIO₄, H₂O₂, urea H₂O₂ (UHP), (Bu)₄NIO₄ and *tert*-BuOOH was explored for the oxidation of $(C_6H_5)_2$ by using **VOL** and **MoO₂L** as catalysts. It was inferred from the results obtained that H₂O₂ can be regarded as the best source for the provision of oxygen. Furthermore, the sulfoxidation can't be carried out without the use of oxidant (Figure S13).

Although diphenyl sulfoxide was obtained as the only product by using < 2 mmol of oxidant, the conversion could not be completed even at a longer period of time. Therefore, at least 2 mmol of H₂O₂ was selected as the optimized amount for oxidizing 1 mmol of sulfide.

2.7.4. Optimization of catalytic amount

The optimization of the amount of catalyst is also very important for developing a catalytic cycle; in this regard, the effect of various amounts of catalysts was explored and the data are presented in Figure S14. It was inferred from the results that the reaction could not be proceeded without the use of a catalyst. The amount of catalyst has a direct relationship with the rate of reaction until the optimum catalytic amount is involved, *i.e.* 0.004 mmol for **VOL** and 0.006 mmol for **MoO**₂**L**, for sulfoxidation of 1 mmol of $(C_6H_5)_2S$.

2.7.5. Oxidation of sulfides

To explore the generalization of the developed procedure, a variety of aliphatic and aromatic sulfides were oxidized under optimal conditions to produce respective sulfoxides and sulfones (Table 1). The data in the table directed us to conclude that the majority of the sulfides were entirely transformed into their respective products, and in many cases, two different reaction times have been reported in which the time taken by **VOL** complex was less than that of **MoO₂L** complex. Also, oxovanadium catalyst showed higher selectivity for the sulfoxide formation over the sulfone. It was found that in these reaction conditions, sulfoxides were produced first which were gradually converted into sulfones with the increase in reaction time.

2.7.6. Mechanism

Based on previously reported mechanisms [53], for the oxidation carried out by oxometal complexes, a probable mechanism for the oxidation of sulfides to the respective sulfoxides and sulfones with H_2O_2 catalyzed by MoO_2L is proposed in Scheme 3. It seems that the metal atom of the catalyst, MoO_2L , can be attacked by nucleophiles. Therefore, on the treatment of molybdenum complexes with H_2O_2 , a peroxomolybdenum moiety is formed. This intermediate is vital for the oxidation of sulfides to sulfoxides *via* a single-step oxygen-transfer reaction. The sulfur atom attacks electrophilically on the oxygen of

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	y Sulfide	VOL complex			MoO ₂ L complex		
Entry		Time (min)	Sulfoxide (%) ^{b,c}	Sulfone (%) ^{b,c}	Time (min)	Sulfoxide (%) ^{b,c}	Sulfone (%) ^{b,c}
1	<u>~s</u> ~	30	100	0	30	95	5
2	<i>∕</i> ∽ ^s √∕∾	60	70	30	70	80	20
3		5	100	0	5	95	5
4	S-CH3	10	100	0	10	70	30
5	s-s-	15	100	0	50	80	20
6	S-CH ₂	15	90	10	15	95	5
7	Me-S-CH ₂ -S-CH ₂ -S-S-S-CH ₂ -S-S-S-CH ₂ -S-S-S-S-CH ₂ -S-S-S-S-S-S-S-S-S-S-S-S-S-S-S-S-S-S-S	30	90	10	35	75	25
8		120	0	0	210	50	50

Table 1. Oxidation of sulfides with H₂O₂ catalyzed by VOL and MoO₂L complexes.^a

^aReaction conditions: sulfide (1 mmol), H_2O_2 (2 mmol), EtOH (10 mL), catalyst (**VOL** = 0.004 mmol or **MoO₂L** = 0.006 mmol).

^bGC (entries 1–4) or isolated yield (entries 5–8).

^cAll products were identified by comparison of their physical and spectral data with those of authentic samples.



Scheme 3. Plausible mechanism for the oxidation of sulfides with H₂O₂ catalyzed by VOL complex.

peroxide followed by the breaking the O–O bond, simultaneously, which causes the transfer of oxygen to sulfide to convert it into sulfoxide. Further oxidation, according to the same mechanism, leads to the formation of sulfone. The same kind of mechanism is also proposed for the **VOL** complex.

3. Conclusion

The current work is based on the synthesis of an ONO-donor tridentate Schiff base and its oxovanadium and dioxomolybdenum complexes, and their characterization by using elemental and various spectroscopic techniques. Only ligand was isolated in the form of single crystal; hence, its theoretical calculations were performed by employing DFT method with the B3LYP/Def2-TZVP level of theory. The computational data for four possible configurations of the ligand including Z and E stereoisomers were also calculated. The exact molecular structure of H_2L ligand determined by single-crystal X-ray crystallography is in agreement with the theoretical results for the keto form of E stereoisomer. Moreover, after preparation and characterization of the VOL and MoO₂L complexes, their catalytic activities were investigated for the oxidation of sulfides by using H_2O_2 in ethanol under reflux conditions. The metal centers of the catalysts are attacked by the hydrogen peroxide to form intermediates which are further ambushed by the sulfur to give sulfoxides by breaking O-O bond. The results showed that oxovanadium catalyst has higher selectivity for the sulfoxide formation over the sulfone. In the future, these catalysts can be employed industrially for hydroxylation, epoxidation and selective oxidation of benzylic alcohols.

4. Experimental

4.1. Materials and methods

All of the chemicals, solvents and reagents mentioned in the current research work were of laboratory/analytical grades and used without adapting any additional purification methods. Percentage composition of C, H and N was calculated by combustion analysis by operating Heraeus CHN-O-FLASH EA 1112 instrument. Nuclear magnetic studies of ¹³C and ¹H were performed by BRUKER AVANCE 400 MHz spectrometer by taking tetramethylsilane (TMS) as a standard reference material to be used internally. All chemical shift values (δ), assigned with respect to TMS, are mentioned in ppm. Infrared spectra were recorded by making the pellets of samples by mixing them with KBr with the assistance of an FT-IR Prestige21 spectrophotometer. The data of X-ray diffraction analysis were recorded on a STOE IPDS-II diffractometer, which generates Mo-K α radiations monochromated by the graphite.

4.2. Synthesis

4.2.1. Synthesis of a tridentate (ONO) Schiff base ligand (H₂L)

To a 15 mL of hot methanolic solution of 5-chlorosalicylaldehyde (10 mmol, 1.57 g), a 15 mL methanolic solution of Nicotinic hydrazide (10 mmol, 1.37 g) was mixed dropwise. The resultant solution was then refluxed by using a water bath for \sim 3 h by using a magnetically equipped hot plate. After that, the contents of the mixture were left as such to procure the room temperature. The precipitates of the anticipated Schiff base product (H₂L) appeared which were then separated by filtration and washed in triplicate with cold MeOH for the purpose of purification. The obtained product was further dissolved in hot MeOH to prepare a saturated solution for the growth of single crystals appropriate for the X-ray single-crystal diffraction analysis.

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H₂L: Yield 73%. *Anal.* Calc. for $C_{13}H_{10}ClN_3O_2$: C, 56.64, H, 3.66; N, 15.24, Found: C, 56.75; H, 3.71; N, 15.15%. FT-IR (KBr, cm⁻¹); 3277 (ν_{N-H}); 1676 ($\nu_{C=O}$); 1616 ($\nu_{C=N}$); 1591, 1477 ($\nu_{C=C}$); 1186 (ν_{C-O}); 1026 (ν_{N-N}).¹H NMR (400 MHz, DMSO-*d*₆, ppm): 6.96–9.10 [7 H, m, Ar-H], 8.63 [1 H, s, (CH=N)], 11.17 [1 H, s, (-NH)], 12.32 [1 H, s, (-OH)]. ¹³C NMR (100 MHz, DMSO-*d*₆, ppm): 118.2, 120.6, 123.0, 123.6, 127.4, 128.6, 130.9, 135.4, 146.1, 148.6, 152.5, 156.0, 161.5.

4.2.2. Synthesis of VOL complex

The oxovanadium complex **VOL** was synthesized by treating equimolar quantities of $[V^{IV}O(acac)_2]$ (0.5 mmol, 0.132 g, acac = acetylacetonate) with H₂L (0.5 mmol, 0.138 g) after dissolving them in hot CH₃OH (25 mL), separately. The mixed stuff was kept under the refluxed condition at least for 3 h until the oxovanadium(V) complex was settled down at the bottom which was then filtered off and washed sensibly with H₂O, CH₃OH and (C₂H₅)₂O and eventually dried in a desiccator by employing anhydrous CaCl₂.

VOL: Yield 66%. *Anal.* Calc. for $C_{14}H_{11}ClN_3O_4V$: C, 45.25; H, 2.98; N, 11.31, Found: C, 45.34; H, 3.03; N, 11.22%. FT-IR (KBr, cm⁻¹); 1600 ($\nu_{C=N}$); 1352 ($\nu_{C=N-N=C}$); 1456, 1544 ($\nu_{C=C}$); 1292 (ν_{C-O}); 1014 (ν_{N-N}); 952($\nu_{V=O}$); 580 (ν_{V-O}); 484 (ν_{V-N}).¹H NMR (400 MHz, DMSO-*d*₆, ppm): 3.19 [3 H, s, (-OCH₃)], 7.01–9.16 [7 H, m, Ar-H], 8.76 [1 H, s, (CH = N)]. ¹³C NMR (100 MHz, DMSO-*d*₆, ppm): 65.7, 119.1, 120.7, 121.7, 123.9, 125.7, 126.2, 135.5, 147.7, 148.8, 149.5, 155.4, 158.7, 167.2.

4.2.3. Synthesis of MoO₂L complex

The same procedure was repeated for the preparation of dioxomolybdenum(VI) complex (MoO_2L), as described above just by replacing the vanadium precursor with molybdenum salt [$Mo^{VI}O_2(acac)_2$]. In this case, the product was obtained by employing an ice bath for the purpose of cooling.

MoO₂L: Yield 72%. *Anal.* Calc. for $C_{14}H_{12}$ ClMoN₃O₅: C, 38.77; H, 2.79; N, 9.69, Found: C, 38.96; H, 2.86; N, 9.53%. FT-IR (KBr, cm⁻¹); 1614 ($\nu_{C=N}$); 1427 ($\nu_{C=N-N=C}$); 1469, 1546 ($\nu_{C=C}$); 1247 (ν_{C-O}); 1035 (ν_{N-N}); 933 ($\nu_{O=Mo=O}$) *asym*; 916 ($\nu_{O=Mo=O}$) *sym*; 572 (ν_{Mo-O}); 478 (ν_{Mo-N}).¹H NMR (400 MHz, DMSO-*d*₆, ppm): 3.37 [3 H, d, (-OCH₃)], 4.07 [1 H, q, (-OH)], 7.01–9.15 [7 H, m, Ar-H], 8.98 [1 H, s, (CH = N)]. ¹³C NMR (100 MHz, DMSO-*d*₆, ppm): 65.5, 120.6, 121.5, 124.0, 124.9, 125.9, 133.0, 134.4, 135.5, 148.8, 152.5, 155.7, 158.1, 167.7.

4.3. X-ray crystallographic data collection H₂L ligand

The diffraction analysis of the ligand H_2L was performed with the help of STOE IPDS-II diffractometer, which employs graphite-based monochromator to generate Mo-K α radiations.

The details of diffractions were obtained at 298(2) K in a series of ω -scans in 1° oscillations and solved with the help of Stöe X-AREA [54] software package. A numerical absorption correction was applied using the X-RED [55] and X-SHAPE [56] software for the compound under investigation. The results were amended for Lorentz and polarizing effects. The molecular structure of the ligand was resolved by direct procedures using SIR2004 [57]. All of the atoms except hydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2 using SHELXL [58]. Table S6 gives a brief overview of diffraction data collected from H₂L.

4.4. Computational details

The calculations based on density functional theory (DFT) were accomplished by employing Gaussian 09 package[59] at the B3LYP level of theory [60] with the help of the Def2-TZVP basis set [61]. The solution phase modulation was processed with the help of IEFPCM by considering the solvent [62]. The optimization of geometrical parameters was analyzed by frequency analysis to make sure that they are at the local minima on the molecular potential energy surface (PES). It was revealed from the data that there is no imaginary frequency. The multinuclear (¹H and ¹³C) NMR magnetic isotropic shielding tensors were obtained by the standard Gauge-Independent Atomic Orbital (GIAO) approach in the solution phase [63]. The chemical shifts of the ligand were calculated with the help of the B3LYP/Def2-TZVP level and IEFPCM model as an implicit model of solvent and equated with the actual experimental results collected in deuterated dimethyl sulfoxide. The same solvent was employed for all IEFPCM calculations for H2L and tetramethylsilane. The chemical shift values (δ) were calculated by subtracting the appropriate isotropic part of the shielding tensor from that of tetramethylsilane $\delta i = \sigma_{TMS} - \sigma i$. The isotropic shielding constants for tetramethylsilane calculated in the solution phase at the B3LYP/Def2-TZVP level of theory were equal to 31.92 and 184.52 ppm for the ¹H nuclei and the ¹³C nuclei, accordingly. The Chemissian program was utilized for the preparation of contour plots of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [64].

4.5. Catalysis experiments

In a typical experiment, to a 1 millimolar solution of diphenyl sulfide and VOL (0.004 mmol) or MoO_2L (0.006 mmol) in EtOH (10 mL), 30% aqueous H₂O₂ (2 mmol) was mixed with the reacting stuff and refluxed along with vigorous stirring for a definite period of time and the results are given in Table 1. The monitoring of the catalytic cycle was ensured by TLC (eluent, *n*-hexane:ethyl acetate, 5:2) while the percentage yield was determined with the help of gas chromatography. The products were then purified with the help of liquid chromatography by using silica gel as a stationary phase and a mixture of *n*-hexane and ethyl acetate (70:30) as a mobile phase. The spectroscopic data of the purified products were then compared with the available data bank of standard samples for their characterization.

Acknowledgments

We gratefully acknowledge the practical support of this study by Ardakan University and Payame Noor University.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Supplementary materials

CCDC 2056759 contains the supplementary crystallographic data of the Schiff base ligand. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving. html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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