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Research paper

Synthesis, structural studies and catalytic activity of a series of dioxidomolybdenum(VI)-thiosemicarbazone complexes

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ABSTRACT

Reaction of the thiosemicarbazone ligands, [4-(*p*-bromophenyl)thiosemicarbazone of salicylaldehyde (H_2L^1), 4-(*p*-X-phenyl)thiosemicarbazone of *o*-vanillin {X = F (H_2L^2), X = Cl (H_2L^3) and X = OMe (H_2L^4)}, 4-(*p*-bromophenyl)thiosemicarbazone of 5-bromosalicylaldehyde (H_2L^5), and 4-(*p*-chlorophenyl) thiosemicarbazone of *o*-hydroxynaphthaldehyde (H_2L^6)] with $[MoO_2(acac)_2]$ afforded a series of new oxidomolybdenum(VI) complexes $[Mo^{(VI)}O_2L^{1-6}(solv)]$ (**1–6**) {where solv (solvent) = DMSO (**1**, **3**, **5** & **6**) and H_2O (**2** & **4**)}. The molecular structures of **2** and **3** were determined by X-ray crystallography, demonstrating the dibasic tridentate behavior of ligands. The cyclic voltammogram pattern is similar for **1–6**, which includes two irreversible reduction processes within the potential window −0.71 to −0.66 V and −0.92 to −0.85 V corresponding to the metal centered reduction from $Mo^{(VI)}/Mo^{(V)}$ and $Mo^{(V)}/Mo^{(IV)}$ respectively. Catalytic potential of **1–6** was tested for the oxidation of styrene and cyclohexene. The effect of various parameters such as the amount of catalyst, oxidant, $NaHCO_3$, and solvent was checked to optimize the conditions for the best performance of the catalyst. 100% product selectivity for the formation of cyclohexene oxide from cyclohexene and ∼98–99% product selectivity for the oxidation of styrene to styrene oxide was observed.

1. Introduction

The transition element molybdenum (Mo) is of essential importance for nearly all biological systems as it is required by enzymes catalyzing diverse key reactions in the global carbon, sulfur and nitrogen metabolism [1]. It occurs in a wide range of metalloenzymes in bacteria, fungi, algae, plants, and animals where it forms part of the active sites of these enzymes [2].

Molybdenum complexes are known for their catalytic applications in the oxidation [3–19] and oxidative bromination of organic substrates [20–23], and the oxidation of sulfides [24–27]. Mo(VI) complexes are also known to be very active as epoxidation catalysts, generally in a solution of an organic solvent, especially for neutral complexes [28–30], much as evidenced by a number of publications [11,16,18,24,31–38]. Oxido-peroxido Mo complexes have been known to exhibit selective catalytic oxidation of alkanes to aldehydes over alcohols [39] and have also demonstrated chemoselective deoxygenation of sulfoxides to sulfides in excellent yields [25]. The catalytic activity of molybdenum complexes are sensitive to the donor/acceptor ability of the ligand and to steric and strain factors.

In addition, thiosemicarbazones are versatile ligands which can coordinate in both their neutral and anionic form [40,41]. Transition metal complexes derived from thiosemicarbazones have shown potent catalytic activity such as oxidation of benzyl alcohol and cyclohexanol [42,43], catalysts for the aryl–aryl coupling reaction [44], reduction and condensation of nitriles [45] and the Suzuki–Miyaura coupling reaction [46]; the catalytic efficiency being dependent on the substituents on the thiosemicarbazone ligand core.

In continuation with our previous studies on the catalytic activity of dioxidomolybdenum(VI) complexes of O, N donating ligands [22,47,48], herein we have tried to explore the catalytic activity of complexes derived from ligands containing ONS donor atoms for epoxide generation. Epoxides are important pharmacophores in

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bioactive natural products, such as dynemicin and fumagillin [49,50] and are readily obtained from alkenes by the use of strong organic oxidants (m-CPBA, $NaClO_4$) [51] or smoother oxidants (THBP, H_2O_2) [28,29,52] with the assistance of metal-based catalysts (Fe, Mn, Re, Mo, V, W) [28,29,52–54]. Among these metals, molybdenum garnered much attention.

In this work, we have described the synthesis of a series of *cis*–dioxidomolybdenum(VI) $[Mo^{(VI)}O_2L^{1/5/6}(DMSO)]$ (**1**, **5** & **6**), $[Mo^{(VI)}O_2L^{2/4}(H_2O)]$ (**2** & **4**), and $[Mo^{(VI)}O_2L^3(DMSO)]_4{\cdot}2DMSO$ (**3**) complexes using tridentate ONS donating thiosemicarbazone ligands. The complexes have been fully characterized by spectroscopic methods and their redox behavior studied by cyclic voltammetry. Molecular structures of **2** and **3** have been determined by X–ray crystallography. The role of the synthesized $Mo^{(VI)}$ complexes (**1**–**6**) as catalysts for the epoxidation of styrene and cyclohexene have also been studied, considering the importance of epoxides as precious precursors in organic synthesis.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from commercial sources and used without further purification. Reagent grade solvents were dried and distilled prior to use. $[Mo^{(VI)}O_2(acac)_2]$ was prepared as described in the literature [55]. The thiosemicarbazides were prepared from distilled substituted aniline by a known method reported earlier [56]. The ligands 4-(*p*-bromophenyl)thiosemicarbazone of salicylaldehyde (H_2L^1), 4-(*p*-X-phenyl)thiosemicarbazone of *o*–vanillin {where X = F (H_2L^2) and X = Cl (H_2L^3) and X = OMe (H_2L^4)}, 4-(*p*-bromophenyl)thiosemicarbazone of 5–bromosalicylaldehyde (H_2L^5), and 4–(*p*-chlorophenyl)thiosemicarbazone of *o*-hydroxynaphthaldehyde (H_2L^6) were prepared by reported methods [41,57,58]. Elemental analyses were performed on a Vario ELcube CHNS Elemental analyzer. IR spectra were recorded on a Perkin–Elmer Spectrum RXI spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker Ultrashield 400 MHz spectrometer using $SiMe_4$ as an internal standard. Electronic spectra were recorded on a Lamda25, PerkinElmer spectrophotometer. Electrochemical data were collected using PAR electrochemical analyzer and a PC–controlled potentiostat/galvanostat (PAR 273A) at 298 K in a dry nitrogen atmosphere, using CH_3CN as the solvent medium. The complex concentration used for cyclic voltammetry was 10^{-3} M. Cyclic voltammetry experiments were carried out with glassy carbon working electrode, platinum auxiliary electrode and Ag/AgCl electrode. The starting potential used for recording the cyclic voltammogram was 0.0 V. Commercially available TEAP (tetraethyl ammonium perchlorate) was dried and used as a supporting electrolyte (0.1 M) for recording cyclic voltammograms of the complexes. ESI-MS was recorded on the SQ–300 MS instrument operating in ESI mode, employing complex concentration of 100 pmol/microliter. The capillary exit voltage was 120 V and the drying gas temperature was 300 °C. The identity of the catalytic products was confirmed using a GC–MS model Perkin–Elmer, Clarus 500 by comparing the fragments of each product with the library available. The percent conversion of the substrate and the selectivity of the products were calculated from GC data using the formulae presented elsewhere [13].

2.2. Synthesis of dioxidomolybdenum(VI) complexes $[Mo^{(VI)}O_2L^{1-6}(solv)]$ (**1**–**6**)

The synthetic procedure for complex preparation is as reported previously [41,57]. To a solution of ligand, H_2L^{1-6} (1.0 mmol), 30 mL of ethanol, $Mo^{(VI)}O_2(acac)_2$ (1.0 mmol) was added. The resulting mixture was refluxed for 2 h and filtered. Dark brown colored microcrystalline residues were obtained in each case, which was recrystallized from DMSO to obtain complexes $[Mo^{(VI)}O_2L^{1-6}(solv)]$ (**1**–**6**).

2.2.1. $[Mo^{(VI)}O_2L^1(DMSO)]$ (**1**)

Yield: 0.40 g (73%). Anal. calc. for $C_{16}H_{16}BrMoN_3O_4S_2$: C, 34.67; H, 2.91; N, 7.58. Found: C, 34.65; H, 2.90; N, 7.60. ^{13}C NMR (DMSO d_6, 100 MHz) δ: 161.55, 159.41, 155.60, 152.56, 147.76, 140.38, 134.74, 134.57, 131.83, 122.02, 121.50, 121.12, 118.58, 114.42, 50.34. ESI-MS (CH_3CN): *m*/*z* 550.44 $[M-4H]^+$, 476.74 $[M-DMSO]^+$.

2.2.2. $[Mo^{(VI)}O_2L^2(H_2O)]$ (**2**)

Yield: 0.31 g (68%). Anal. calc. for $C_{15}H_{14}FMoN_3O_5S$: C, 38.89; H, 3.05; N, 9.07. Found: C, 38.87; H, 3.02; N, 9.10. ^{13}C NMR (DMSO d_6, 100 MHz) δ: 172.74, 163.51, 155.51, 147.67, 146.86, 143.83, 143.74, 137.75, 134.33, 127.54, 125.59, 124.76, 120.68, 118.47, 51.56. ESI-MS (CH_3CN): *m*/*z* 463.29 $[M]^+$.

2.2.3. $[Mo^{(VI)}O_2L^3(DMSO)]_4{\cdot}2DMSO$ (**3**)

Yield: 1.20 g (52%). Anal. calc. for $C_{72}H_{84}Cl_4Mo_4N_{12}O_{22}S_{10}$: C, 37.34; H, 3.66; N, 7.26. Found: C, 37.37; H, 3.68; N, 7.25. ^{13}C NMR (DMSO d_6, 100 MHz) δ: 169.49, 167.35, 162.37, 158.23, 155.06, 148.98, 146.77, 144.58, 140.30, 137.67, 135.53, 131.47, 126.46, 120.96, 53.35, 48.27. ESI-MS (CH_3CN): *m*/*z* 2159.67 $[M-2DMSO]^+$.

2.2.4. $[Mo^{(VI)}O_2L^4(H_2O)]$ (**4**)

Yield: 0.31 g (67%). Anal. calc. for $C_{16}H_{17}MoN_3O_6S$: C, 40.43; H, 3.60; N, 8.84. Found: C, 40.45; H, 3.62; N, 8.81. ^{13}C NMR (DMSO d_6, 100 MHz) δ: 176.34, 172.45, 167.53, 160.43, 158.76, 150.88, 144.14, 142.46, 140.21, 135.54, 129.23, 123.52, 119.74, 113.45, 56.13, 50.24. ESI-MS (CH_3CN): *m*/*z* 475.40 $[M]^+$.

2.2.5. $[Mo^{(VI)}O_2L^5(DMSO)]$ (**5**)

Yield: 0.43 g (68%). Anal. calc. for $C_{16}H_{15}Br_2MoN_3O_4S_2$: C, 30.35; H, 2.39; N, 6.64. Found: C, 30.38; H, 2.40; N, 6.65. ^{13}C NMR (DMSO d_6, 100 MHz) δ: 168.63, 159.45, 154.72, 151.35, 144.74, 141.33, 135.56, 132.35, 130.54, 128.01, 123.65, 120.64, 117.87, 112.53, 52.67. ESI-MS (CH_3CN): *m*/*z* 633.80 $[M]^+$.

2.2.6. $[Mo^{(VI)}O_2L^6(DMSO)]$ (6)

Yield: 0.39 g (71%). Anal. calc. for $C_{20}H_{18}ClMoN_3O_4S_2$: C, 42.90; H, 3.24; N, 7.50. Found: C, 42.92; H, 3.22; N, 7.51. ^{13}C NMR (DMSO d_6, 100 MHz) δ: 168.53, 167.12, 165.53, 158.80, 156.35, 153.65, 146.34, 143.67, 140.64, 139.12, 136.57, 130.76, 126.36, 122.56, 120.65, 117.87, 113.77, 112.63, 56.32. ESI-MS (CH_3CN): *m*/*z* 557.30 $[M-2H]^+$.

2.3. X-ray crystallography

Single crystals of complexes were mounted on, Rigaku XtaLAB mini diffractometer (**2** and **3**), equipped with a graphite monochromator and a Mo Kα source (λ = 0.71073 Å). Crystallographic data and details of refinement of **2** and **3** are given in Table 1. The unit cell dimensions and intensity data were measured at 293 K for **2** and **3**. The data were integrated and scaled using SAINT, SADABS within the APEX2 software package by Bruker [59]. Absorption corrections were applied using SADABS [60] and the structures were solved by direct methods using the program SHELXS-97 [61] and refined using least squares with the SHELXL-97 [61] software program. Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C–H distances in the range 0.95–1.00 Å. The non–hydrogen atoms were refined anisotropically.

Table 1
Crystal data and refinement details of $[Mo^{(VI)}O_2L^{2,3}(solv)]$ (**2** and **3**).

Compound	2	3
Formula	$C_{15}H_{14}FMoN_3O_5S$	$C_{72}H_{84}Cl_4Mo_4N_{12}O_{22}S_{10}$
M	463.29	2315.67
Crystal system	Monoclinic	Monoclinic
Space group	$P\,2_1/c$	$C\,2/c$
a (Å)	15.082(15)	22.871(13)
b (Å)	13.711(13)	17.611(10)
c (Å)	10.399(10)	11.323(8)
α (°)	90	90
β (°)	93.938(7)	92.129(7)
γ (°)	90	90
V (Å^3)	2145.3(4)	4557.3(5)
Z	4	2
D_{calc} (Mg.m^{-3})	1.434	1.688
F(0 0 0)	928	2344
μ(Mo–Kα) (mm^{-1})	0.743	0.959
max./min. trans.	0.8778/0.8189	0.8313/0.8313
2θ(max) (°)	27.48	27.48
Reflections collected/ unique	4912/4912 [R(int) = 0.0293]	23,695/5226 [R(int) = 0.0226]
$R_1[I > 2\sigma(I)]$	$R1 = 0.0332$, $wR2 = 0.0973$	$R1 = 0.0214$, $wR2 = 0.0548$
wR_2 [all data]	$R1 = 0.0383$, $wR2 = 0.1003$	$R1 = 0.0233$, $wR2 = 0.0557$
S [goodness of fit]	1.076	1.052
min./max. res. (e.Å^{-3})	0.720/−0.459	0.277/−0.532
CCDC deposition number	1408558	1408559

2.4. Catalytic reactions of $[Mo^{(VI)}O_2L^{1-6}(solv)]$ (**1**–**6**)

2.4.1. Oxidation of styrene

In a typical oxidation reaction, styrene (0.520 g, 5 mmol), aqueous 30% H_2O_2 (2.27 g, 20 mmol), catalyst (0.0010 g, 1.8×10^{-6} mmol) and $NaHCO_3$ (0.126 g, 1.5 mmol) were mixed in 5 mL of CH_3CN. The reaction mixture was heated at 60 °C for 4 h. The progress of the reaction was monitored by withdrawing samples at different time intervals and extracted with n-hexane, which were then analyzed quantitatively using gas chromatography. The effect of various parameters such as the amount of catalyst, oxidant, $NaHCO_3$, and solvent were checked to optimize the conditions for the best performance of the catalyst. The identity of the products was confirmed by GC mass.

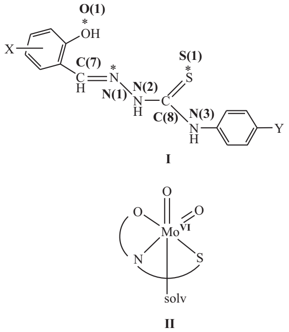
2.4.2. Oxidation of cyclohexene

Aqueous 30% H_2O_2 (1.70 g, 15 mmol), cyclohexene (0.41 g, 5 mmol), $NaHCO_3$ (0.126 g, 1.5 mmol) and catalyst (0.0010 g, 1.8×10^{-6} mmol) were mixed in CH_3CN (5 mL) and the reaction mixture was heated at 60 °C with continuous stirring in an oil bath for 4 h. The reaction was monitored by withdrawing small aliquots of the reaction mixture at every 60 min and analyzing them quantitatively by gas chromatography. The identities of the products were confirmed as mentioned above. The effects of various parameters, such as amounts of oxidant, amount of sodium bicarbonate, catalyst, temperature, and solvent were studied to see their effect on the conversion.

3. Result and discussion

3.1. Synthesis

The ligands H_2L^{1-6} (I, Chart 1) and complexes $[Mo^{(VI)}O_2L^{1-6}(solv)]$ {where solv = DMSO (**1**, **3**, **5** & **6**) and H_2O (**2** & **4**)} (II, Chart 1) used in this work have been synthesized by refluxing an equimolar ratio of $[Mo^{(VI)}O_2(acac)_2]$ and ligands in an ethanolic medium, followed by recrystallisation of the product in DMSO. Proposed structures of these complexes are based on elemental analyses, spectroscopic characteristics (IR, electronic, ^{1}H and ^{13}C NMR), ESI-MS, and single crystal X-ray diffraction studies of **2** and **3**. All the complexes are highly soluble in aprotic solvents, *viz.* DMF or DMSO and are sparingly soluble in CH_3OH, CH_3CN, and $CHCl_3$.



X	Y	Ligand	solv	Complex
H	Br	H_2L^1	DMSO	**1**
o-OCH_3	F	H_2L^2	H_2O	**2**
	Cl	H_2L^3	DMSO	**3**
	OCH_3	H_2L^4	H_2O	**4**
p-Br	Br	H_2L^5	DMSO	**5**
Ph	Cl	H_2L^6	DMSO	**6**

Chart 1. Representation of ligands (I) and dioxidomolybdenum complexes (II), $[Mo^{(VI)}O_2L^{1-6}(solv)]$ (**1**–**6**); * = donor sites.

3.2. Spectral characteristics

3.2.1. IR spectroscopy

The infrared spectra of complexes **1**–**6** exhibits two strong absorptions in the range 933–887 cm^{-1}, besides typical ligand vibrations, which are attributed to the symmetric and antisymmetric ν(Mo=O) vibrations of the C_{2v} *cis*-MoO_2^{2+} groups [33], thus confirming the formation of dioxidomolybdenum(VI) complexes. The sharp band in the range 780–792 cm^{-1} due to ν(C(8)–S(1)) stretching in the ligand is lowered by 10–15 cm^{-1} upon complexation, indicating participation of the thione sulfur in coordination. The infrared spectra of all the complexes are mostly similar. The ligands exhibit bands due to ν(–C(1)O(1)–H) moiety in the 3357–3300 cm^1 region, however except complexes **2** and **4** (having coordinated H_2O molecule to the Mo center) other complexes do not exhibit bands in the region beyond 3300 cm^{-1}. Thus it reveals that the ligands coordinate to the metal centre in their phenolate form. The detailed IR data has been tabulated in Table 2.

3.2.2. UV–vis spectroscopy

The electronic spectra of complexes **1**–**6** were recorded in CH_3CN and are listed in Table 3. The representative UV–vis spectrum of $[Mo^{(VI)}O_2L^2(H_2O)]$ (**2**) is shown in Fig. 1. Complexes **1**–**6** display medium intensity band in 442–417 nm region and two strong absorptions in 346–243 nm range, for the LMCT and intraligand transitions, respectively [62,63]. As compared to the ligands, the complexes have an extra peak in 442–417 nm region, which indicates coordination of the ligand upon complexation. We have assigned the LMCT signals of metal based transitions on the basis of previous reports by our group [47,48,64,65]. Therefore we did not go for the theoretical study.

3.2.3. NMR spectroscopy

The NMR spectra (^{1}H and ^{13}C) of the dioxidomolybdenum(VI) complexes **1**–**6** were recorded using DMSO d_6. The ^{1}H NMR spectra exhibit two singlets in the range 9.83–8.56 ppm due to NH (–C(8)–N(3)H) and CH (–N(1)=C(7)–H) groups. Signals for aromatic protons were found as multiplets in 7.78–6.56 ppm. The detailed ^{1}H NMR data of dioxidomolybdenum(VI) complexes are summarized in Table 4. In complexes **2** and **4** the peak for the H_2O molecule overlapped with the signal for the presence of H_2O in the solvent molecule. The representative ^{1}H NMR of $[Mo^{(VI)}O_2L^1(DMSO)]$ (**1**) is shown in Fig. S1.

Table 2
IR spectral data (in cm^{-1}) of [Mo$^{(VI)}$O$_2$L$^{1/5/6}$(DMSO)] (**1**, **5** & **6**), [Mo$^{(VI)}$O$_2$L$^{2/4}$(H$_2$O)] (**2** & **4**), and [Mo$^{(VI)}$O$_2$L^3(DMSO)]$_4$·2DMSO (**3**).

Complexes	$\nu(H_2O)$	ν(N(3)–H)	ν(C(7)–H)	ν(C=C)	ν(C(7)=N(1))	ν(Mo=O)	ν(C(8)–S(1))
1	–	3271	3018	1598 s	1504 m	920 s, 896 s	760 s
2	3395	3285	2968	1603 s	1516 m	931 s, 887 s	738 s
3	–	3278	3015	1592 s	1521 m	916 s, 893 s	778 s
4	3401	3299	2978	1591 s	1517 m	925 s, 895 s	735 s
5	–	3211	2915	1594 s	1554 m	938 s, 892 s	767 s
6	–	3282	3013	1589 s	1512 m	933 s, 887 s	766 s

Table 3
Electronic spectral and Cyclic voltammetric[a] results for complexes **1**–**6**.

Complex	λ_{max}/nm(ε/dm^3 mol^{-1} cm^{-1})	Potentials (V) versus Ag/AgCl	
		Mo$^{(VI)}$/Mo$^{(V)}$ E$_{pc}$	Mo$^{(V)}$/Mo$^{(IV)}$ E$_{pc}$
1	268(17,072), 341(14,323), 433(3370)	−0.66	−0.87
2	263(16,341), 335(12,543), 417(2789)	−0.71	−0.92
3	264(17,534), 346(13,535), 436(5422)	−0.70	−0.92
4	274(16,432), 328(14,212), 442(3856)	−0.68	−0.85
5	270 (16,322), 343(13,648), 439(3922)	−0.66	−0.87
6	243(16,429), 338(13,768), 437(3425)	−0.70	−0.88

[a] In CH$_3$CN at a scan rate 100 mV/s. E_{pc} is cathodic peak potentials vs. Ag/AgCl.

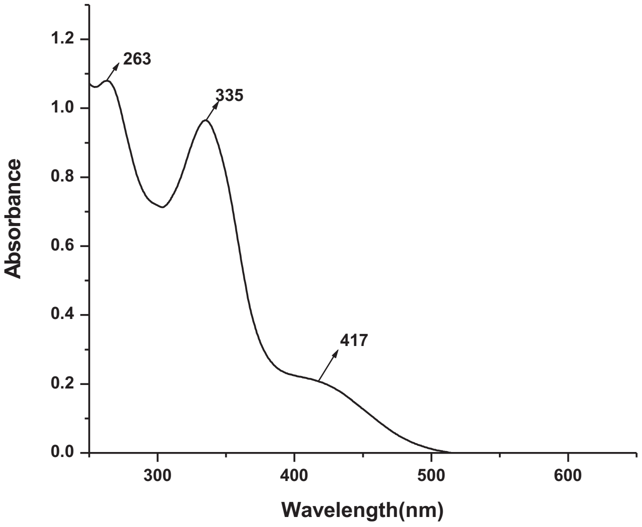


Fig. 1. UV–vis spectrum of [Mo$^{(VI)}$O$_2$L^2(H$_2$O)] (**2**) in CH$_3$CN.

3.3. ESI-MS

The ESI-MS data are summarized in the experimental section. Figs. S2 and S3 depict the representative ESI-MS of **1** and **4** respectively.

3.4. Electrochemical properties

The electrochemical properties of **1**–**6** were examined in CH$_3$CN solution (0.1 M TEAP) by cyclic voltammetry using a glassy carbon working electrode, platinum auxiliary electrode, and Ag/AgCl as the reference electrode. The potential data are listed in Table 2 and Fig. 2 depicts the representative voltammogram of [Mo$^{(VI)}$O$_2$L^2(H$_2$O)] (**2**). The voltammogram pattern is similar for **1**–**6**, which includes two irreversible reduction processes within the potential window −0.71 to −0.66 V and −0.92 to −0.85 V corresponding to metal centered reduction from Mo$^{(VI)}$/Mo$^{(V)}$ and Mo$^{(V)}$/Mo$^{(IV)}$ respectively [66–68]. Similar cyclic voltammogram pattern was observed in our previous reports on dioxidomolybdenum(VI) complexes [22,47,48]. We had varied the ligands to see their effect, if any, on their redox properties, however no significant changes in the values could be observed.

3.5. Description of X–ray structure of dioxidomolybdenum(VI) complexes **2** and **3**

Although the preliminary characterization data (elemental analysis, ^{1}H and ^{13}C NMR and IR) indicated the presence of the ligand, two oxido groups and solvent in the complexes **1**–**6**, they could not point to any definite stereochemistry of the complexes, or the coordination mode of H$_2$L$^{1-6}$. For an unambiguous characterization of these complexes, structures of **2** and **3** were determined by X-ray crystallography. The X-ray structures show that all the indications given by the ^{1}H NMR spectra are indeed correct. The molecular structure and the atom numbering scheme for **2** and **3** are shown in Figs. 3 and 4, respectively. The relevant bond distances and angles are collected in Table 5. The coordination geometry around the molybdenum(VI) atom in **2** and **3** reveals a distorted octahedral environment with NO$_4$S coordination sphere (Chart 1). Complex **3** contains two DMSO molecules as solvent of crystallization. Each ligand molecule behaves as a dianionic tridentate one and is bonded to the metal centre through the phenolate

Table 4
^{1}H NMR data of [Mo$^{(VI)}$O$_2$L$^{1/5/6}$(DMSO)] (**1**, **5** & **6**), [Mo$^{(VI)}$O$_2$L$^{2/4}$(H$_2$O)] (**2** & **4**), and [Mo$^{(VI)}$O$_2$L^3(DMSO)]$_4$·2DMSO (**3**).

Complexes	C(8)–N(3)H	N(1)=C(7)H	Ar-H	OCH$_3$	DMSO
1	9.83 (s, 1H)	8.82 (s, 1H)	7.74–6.90 (m, 8H)	–	2.54 (s, 6H)
2	9.72 (s, 1H)	8.75 (s, 1H)	7.77–6.94 (m, 7H)	3.78 (s, 3H)	–
3	9.81 (s, 1H)	8.79 (s, 1H)	7.78–6.97 (m, 7H)	3.79 (s, 3H)	2.54 (s, 6H)
4	9.56 (s, 1H)	8.70 (s, 1H)	7.64–6.85 (m, 7H)	3.78 (s, 3H) 3.72 (s, 3H)	–
5	9.34 (s, 1H)	8.76 (s, 1H)	7.63–6.56 (m, 7H)	–	2.53 (s, 6H)
6	9.34 (s, 1H)	8.56 (s, 1H)	7.35–6.65 (m, 10H)	–	2.53 (s, 6H)

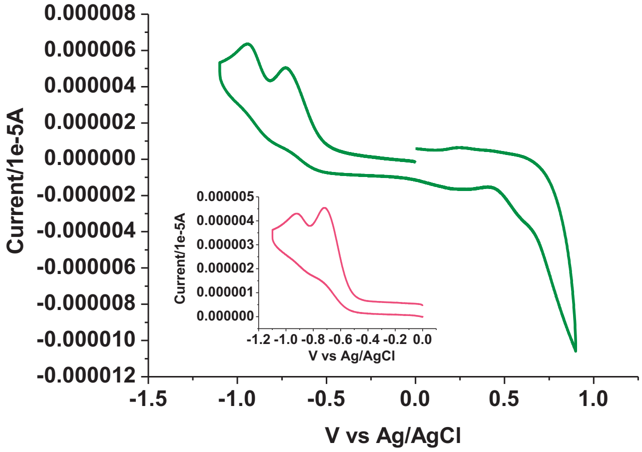


Fig. 2. Cyclic voltammogram of $[Mo^{(VI)}O_2L^2(H_2O)]$ (**2**) in CH_3CN (Inset: metal centered reduction from $Mo^{(VI)/}Mo^{(V)}$ and $Mo^{(V)/}Mo^{(IV)}$ in the cathodic region).

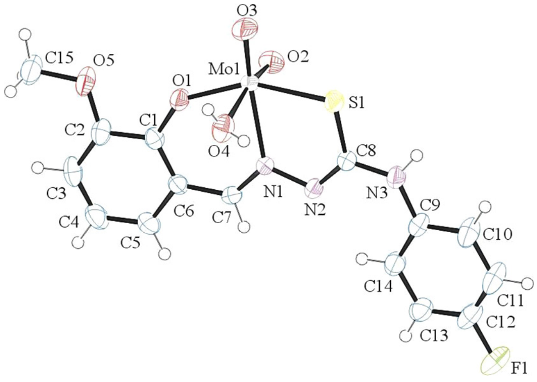


Fig. 3. ORTEP diagram of $[Mo^{(VI)}O_2L^2(H_2O)]$ (**2**) with atom labeling scheme.

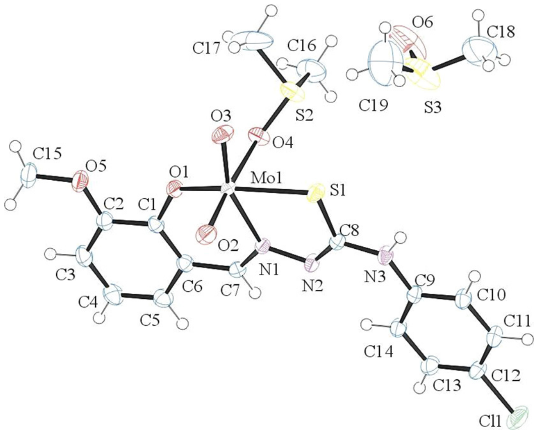


Fig. 4. ORTEP diagram of asymmetric unit of $[Mo^{(VI)}O_2L^3(DMSO)]_4{\cdot}2DMSO$ (**3**) with atom labeling scheme.

oxygen O(1), thiolate sulfur S(1) and the imine nitrogen N(1) forming a five membered and a six membered chelate ring with S(1)–Mo(1)–N(1) and O(1)–Mo(1)–N(1) bite angles of 75.74(5)°–75.49(3)° and 83.52(7)°–82.05(2)° respectively. In all the complexes, one of the two oxido groups, O(3) is located *trans* to the imine nitrogen N(1) and the other oxido group O(2) is located in the axial plane along with the solvent molecule, H_2O (**2**) and DMSO (**3**). The bond length values examined in the X-ray data give an indication for the presence of the enethiol form of the ligand coordinated to the Mo(1) center. Also, in our previous reports [57,69], the presence of the enethiol form was predominant in the thiosemicarbazone complexes.

Table 5
Selected geometric parameters (Å, °) for **2** and **3**.

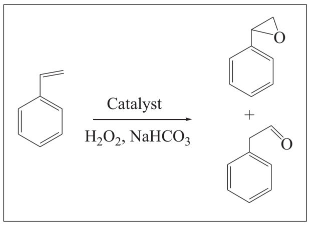
	2	**3**
Bond lengths		
Mo(1)–O(1)	1.926(2)	1.929(1)
Mo(1)–O(2)	1.706(2)	1.703(1)
Mo(1)–O(3)	1.690(2)	1.707 (1)
Mo(1)–O(4)	2.342(2)	2.314(1)
Mo(1)–N(1)	2.266(2)	2.275(1)
Mo(1)–S(1)	2.426(7)	2.438(4)
Bond angles		
O(2)–Mo(1)–O(3)	105.41(1)	104.95(6)
O(2)–Mo(1)–O(1)	100.16(9)	98.15(6)
O(3)–Mo(1)–O(1)	104.05(9)	107.68(5)
O(2)–Mo(1)–N(1)	90.79(9)	91.12(5)
O(3)–Mo(1)–N(1)	160.30(1)	158.93(5)
O(1)–Mo(1)–N(1)	83.52(7)	82.85(5)
O(2)–Mo(1)–O(4)	168.07(9)	169.92(5)
O(3)–Mo(1)–O(4)	86.42(1)	85.08(5)
O(1)–Mo(1)–O(4)	77.90(8)	77.48(5)
N(1)–Mo(1)–O(4)	77.31(8)	79.38(4)
O(2)–Mo(1)–S(1)	96.61(8)	97.32(4)
O(3)–Mo(1)–S(1)	91.06(8)	88.79(4)
O(1)–Mo(1)–S(1)	153.42(6)	153.53(4)
N(1)–Mo(1)–S(1)	75.74(5)	75.49(3)
O(4)–Mo(1)–S(1)	81.42(6)	83.66(3)

Mo–O(2) and Mo–O(3) bond distances of the $[MoO_2]^{2-}$ group are unexceptional [62,70] and almost equal 1.707(1)–1.690(2) Å for complexes **2** and **3**. The bond between Mo and the azomethine nitrogen in the complexes are within the range of 2.275(1)–2.266(2) Å, which is comparatively longer than other Mo–N single bonds. This is due to the *trans* effect generated by the oxido group *trans* to the Mo–N bond [63,70]. The other Mo–hetero atom (O and S) distances are normal, as observed in other structurally characterized complexes of molybdenum containing these bonds [71]. In complexes **2** and **3**, $[MoO_2L^{2,3}(solv)]$, a solvent molecule completes the distorted octahedral coordination sphere, which lies *trans* to the other oxido group O(2). The Mo–O(solvent) bond in the range 2.342(2)–2.314(1) Å is significantly longer than the other Mo–O bonds (1.929(1)–1.690(2) Å) indicating that the solvent molecule is weakly bonded to the $[MoO_2]^{2-}$ core.

3.6. Catalytic activity studies of *1*–*6*

3.6.1. Oxidation of styrene

There are many reports of oxidation of styrene catalyzed by molybdenum complexes, where H_2O_2 has been used as an oxidant in the presence of $NaHCO_3$ [72]. Aqueous 30% H_2O_2 as the sole oxidant in presence of dioxidomolybdenum(VI) complexes as catalyst gave poor catalytic efficiency, whereas the addition of $NaHCO_3$ as an additive activated the catalytic oxidation process and gave two products, namely styrene oxide (major) and phenyl acetaldehyde (minor) (Scheme 1). Such $NaHCO_3$ assisted oxidation of



Scheme 1. Oxidation of styrene with H_2O_2 and $NaHCO_3$.

styrene has been reported in the literature and gave styrene oxide selectively [73–75].

[Mo$^{(VI)}$O$_2$L^1(DMSO)] (**1**) was considered as a representative catalyst to optimize the reaction conditions for the maximum oxidation of styrene, by studying five different parameters *viz.* the effect of amount of oxidant, amount of catalyst, amount of $NaHCO_3$, solvent and temperature of the reaction mixture in detail. The effect of oxidant was studied considering styrene:aqueous 30% H_2O_2 in the molar ratios of 1:3, 1:4 and 1:5, where the mixture of styrene (0.520 g, 5 mmol), catalyst (0.0010 g, 1.8 × 10^{-6} mmol), $NaHCO_3$ (0.126 g, 1.5 mmol) and oxidant were taken in 5 mL of CH_3CN and the reaction was carried out at 60 °C. As illustrated in entries No. 2, 6 and 7 of Table S1, the percent conversion of styrene improved from 77.7% to 92.5% on increasing the styrene to oxidant ratio from 1:3 to 1:4 but on further increment of ratio (1:5) there is no remarkable improvement in conversion, suggesting that 1:4 (styrene:H_2O_2) molar ratio is sufficient enough to perform the reaction with good conversion. Similarly, for three different amounts *viz.* 0.0005 (1.0 × 10^{-6} mmol), 0.0010 (1.8 × 10^{-6} mmol) and 0.0015 g (2.7 × 10^{-6} mmol) of catalyst, at styrene to H_2O_2 molar ratio of 1:4 under above reaction conditions, 79.0%, 92.5% and 93.4% conversion was observed. The increase of catalyst

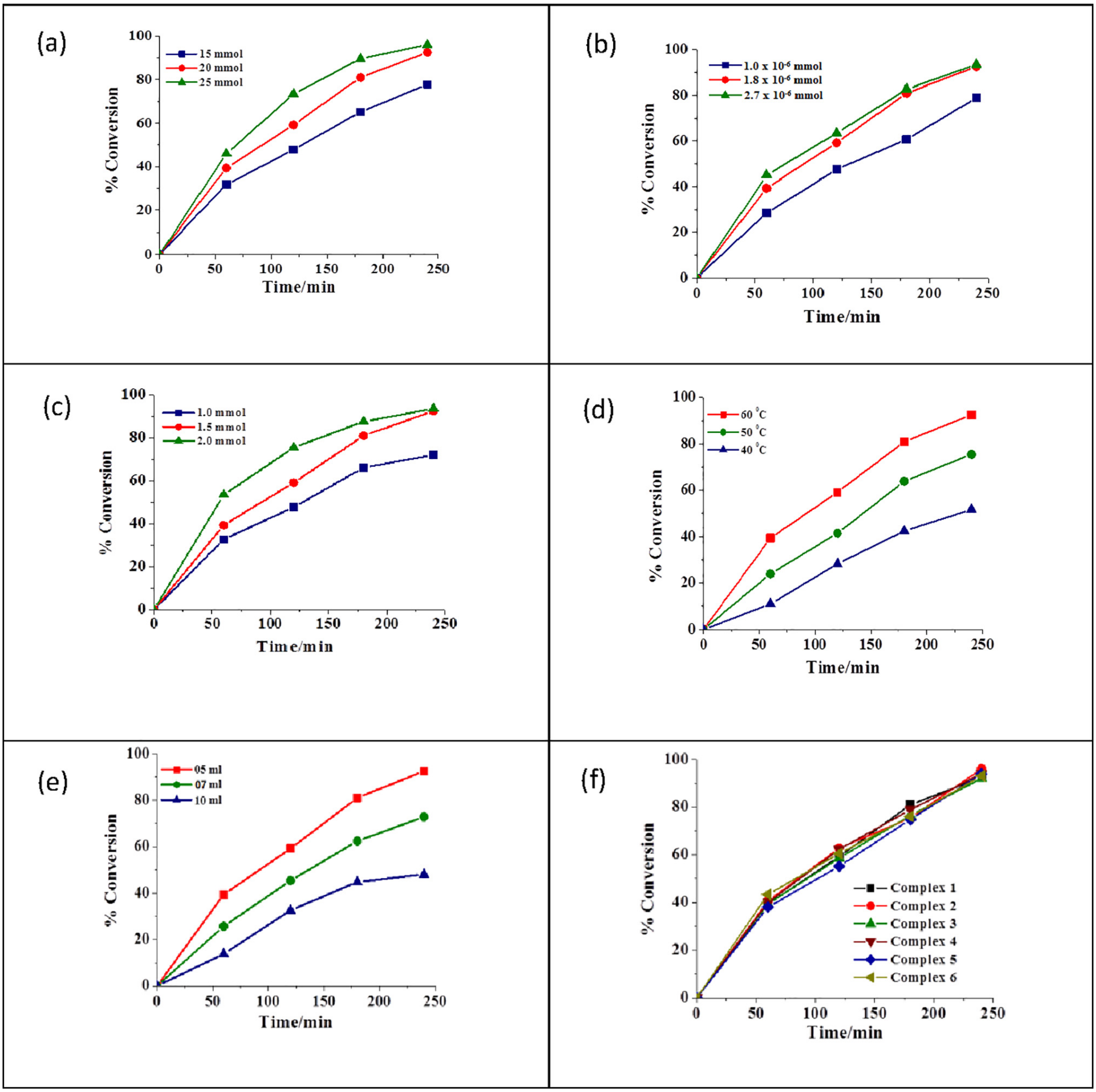


Fig. 5. (a) Effect of oxidant amount on the oxidation of styrene. Reaction condition: styrene (0.520 g, 5 mmol), catalyst [Mo$^{(VI)}$O$_2$L^1(DMSO)] (**1**) (0.0010 g, 1.8 × 10^{-6} mmol), $NaHCO_3$ (0.126 g, 1.5 mmol), temperature 60 °C and acetonitrile (5 mL). (b) Effect of catalyst [Mo$^{(VI)}$O$_2$L^1(DMSO)] (**1**) amount on the oxidation of styrene. Reaction condition: styrene (0.520 g, 5 mmol), 30% H_2O_2 (2.27 g, 20 mmol), $NaHCO_3$ (0.126 g, 1.5 mmol), temperature 60 °C and acetonitrile (5 mL). (c) Effect of $NaHCO_3$ amount on the oxidation of styrene. Reaction condition: styrene (0.520 g, 5 mmol), catalyst [Mo$^{(VI)}$O$_2$L^1(DMSO)] (**1**) (0.0010 g, 1.8 × 10^{-6} mmol), 30% H_2O_2 (2.27 g, 20 mmol), temperature 60 °C and acetonitrile (5 mL). (d) Effect of temperature on the oxidation of styrene. Reaction conditions: styrene (0.520 g, 5 mmol), 30% H_2O_2 (2.27 g, 20 mmol), $NaHCO_3$ (0.126 g, 1.5 mmol), catalyst [Mo$^{(VI)}$O$_2$L^1(DMSO)] (**1**) (0.0010 g, 1.8 × 10^{-6} mmol) and acetonitrile (5 mL). (e) Effect of solvent amount on the oxidation of styrene. Reaction conditions: styrene (0.520 g, 5 mmol), 30% H_2O_2 (2.27 g, 20 mmol), $NaHCO_3$ (0.126 g, 1.5 mmol), catalyst [Mo$^{(VI)}$O$_2$L^1(DMSO)] (**1**) (0.0010 g, 1.8 × 10^{-6} mmol) and temperature 60 °C. (f) Plot showing conversion of all metal complexes.

amount from 0.0010 to 0.0015 g shows very minor improvement in the conversion (entries No. 1, 2 and 3 of Table S1). The amount of $NaHCO_3$ has played a significant role in the conversion of styrene and best conversion was obtained with 1.5 mmol of $NaHCO_3$ (entries No. 2, 4 and 5 in Table S1). There was no conversion of substrate in the absence of $NaHCO_3$. Among three selected temperatures of 40, 50 and 60 °C, running the reaction at 60 °C for the following fixed operating condition of styrene (0.52 g, 5 mmol), H_2O_2 (2.27 g, 20 mmol), $[Mo^{(VI)}O_2L^1(DMSO)]$ (**1**) (0.0010 g, 1.8×10^{-6} mmol), $NaHCO_3$ (0.126, 1.5 mmol) and CH_3CN (5 mL), gave best conversion (entries No. 2, 10 and 11 of Table S1). Variation in the volume of CH_3CN (5, 7 and 10 mL) was also studied (entries No. 2, 8 and 9 of Table S1) and it was observed that 5 mL of CH_3CN was sufficient enough to get good transformation of styrene while running the reaction at 60 °C under above conditions. Thus, the best reaction conditions as concluded above (i.e. styrene 0.52 g, 5 mmol, H_2O_2 2.27 g, 20 mmol, $[Mo^{(VI)}O_2L^1(DMSO)]$ (**1**) 0.0010 g, 1.8×10^{-6} mmol, $NaHCO_3$ 0.126, 1.5 mmol, CH_3CN 5 mL and reaction temperature 60 °C) were further applied for the maximum transformation of styrene. Table S1 and Fig. 5 summarize all the conditions and conversions obtained in this work.

$[Mo^{(VI)}O_2L^1(DMSO)]$ (**1**) as catalyst under the optimized reaction conditions (entry No. 2 of Table S1) has been analyzed as a function of time and is presented in Fig. 6 and Table 6. Thus, under optimized reaction conditions, the selectivity of the two oxidation products varies in the order: styrene oxide (98.6%) > phenyl acetaldehyde (1.4%). Complexes $[Mo^{(VI)}O_2L^{1-6}(solv)]$ (**1**–**6**) cause the same order of the selectivity of products with an almost identical conversion. Blank reaction under above reaction conditions gave 30.0% conversion.

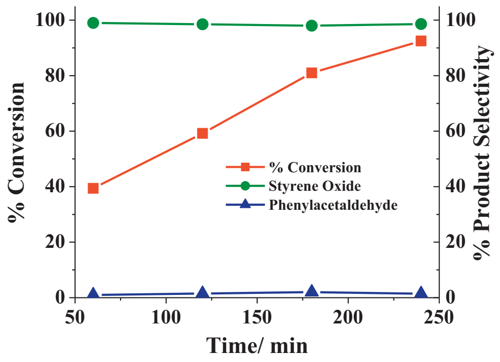
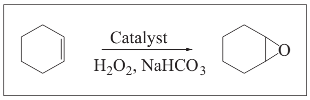


Fig. 6. Plot showing conversion and product selectivity as a function of time in the optimized reaction condition.

3.6.2. Oxidation of cyclohexene

Oxidation of cyclohexene, catalyzed by dioxidomolybdenum (VI) complexes using aqueous 30% H_2O_2 as oxidant in the presence of $NaHCO_3$ gave one product, namely cyclohexene oxide (Scheme 2).

$[Mo^{(VI)}O_2L^1(DMSO)]$ (**1**) was again considered as a representative catalyst for the oxidation of cyclohexene by H_2O_2 in presence of $NaHCO_3$. In order to achieve optimum reaction conditions, the effect of catalyst considering three different amounts *viz.* 0.0005 g (1.0×10^{-6} mmol), 0.0010 g (1.8×10^{-6} mmol) and 0.0015 g (2.7×10^{-6} mmol) as a function of time was studied for the fixed amount of cyclohexene (0.41 g, 5 mmol), $NaHCO_3$ (0.126 g, 1.5 mmol) and 30% H_2O_2 (1.70 g, 15 mmol) in 5 mL of CH_3CN and reaction was carried out at 60 °C. The results are illustrated in Fig. 7(a) (entries No. 1, 2 and 3 of Table S2). It is evident from the plot that 0.0005 g (1.0×10^{-6} mmol) gave 81.0% conversion of the substrate, whereas 0.0010 g (1.8×10^{-6} mmol) and 0.0015 g (2.7×10^{-6} mmol) of catalyst gave 93.0% and 95.0% respectively. Out of these 0.0010 g (1.8×10^{-6} mmol) was the best one to obtain a maximum of 93.0% conversion of cyclohexene. For the effect of oxidant three different cyclohexene to aqueous 30% H_2O_2 molar ratios *viz.* 1:2, 1:3 and 1:4 were considered for the fixed amount of cyclohexene (0.41 g, 5 mmol), $NaHCO_3$ (0.126 g, 1.5 mmol) and catalyst (0.0010 g, 1.8×10^{-6} mmol) in 5 mL of CH_3CN and reaction was carried out at 60 °C. As presented in entries No. 2, 6 and 7 of Table S2 and Fig. 7(b), a maximum of 63.6% conversion was obtained at a cyclohexene to H_2O_2 molar ratio of 1:2 in 4 h of reaction time. This conversion reached 93.0% on increasing this ratio to 1:3 while 1:4 ratios improve the conversion slightly (99.0%). The best conditions as found above were cyclohexene (0.41 g, 5 mmol), 30% H_2O_2 (1.70 g, 15 mmol), $NaHCO_3$ (0.126 g, 1.5 mmol) in 5 mL of CH_3CN. We have also optimized the amount of $NaHCO_3$ (entries No. 2, 4 and 5), the amount of solvent (acetonitrile, entries No. 2, 8 and 9) and temperature (entries No. 2, 10 and 11) of the reaction and found that 1.5 mmol of $NaHCO_3$, 5 mL of solvent and 60 °C reaction temperature were sufficient enough to obtain 93.0% conversion under above reaction conditions. Table S2 and Fig. 7 summarize all the conditions and the conversions obtained under several selected conditions. No conversion of the substrate in the absence of $NaHCO_3$ was obtained. Blank reaction under above reaction conditions gave 32.0% conversion.



Scheme 2. Oxidation of cyclohexene with H_2O_2 and $NaHCO_3$.

Table 6
Oxidation of styrene, TOF and product selectivity using **1**–**6** as catalyst.

Catalyst	TOF $[h^{-1}]$[a]	Conv. [%]	Selectivity [%][b]	
			phac	so
$[Mo^{(VI)}O_2L^1(DMSO)]$ (**1**)	642	92.5	1.4	98.6
$[Mo^{(VI)}O_2L^2(H_2O)]$ (**2**)	600	96.0	1.3	98.7
$[Mo^{(VI)}O_2L^3(DMSO)]_4{\cdot}2DMSO$ (**3**)	676	92.0	0.8	99.2
$[Mo^{(VI)}O_2L^4(H_2O)]$ (**4**)	586	94.0	0.9	99.1
$[Mo^{(VI)}O_2L^5(DMSO)]$ (**5**)	651	93.8	1.1	98.9
$[Mo^{(VI)}O_2L^6(DMSO)]$ (**6**)	647	93.0	0.6	99.4
Blank reaction	–	30.0	3.0	97.0

[a] TOF values calculated at 4 h of reaction time.
[b] so: styrene oxide; phac: phenyl acetaldehyde.

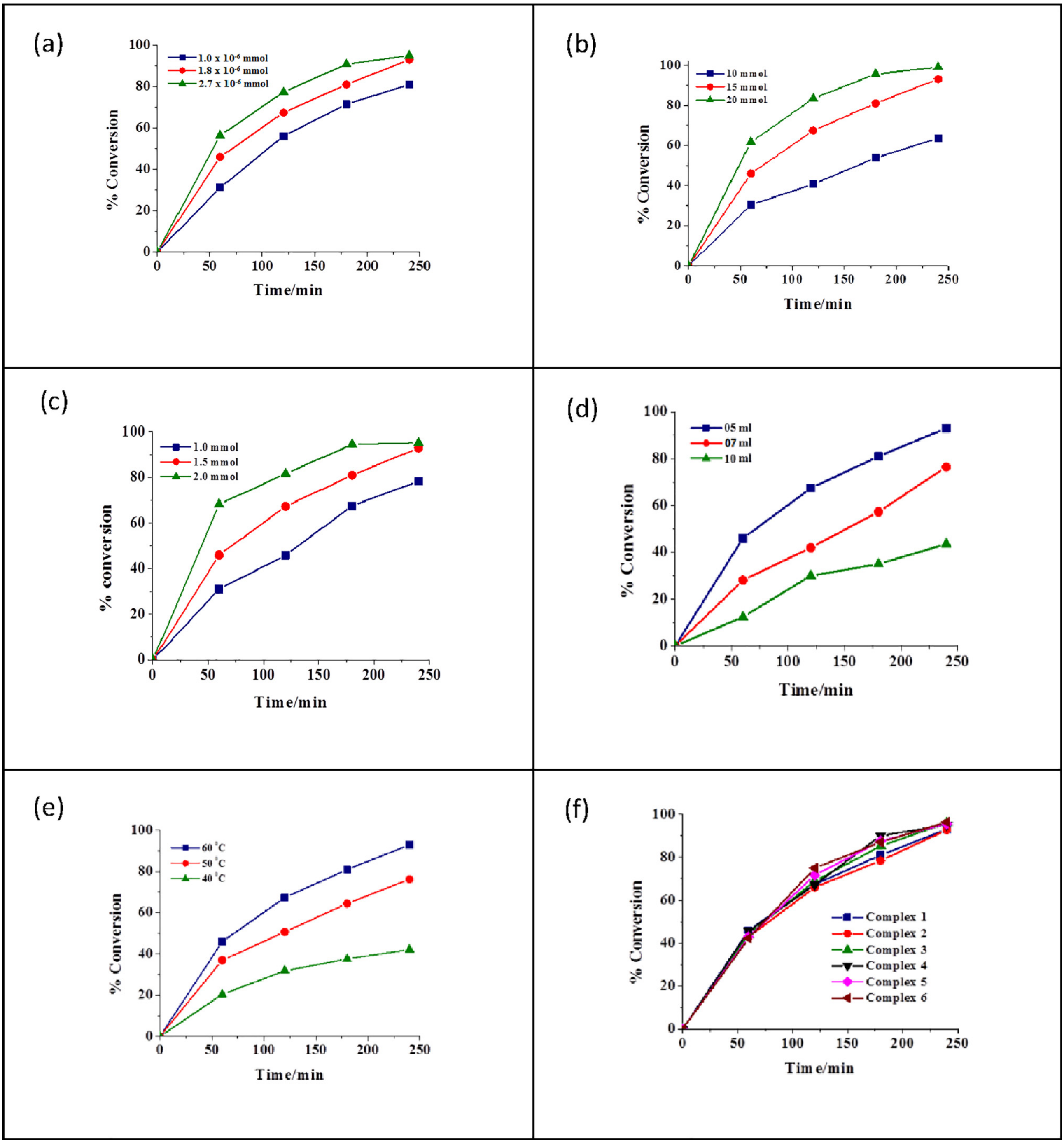


Fig. 7. (a) Effect of catalyst [$Mo^{(VI)}O_2L^1$(DMSO)] (**1**) amount on the oxidation of cyclohexene. Reaction conditions: cyclohexene (0.410 g, 5 mmol), 30% H_2O_2 (1.70 g, 15 mmol), $NaHCO_3$ (0.126 g, 1.5 mmol), temperature 60 °C and acetonitrile (5 mL). (b) Effect of oxidant amount on the oxidation of cyclohexene. Reaction condition: cyclohexene (0.410 g, 5 mmol), catalyst [$Mo^{(VI)}O_2L^1$(DMSO)] (**1**) (0.0010 g, 1.8×10^{-6} mmol), $NaHCO_3$ (0.126 g, 1.5 mmol), temperature 60 °C and acetonitrile (5 mL). (c) Effect of $NaHCO_3$ amount on the oxidation of cyclohexene. Reaction condition: cyclohexene (0.410 g, 5 mmol), catalyst [$Mo^{(VI)}O_2L^1$(DMSO)] (**1**) (0.0010 g, 1.8×10^{-6} mmol), 30% H_2O_2 (1.70 g, 15 mmol), temperature 60 °C and acetonitrile (5 mL). (d) Effect of solvent amount on the oxidation of cyclohexene. Reaction conditions: cyclohexene (0.410 g, 5 mmol), 30% H_2O_2 (1.70 g, 15 mmol), $NaHCO_3$ (0.126 g, 1.5 mmol), catalyst [$Mo^{(VI)}O_2L^1$(DMSO)] (**1**) (0.0010 g, 1.8×10^{-6} mmol) and temperature 60 °C. (e) Effect of temperature on the oxidation of cyclohexene. Reaction conditions: cyclohexene (0.410 g, 5 mmol), 30% H_2O_2 (1.70 g, 15 mmol), $NaHCO_3$ (0.126 g, 1.5 mmol), catalyst [$Mo^{(VI)}O_2L^1$(DMSO)] (**1**) (0.0010 g, 1.8×10^{-6} mmol) and acetonitrile (5 mL). (f) Plot showing conversion of all metal complexes on the oxidation of cyclohexene.

The oxidation of cyclohexene, TOF and selectivity of cyclohexene oxide using different dioxidomolybdenum(VI) complexes (**1**–**6**) as catalyst is given in Table 7.

The possible side products for oxidation of cyclohexene could be 2-cyclohexene-1-ol, 2-cyclohexene-1-one and cyclohexane-1,2-diol [76]. The catalytic potential of our synthesized complexes in terms of selectivity towards epoxydation of cyclohexene and styrene oxide was found to be comparable to many related dioxidomolybdenum(VI) complexes [23,47,60,77–83].

3.6.3. Reactivity of complexes with H_2O_2

Dioxidomolybdenum(VI) complexes (**1**–**6**) react with H_2O_2 to give the corresponding oxido–peroxido complexes. The generation of such species has been established in DMSO by electronic

Table 7
Oxidation of cyclohexene, TOF and selectivity of cyclohexene oxide using **1**–**6** as catalyst.

Catalyst	TOF $[h^{-1}]$[a]	Conv. [%]	Selectivity [%]
$[Mo^{(VI)}O_2L^1(DMSO)]$ (**1**)	646	93.0	100
$[Mo^{(VI)}O_2L^2(H_2O)]$ (**2**)	579	92.7	100
$[Mo^{(VI)}O_2L^3(DMSO)]_4{\cdot}2DMSO$ (**3**)	705	96.0	100
$[Mo^{(VI)}O_2L^4(H_2O)]$ (**4**)	593	95.0	100
$[Mo^{(VI)}O_2L^5(DMSO)]$ (**5**)	664	95.6	100
$[Mo^{(VI)}O_2L^6(DMSO)]$ (**6**)	670	96.4	100
Blank reaction	–	32.0	100

[a] TOF values calculated at 4 h of reaction time.

absorption spectroscopy. In a typical reaction, 20 mL of ca. 3.6×10^{-5} M solution of $[Mo^{(VI)}O_2L^1(DMSO)]$ (**1**) was treated with one drop of 30% aqueous H_2O_2 (0.260 g, 2.3 mmol) dissolved in 5 mL of DMSO and the resultant spectroscopic changes are presented in Fig. 8. The intensity of bands at 312 and 343 nm increases, while 267 and 420 nm decreases considerably. These changes indicate the interaction of $[Mo^{(VI)}O_2L^1(DMSO)]$ (**1**) with H_2O_2 and formation of oxido–peroxido species [22].

During catalytic action, $NaHCO_3$ and H_2O_2 jointly affect the reactivity of **1**. To understand the mechanism, a mixture of $NaHCO_3$ (0.13 mmol) and 30% H_2O_2 (0.58 mmol) dissolved in 5 mL of DMSO was treated with 20 mL of 3.6×10^{-5} M solution of **1**. Fig. S4 of the Supporting Information represents the very similar spectral changes as shown by H_2O_2 alone. The oxido–peroxido species is formed immediately on addition of only few drops of a mixture of $NaHCO_3$ and H_2O_2. It has been accounted that HCO_4^- (peroxymonocarbonate) species generates quickly on the reaction of $NaHCO_3$ and H_2O_2 [72–75], and then this species reacts with dioxidomolybdenum(VI) complex to give oxido-peroxidomolybdenum (VI) intermediate instantly as compared to H_2O_2 alone. Exact mechanism for the oxidation of olefins by oxidomolybdenum complexes in presence of H_2O_2 is not clear at present. However, the formation of relevant oxido-peroxido complexes has been reported by us [47,48,84] and some other groups in the past [74,85–90]. Alternative plausible mechanisms of epoxidation have also been theoretically proved, wherein the peroxido complexes were established to be less active than the oxido complexes [91–93]. Although no attempts to isolate appropriate intermediates for our system have been performed, based on the oxidation products obtained and experiments carried out above, a reaction pathway including oxido-peroxido intermediates can be proposed as shown in Scheme 3. The changes in the electronic absorption spectra (Fig. 8) indicate the interaction of $[MoO_2L^1(DMSO)]$ with H_2O_2 with the formation of a oxido-peroxido species. The same has been confirmed in a study reported by Maurya et al. [94], wherein the molybdenum peroxide species had been successfully isolated.

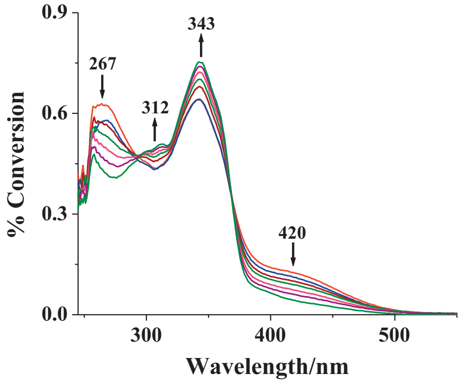
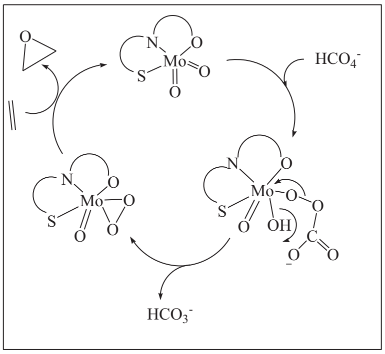


Fig. 8. UV–vis spectral changes observed during titration of complex **1** with H_2O_2. The spectra were recorded after successive additions of 1 drop of 30% H_2O_2 (2.3 mmol) dissolved in 5 mL of DMSO to 20 mL of 3.6×10^{-5} M solution of complex **1** in DMSO.



Scheme 3. Proposed catalytic mechanism for the oxidation of alkenes.

The percent conversion values indicate that the synthesized complexes (**1**–**6**) have shown better activity than some of the previous reports on Mo(VI) epoxidation catalysts, such as those of Mo (VI) hydroxamates and pyrazole based aryloxide ligands [89,95]. There is a marginal increase in the percent conversion values of epoxidation of cyclohexene as compared to our previous catalytic report on Mo(VI) complexes of Schiff bases [47].

Though no direct correlation of the substituent effect on the catalytic efficacy could be observed, however, both the percent conversion to cyclohexene oxide from cyclohexene and the percent selectivity for oxidation of styrene to styrene oxide were found to be marginally higher for the chloro substituted complexes (**3** and **6**).

4. Conclusion

In this work, six hexacoordinated molybdenum(VI) thiosemicarbazone complexes (**1**–**6**) have been prepared and characterized by spectroscopic and electrochemical techniques. The molecular structures of two of the synthesized complexes (**2** and **3**) have been successfully solved. The catalytic activity (oxidation of styrene and cyclohexene) of $Mo^{(VI)}$ complexes (**1**–**6**) have been successfully evaluated. In all the cases, the percent conversion is increased significantly (>92%) in the presence of the catalysts. Moreover, there is 100% product selectivity for the formation of cyclohexene oxide from cyclohexene and ~98–99% product selectivity for the oxidation of styrene to styrene oxide. In view of the above results, it can be concluded that molybdenum complexes derived from thiosemicarbazone ligands have the potential to stimulate the research for the synthesis of a better catalyst.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ica.2018.01.023.

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