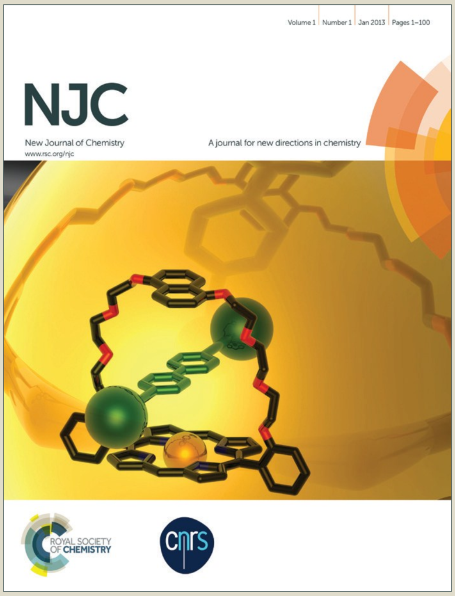
Volume 1 | Number 1 | Jan 2013 | Pages 1–100
NJC
New Journal of Chemistry
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ROYAL SOCIETY OF CHEMISTRY
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Oxidation of secondary alcohols by conventional and microwave-assisted methods using molybdenum complexes of ONO donor ligands†

Mannar R. Maurya, [a]* Sarita Dhaka, [a] and Fernando Avecilla[b]

[a] *Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India. E-mail address: rkmanfcy@iitr.ac.in. Tel.: +91 1332 285327; Fax: +91 1332 273560.*

[b] *Departamento de Química Fundamental, Universidade da Coruña, Campus de A Zapateira, 15071 A Coruña, Spain*

((Abstract))

New dioxidomolybdenum(VI) complexes, $[Mo^{VI}O_2\{Hdfmp(bhz)_2\}(MeOH)]$ **1**, $[Mo^{VI}O_2\{Hdfmp(inh)_2\}(MeOH)]$ **2** and $[Mo^{VI}O_2\{Hdfmp(nah)_2\}(MeOH)]$ **3** of ligand $H_3dfmp(L)_2$ **I**, obtained by the condensation of 2,6-diformyl-4-methylphenol (dfmp) and hydrazides (L) [L = benzoylhydrazide (bhz), isonicotinoylhydrazide (inh), and nicotinoylhydrazide (nah)], respectively. All these complexes are characterized in the solid state and in solution namely by elemental analyses, spectroscopic techniques (IR, electronic, ^1H and ^{13}C NMR) and thermogravmetric analyses. Single crystal X-ray analysis of complexes **1** and **3** confirms the coordination of the ligand in the dianionic (ONO^{2-}) enolate-tautomeric form and one of the hydrazido moieties remains non-coordinated. Oxidation of secondary alcohols: 1-phenyl ethanol, 2-propanol and 2-butanol, catalyzed by these molybdenum complexes, using conventional liquid phase and microwave-assisted methods in the presence of 30 % H_2O_2 as an oxidant have been tested. The effects of various factors, such as temperature and amounts of catalyst, H_2O_2 and solvent have been investigated. These alcohols under the optimized reaction conditions gave high yields of the respective ketone. Addition of an N-based additive reduces the reaction time considerably. Amongst the two methods studied, the microwave technique proves to be a time efficient system.

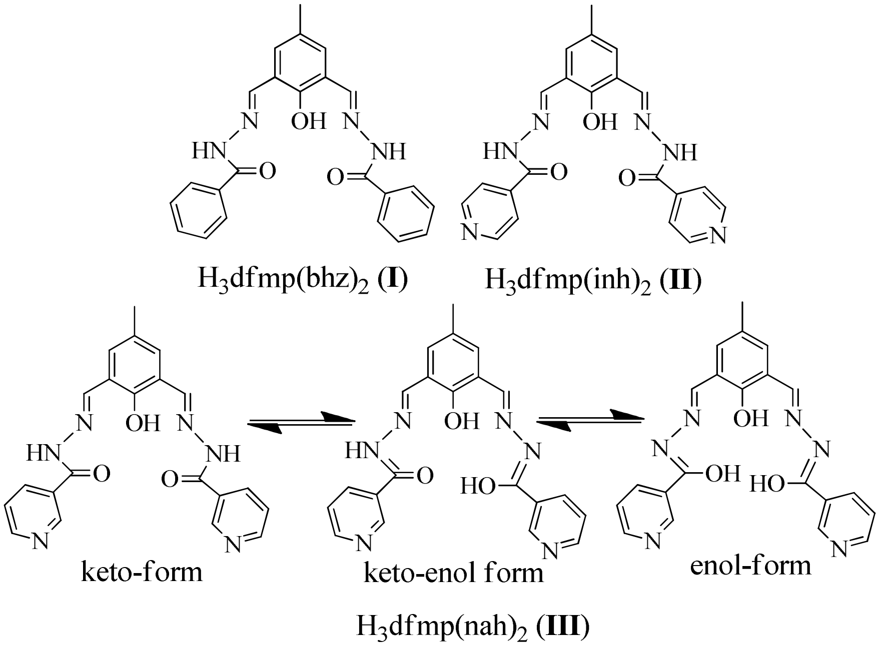
† **Electronic supplementary information (ESI) available:** ^{1}H and ^{13}C NMR description and related figures of complexes, CCDC 1037148 for **1a** and 1037149 for **3**·DMSO contain the supplementary crystallographic data for the structure reported in this paper. The supplementary data for crystals 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.

Introduction

The oxidation of volatile organic compounds e.g. secondary alcohols to respective carbonyl compounds as crucial precursors of drugs, dyes and fine chemicals have attracted much attention in chemical research during last decades.[1-3] Recently, considerable efforts have been paid in investigating highly efficient catalytic processes for oxidation of alcohols.[4,5] Traditional oxidation reactions can be efficient and selective but they often involve the use of harmful oxidants, such as CrO_3, $KMnO_4$ etc. in the presence of halogenated/non-halogenated solvents, which result in the generation of large amounts of waste. To minimize harmful wastes, the development of catalytic oxidation procedures that involve green oxidants, e.g. dioxygen or peroxides [H_2O_2, *tert*-butylhydroperoxide (TBHP)], is a matter of current interest and out of these H_2O_2 is widely used in liquid oxidation of organic compounds due to its clean and environment friendly nature.[6,7] Molybdenum compounds are considered to be very effective catalysts for the oxidation of organic compounds with TBHP and H_2O_2.[8,9] A number of soluble molybdenum complexes bearing different ligands have been synthesized and employed as homogeneous catalysts for the epoxidation of alkenes;[10,11] molybdenum complexes catalyzed oxidation of alcohols are also reported in the literature.[12,13]

The microwave irradiation is an alternate method compared to conventional liquid phase method and has widely been applied in syntheses of organic compounds.[14–19] Here, the energy is transferred directly to the reaction components resulting in shorter reaction time compared to conventional reactions [14] and cleaner reaction with a better yield and selectivity.[20,21] Addition of small amount of solvent to the reaction mixture generally improves efficiency of the catalyst due to its smooth and homogenous heating.

The hydrazones are relatively cheap and environmentally tolerable ligands, which are available commercially or can be synthesize through simple synthetic procedures.[22–24] The *cis*-$[Mo^{VI}O_2]^{2+}$ complexes of Schiff bases having ONO donor sites have drawn much attention due to their interesting catalytic properties.[9,22,25-27] Herein, we have selected ligands derived from 2,6-diformyl-4-methylphenol (dfmp) and aromatic hydrazides [benzoylhydrazide (bhz), isonicotinoylhydrazide (inh) and nicotinoylhydrazide (nah)] which are potential tribasic pentadenate O, N and O donors (Scheme 1) but they sometimes behave only as tridentate ONO due to non-participation of the potential coordination sites of one of the arms. Their new *cis*-$[Mo^{VI}O_2]^{2+}$ complexes, characterization and catalytic potential in the production of ketones by conventional liquid phase and microwave assisted peroxidative oxidation of secondary alcohols are reported.



Scheme 1 Structure of the ligands designated by **I**, **II** and **III** used in this work.

Experimental Section

Materials

Analytical reagent grade ammonium molybdate, ethyl benzoate, hydrazine hydrate, isonicotinoylhydrazide (Loba Chemie, Mumbai, India), nicotinic acid hydrazide (Acros organics, New Jersey, USA), acetylacetone, 1-phenyl ethanol (Aldrich Chemicals Co., U.S.A.), 30% aqueous H_2O_2 (Rankem, New Delhi, India), 2-propanol (Thomas Baker, Mumbai, India) and 2-

butanol (Sisco research laboratory, Mumbai, India) were used as obtained. Other chemicals and solvents were of analytical reagent grade. The precursors, $[MoO_2(acac)_2]$[28] and 2,6-diformyl-4-methylphenol[29] were prepared according to methods reported in the literature. The ligands H_3dfmp(bhz)$_2$ **I**, H_3dfmp(inh)$_2$ **II** and H_3dfmp(nah)$_2$ **III** were prepared according to the reported method.[31] Benzoyl hydrazide was prepared by the reaction of a twofold excess of hydrazine hydrate with ethyl benzoate in ethanol.

Instrumentation and characterization Procedures

Elemental analyses of the compounds were carried out on an Elementar model Vario-El-III. Thermogravimetric analyses of the complexes were carried out under an oxygen atmosphere using a TG Stanton Redcroft STA 780 instrument. IR spectra were recorded as KBr pellets on a Nicolet NEXUS Aligent 1100 series FT-IR spectrometer. Electronic spectra of ligand and complexes were recorded in DMSO or methanol using Shimadzu 1601 UV-vis spectrophotometer. ^{1}H and ^{13}C NMR spectra of complexes were recorded on a Bruker Avance 500 MHz spectrometer with the common parameter settings in DMSO-d_6. The δ values are quoted relative to TMS as internal standard. A Shimadzu 2010 plus gas-chromatograph fitted with a Rtx-1 capillary column (30 m × 0.25 mm × 0.25 μm) and a FID detector was used to analyze the catalytic reaction products. The identity of the 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 substrate and selectivity of products were calculated from GC data using the formulae presented elsewhere.[30]

Preparations

$[Mo^{VI}O_2\{Hdfmp(bhz)_2\}(MeOH)]$ 1. A solution of $[Mo^{VI}O_2(acac)_2]$ (0.66 g, 2 mmol) dissolved in 10 ml of methanol was added to a stirred solution of H_3dfmp(bhz)$_2$ (0.80 g, 2 mmol) in methanol (20 ml) and the obtained reaction mixture was stirred at room temperature whereupon an yellow solid started to form. After 3 h of stirring, the separated solid was filtered, washed with cold methanol followed by petroleum ether and dried in a vacuum desiccator over silica gel. Yield: 1.03 g (92.0%). (Found: C, 51.93; H, 3.86; N, 10.24 %. Calc'd. for $C_{24}H_{22}N_4O_6Mo$ (558.39): C, 51.62; H, 3.97; N, 10.03%). X-ray diffraction quality crystals of **1** having formulation [Mo^{VI}O$_2${Hdfmp(bhz)$_2$}(H$_2$O)]·DMSO (**1a**) were grown by diffusing MeOH to a DMSO-water (95:5) solution of complex.

[Mo^{VI}O$_2${Hdfmp(inh)$_2$}(MeOH)] 2. Complex **2** was prepared from [Mo^{VI}O$_2$(acac)$_2$] (0.66 g, 2 mmol) and H$_3$dfmp(inh)$_2$ (0.804, 2 mmol) in methanol by the method used for **1**. The separated yellow solid was filtered, washed with cold methanol followed by petroleum ether and dried in a vacuum desiccator over silica gel. Yield: 1.02 g (91.0%). (Found: C, 47.68; H, 3.56; N, 15.20%. Calc'd. for $C_{22}H_{20}N_6O_6Mo$ (560.37): C, 47.15; H, 3.60; N, 15.00%).

[Mo^{VI}O$_2${Hdfmp(nah)$_2$}(MeOH)] 3. Complex **3** was prepared from [Mo^{VI}O$_2$(acac)$_2$] (0.66 g, 2 mmol) and H$_3$dfmp(nah)$_2$(0.804 g, 2 mmol) in methanol following the method described for **1**. After 3 h of stirring, the separated yellow solid was filtered, washed with cold methanol followed by petroleum ether and dried in a vacuum desiccator over silica gel. Yield: 1.00 g (89.3%). (Found: C, 47.28; H, 3.68; N, 15.23%. Calc'd. for $C_{22}H_{20}N_6O_6Mo$ (560.37): C, 47.15; H, 3.60; N, 15.00 %). X-ray diffraction quality crystals of **3** having formulation [Mo^{VI}O$_2${Hdfmp(nah)$_2$}(MeOH)]·DMSO (**3**·DMSO) were grown by diffusing MeOH to a DMSO solution of complex.

X-Ray single crystal diffraction studies

Three-dimensional X-ray data were collected on a Bruker Kappa Apex CCD diffractometer at room temperature for **1a** and low temperature for **3**·DMSO by the ϕ-ω scan method. Reflections were measured from a hemisphere of data collected from frames each of them covering 0.3° in ω. Of the 18084 for **1a** and 17509 for **3**·DMSO reflections measured, all were corrected for Lorentz and polarization effects and for absorption by multi-scan methods based on symmetry-equivalent and repeated reflections, 4894 and 2699, respectively, independent reflections exceeded the significance level ($|F|/\sigma|F|$) > 4.0. Complex scattering factors were taken from the program package SHELXTL.[32] The structures were solved by direct methods and refined by full matrix least-squares on F^2. In **1a**, hydrogen atoms were located in the difference Fourier map and left to refine freely, except for C(2), C(5), C(15), C(22) and N(4), which were included in calculated positions and refined in the riding mode. Hydrogen atoms of O(1W), C(1S) and C(2S), were located in the difference Fourier map and fixed to the corresponding atoms. In **3**·DMSO, hydrogen atoms were included in calculation positions and refined in the riding mode, except for C(7), C(15) and N(5), which were located in the difference Fourier map and left to refine freely. Refinements were done with allowance for thermal anisotropy of all non-hydrogen atoms. Further details of the crystal structure determination are given in Table 1. A final difference Fourier map showed no residual density outside: 0.504 and -0.825 e.Å^{-3} for **1a** and 1.167 and -1.259 e.Å^{-3} for **3**·DMSO. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.068800\ P)^2 + 0.282000\ P]$ for **1a** and $w = 1/[\sigma^2(F_o^2) + (0.060200\ P)^2 + 12.752000\ P]$ for **3**·DMSO, where $P = (|F_o|^2 + 2|F_c|^2)/3$, were used in the latter stages of refinement. The crystal of **1a** presents important disorder on DMSO molecule. The disorder on DMSO molecule was solved and the atomic sites have been observed and refined with anisotropic atomic displacement parameters. The site occupancy factor was 0.88613 for S(1S). This disorder was refined using 43 restraints (SADI, SIMU and DELU restraints were used).

Table 1 Crystal data and structure refinement for $[\mathrm{Mo^{VI}O_2\{Hdfmp(bhz)_2\}(H_2O)}]\cdot$DMSO **1a** and for $[\mathrm{Mo^{VI}O_2\{Hdfmp(nah)_2\}(MeOH)}]\cdot$DMSO **3**·DMSO.

	1a	**3**·DMSO
Formula	$C_{25}H_{26}MoN_4O_7S$	$C_{24}H_{26}MoN_6O_7S$
Formula weight	622.50	638.51
T, *K*	293(2)	100(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$
a/Å	8.782(5)	7.3114(10)
b/Å	11.521(5)	13.174(2)
c/Å	14.083(5)	13.6623(19)
α/º	106.769(5)	98.512(7)
β/º	98.537(5)	91.457(6)
γ/º	91.636(5)	90.513(7)
V/Å^3	1345.3(11)	1300.9(3)
Z	2	2
F_{000}	636	652
D_{calc}/g cm^{-3}	1.537	1.630

μ/mm^{-1}	0.616	0.641
θ/ (°)	1.53 to 32.79	1.51 to 26.20
R_{int}	0.0386	0.1632
Crystal size/ mm^3	0.29 × 0.24 × 0.21	0.10 × 0.06 × 0.03
Goodness-of-fit on F^2	1.094	1.112
R_1 [a]	0.0460	0.0830
wR_2 (all data) [b]	0.1421	0.2258
Largest differences peak and hole (eÅ^{-3})	0.504 and -0.825	1.167 and -1.259

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(|F_o|^2-|F_c|^2|)^2]|/\Sigma[w(F_o^4)]\}^{1/2}$

Catalytic activity studies-Oxidation of secondary alcohols with aqueous H_2O_2

Conventional liquid phase method. Oxidation reactions were carried out in a 50 mL round-bottom flasks equipped with a reflux condenser. Under typical conditions, secondary alcohol 5 mmol {1-phenyl ethanol (0.610 g), 2- propanol (0.300 g) or 2- butanol (0.370 g)}, aqueous 30% H_2O_2 (1.69 g, 15 mmol), additive (250 µmol) and catalyst (0.002 g) were dissolved in acetonitrile (5 mL) and the obtained solution was stirred for a particular time depending upon the substrate using magnetic stirrer. The desired reaction temperature (typically 80 °C) was maintained using an oil bath. The reaction was monitored by withdrawing small aliquots of the reaction mixture at definite time interval, extracting with hexane and analyzing quantitatively by gas chromatograph. The identities of the products were confirmed by GC–MS.

Microwave-assisted method. Anton Paar Monowave 300 Microwave synthesis reactor equipped with IR sensing probe to control the reaction temperature was used to carry out all catalytic reactions. Non-thermal effects were not studied as the instrument does not permit to work below 40 °C. The oxidation of secondary alcohols was carried out in a sealed Pyrex tube under focused microwave irradiation under the reaction conditions pre-fixed for conventional liquid phase method in the minimum amount of solvent. The reaction mixture was irradiated (25 W) along with stirring for 30–120 min (depending up on the substrate) at 80 °C. After cooling the reaction mixture to room temperature, it was extracted with hexane and analyzed by GC and GC–MS.

Results and discussion

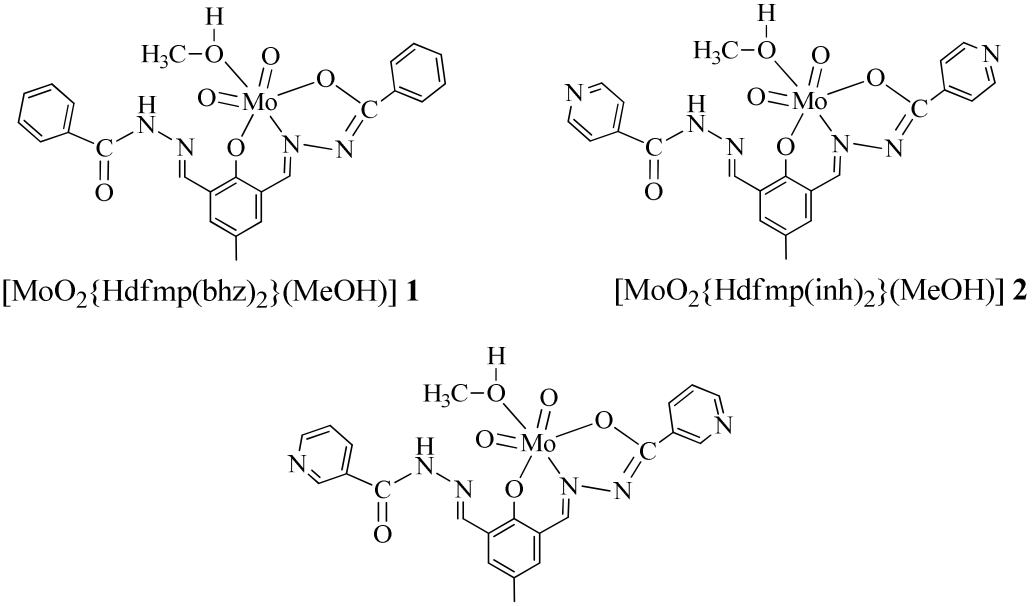
Synthesis and characterization of complexes

Scheme 2 provides idealized structures of the complexes, which are based on the spectroscopic (IR, UV/Vis, ^{1}H and ^{13}C NMR) data, elemental analyses and X-ray diffraction studies of $[\mathrm{Mo^{VI}O_2\{Hdfmp(bhz)_2\}(H_2O)]\cdot DMSO}$ **1a** and $[\mathrm{Mo^{VI}O_2\{Hdfmp(nah)_2\}(MeOH)]\cdot DMSO}$ **3**·DMSO.

The dioxidomolybdenum(VI) precursor $[\mathrm{Mo^{VI}O_2(acac)_2}]$ reacts with the ligands $\mathrm{H_3dfmp(bhz)_2}$ **I**, $\mathrm{H_3dfmp(inh)_2}$ **II** and $\mathrm{H_3dfmp(nah)_2}$ **III** (*c.f.* Scheme 1) in methanol to give dioxidomolybdenum(VI) complexes $[\mathrm{Mo^{VI}O_2\{Hdfmp(bhz)_2\}(MeOH)]}$ **1**, $[\mathrm{Mo^{VI}O_2\{Hdfmp(inh)_2\}(MeOH)]}$ **2** and $[\mathrm{Mo^{VI}O_2\{Hdfmp(nah)_2\}(MeOH)]}$ **3**, respectively. The ligands coordinate via the dianionic (ONO(2−)) enolate-tautomeric moiety, while other potential coordination sites remain free. [Eqn (1) taking **I** as a representative example].

$$[\mathrm{Mo^{VI}O_2(acac)_2}] + \mathrm{H_3dfmp(bhz)_2} + \mathrm{MeOH} \rightarrow$$
$$[\mathrm{Mo^{VI}O_2\{Hdfmp(bhz)_2\}(MeOH)]} + 2\mathrm{Hacac} \qquad (1)$$

All these complexes are soluble in methanol, ethanol and acetonitrile. In these complexes, the sixth coordination site is occupied by methanol.



$[MoO_2\{Hdfmp(bhz)_2\}(MeOH)]$ **1**

$[MoO_2\{Hdfmp(inh)_2\}(MeOH)]$ **2**

$[MoO_2\{Hdfmp(nah)_2\}(MeOH)]$ **3**

Scheme 2 Structure of metal complexes.

The thermal stability of monomeric complexes **1**, **2** and **3** has been studied under an oxygen atmosphere. These complexes lose mass roughly equal to one methanol molecule in the temperature range 100-140 °C, indicating the presence of coordinated methanol. On further increasing the temperature the solvent free complexes decompose exothermically in two/ three overlapping steps and form MoO_3 as a final product. The observed MoO_3 contents of 25.7 % at ca. 510 °C for **1**, 25.0 % at 470 °C for **2** and 24.7 % at 475 °C for **3** match closely with the calculated values of 25.9, 25.8 and 25.8 %, respectively.

Structure descriptions

The ORTEP diagrams of complexes **1a** and **3**·DMSO are shown in Figs. 1 and 2, respectively. Fig. 3 presents the intermolecular π-π interactions. Selected bond distances and angles are given in Table 2. These complexes adopt a six-coordinated structure in a distorted octahedral geometry. In the complexes, the phenolic oxygen, hydrazide oxygen and the azomethine nitrogen atoms of the ligands coordinate to the molybdenum while other set of hydrazide oxygen and azomethine nitrogen atoms of the ligands do not participate in coordination, as in other similar compounds.[31] One water molecule in **1a**, one methanol molecule in **3**·DMSO and two oxido groups complete the coordination sphere. One DMSO molecule in **1a** and other DMSO molecule in **3**·DMSO are present in the crystal packing. The DMSO molecule of **1a** presents a disorder on sulphur atom. Two atomic sites have been observed for the first DMSO molecule [site occupancy factor for S(1S) is 0.88613].

In complex **1a**, the phenyl groups of the coordinated set of two complexes interact by π-π interactions. The steric requirements, derived from coordination sphere around Mo, prevent π-π interactions between the phenol rings (see Fig. 3). The distances between centroids are: $d_{c1\text{-}c2}$ = 3.727 Å [c1(C1G-C2G-C3G-C4G-C5G-C6G), c2 (C1K-C2K-C3K-C4K-C5K-C6K)]. Intermolecular hydrogen bonds are present in the crystal packing in the three structures (see Table 3).

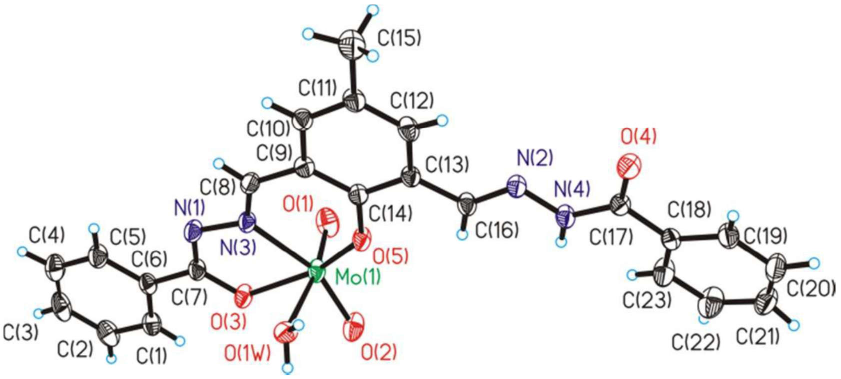


Fig. 1 ORTEP plot of complex **1a**. All the non-hydrogen atoms are presented by their 30% probability ellipsoids. DMSO is omitted for clarity.

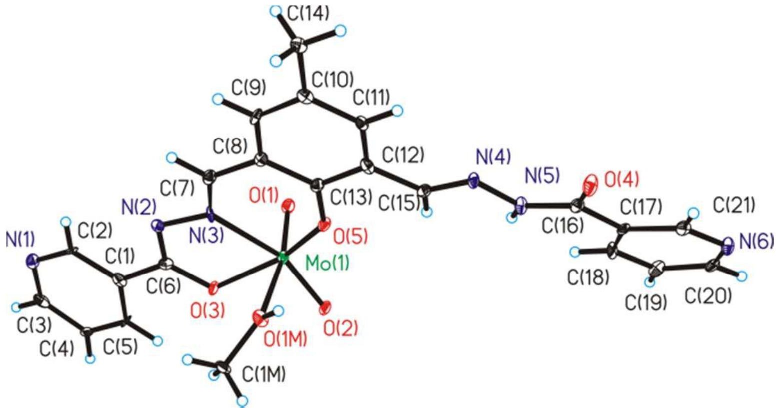


Fig. 2 ORTEP plot of complex **3**·DMSO. All the non-hydrogen atoms are presented by their 30% probability ellipsoids. DMSO is omitted for clarity.

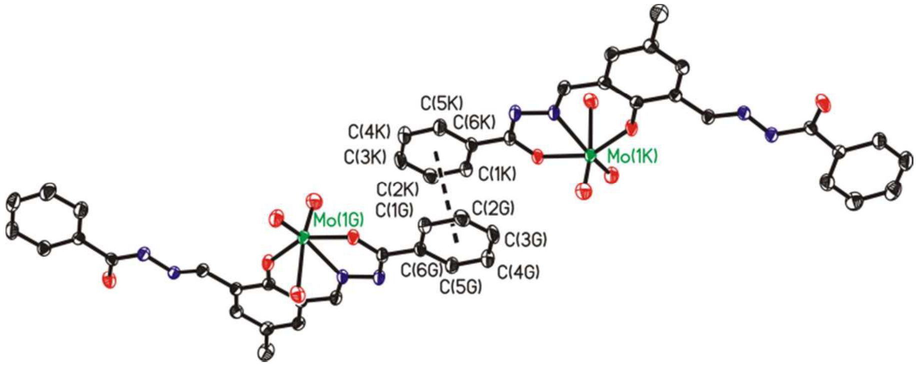


Fig. 3 Intermolecular π-π interactions in **1a**. Dashed lines link the centres of the π clouds involving in each interaction.

Table 2 Bond lengths [Å] and angles [°] for **1a** and **3**·DMSO

Bond lengths **1a**		Bond lengths **3**·DMSO	
Mo(1)-O(1)	1.689(3)		1.704(7)
Mo(1)-O(2)	1.697(3)		1.705(7)
Mo(1)-O(3)	2.008(2)		1.999(6)
Mo(1)-O(5)	1.922(2)		1.900(7)
Mo(1)-O(1W)	2.338(3)	Mo(1)-O(1M)	2.288(7)
Mo(1)-N(3)	2.239(3)		2.234(9)

Bond angles **1a**		Bond angles **3**·DMSO	
O(1)-Mo(1)-O(2)	105.73(16)		105.8(4)
O(1)-Mo(1)-O(5)	99.23(14)		100.2(3)
O(2)-Mo(1)-O(5)	104.24(11)		103.9(3)
O(1)-Mo(1)-O(3)	95.82(13)		95.6(3)
O(2)-Mo(1)-O(3)	96.37(11)		96.4(3)
O(5)-Mo(1)-O(3)	149.99(11)		149.6(3)
O(1)-Mo(1)-N(3)	94.05(13)		91.8(3)
O(2)-Mo(1)-N(3)	157.96(13)		160.0(3)
O(5)-Mo(1)-N(3)	81.55(10)		81.6(3)
O(3)-Mo(1)-N(3)	71.57(10)		72.1(3)

O(1)-Mo(1)-O(1W)	169.45(12)	O(1)-Mo(1)-O(1M)	167.9(3)
O(2)-Mo(1)-O(1W)	84.30(13)	O(2)-Mo(1)-O(1M)	86.1(3)
O(5)-Mo(1)-O(1W)	81.07(11)	O(5)-Mo(1)-O(1M)	77.9(3)
O(3)-Mo(1)-O(1W)	79.52(10)	O(3)-Mo(1)-O(1M)	81.2(3)
N(3)-Mo(1)-O(1W)	75.52(10)	N(3)-Mo(1)-O(1M)	76.1(3)

Table 3 Hydrogen bonds for complex **1a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1WB)...O(4)#1	0.87	1.86	2.726(4)	173.5
O(1W)-H(1WA)...O(4)#2	0.84	2.28	2.919(3)	132.8
O(1W)-H(1WA)...N(2)#2	0.84	2.27	3.047(4)	154.6
N(4)-H(4N)...O(1S)	0.86	2.04	2.864(4)	159.9

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1 #2 x-1,y,z

Spectral studies

A partial list of IR spectral data of ligands and complexes are presented in Table **4**. Though, there are two azomethine, ketonic and NH groups present in all the ligands, they exhibit single band for each. The IR spectra of the ligands exhibit ν(NH) and ν(C=O) at 3021–3064 and 1645–1665 cm^{-1}, respectively. These bands indicate their ketonic nature in the solid state (*cf.* Scheme 1). All the complexes retain the positions of these bands with slight deviations along with the appearance of a new band at 1246–1259 cm^{-1} due to the ν(C-O) stretch. This observation suggests the enolization of one of the ketonic groups and replacement of H by the metal ion while the presence of a ketonic band suggests that all the ligands have at least one ketonic group free from coordination. Recently reported DFT calculations on vanadium complexes with these ligands have suggested the mixing of the enolic ν(C-O) stretch with a number of δ(CH) and δ(NH) bending modes.[31] Similarly, all complexes exhibit two azomethine stretches; one at nearly same position to that of respective ligand while other one at lower wave number (1571 – 1617 cm^{-1}). This shows the coordination of only one of the azomethine nitrogen to the metal ion. The presence of several medium intensity bands between 2800 and 2500 cm^{-1} in the ligands as well as in complexes suggest the existence of C-H stretching bands due to -CH_2. In addition, these complexes display two sharp bands at 933–944 and 914–920 cm^{-1} due to the ν_{asym}(O=Mo=O) and ν_{sym}(O=Mo=O) streching modes, respectively due to the presence of *cis*-[$Mo^{VI}O_2$] moiety.[33]

Table 4 IR spectral data [in cm^{-1}] of compounds

Compounds	ν(NH)	ν(C=O)	ν(C=N)	ν(C-O)	ν(O=Mo=O)[a]
H_3dfmp(bhz)$_2$ **I**	3050	1665	1619		
[$Mo^{VI}O_2${Hdfmp(bhz)$_2$}(MeOH)] **1**	3064	1651	1571,1616	1259	933, 914
H_3dfmp(inh)$_2$ **II**	3030	1655	1618		
[$Mo^{VI}O_2${Hdfmp(inh)$_2$}(MeOH)] **2**	3021	1663	1577,1615	1246	944, 920
H_3dfmp(nah)$_2$ **III**	3050	1645	1616		
[$Mo^{VI}O_2${Hdfmp(nah)$_2$}(MeOH)] **3**	3040	1652	1594,1617	1254	935, 920

[a] Asymmetric and symmetric ν(O=Mo=O) values.

The electronic absorption spectra of ligands and metal complexes were recorded in methanol successfully. Table **5** presents absorption maxima of the ligands and complexes with their extinction coefficients. The electronic spectra of ligands **I**, **II** and **III** exhibit three spectral bands at 427-453, 363-364, 300-303 and 201-218 nm.[31] Based on their extinction coefficients, these bands are interpreted as split n→π* (first two bands), π→π* and φ → φ* transitions, respectively. All these bands are present in complexes with slight variations. In addition, all complexes exhibit a medium intensity band at 430 – 450 nm due to ligand to metal charge transfer (LMCT) transition from the phenolate oxygen atom to an empty d-orbital of the molybdenum and n → p* (imine type) transitions.[34,35] As Mo^{VI}-complexes have $4d^0$ configuration, the d→d band is not expected.

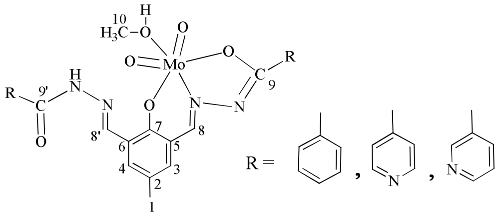
Table 5 Electronic spectral data of ligands and complexes recorded in methanol

Compound	λ_{max} /nm (ε/ $M^{-1}cm^{-1}$)
H_3dfmp(bhz)$_2$ **I**	203(5.0 × 10^3), 300(7.0 × 10^3), 363(2.5 × 10^3), 427(4.0 × 10^2)
[Mo^{VI}O$_2${Hdfmp(bhz)$_2$}(MeOH)] **1**	299(2.5 × 10^4), 358(9.0 × 10^3), 430(5.2 × 10^3)
H_3dfmp(inh)$_2$ **II**	201(2.5 × 10^4), 303(3.4 × 10^4), 364(1.7 × 10^4), 453(2.8 × 10^3)
[Mo^{VI}O$_2${Hdfmp(inh)$_2$}(MeOH)] **2**	304(1.8 × 10^4), 360(1.3 × 10^4), 450(5.4 × 10^3)
H_3dfmp(nah)$_2$ **III**	218(1.1 × 10^4), 300(2.0 × 10^4), 363(8.7 × 10^3), 453(1.2 × 10^3)
[Mo^{VI}O$_2${Hdfmp(nah)$_2$}(MeOH)] **3**	300(3.0 × 10^4), 360(1.6 × 10^4), 446(6.1 × 10^3)

The ^{1}H NMR spectra of ligands and the corresponding complexes were recorded to confirm their coordinating modes. Fig. S1 presents the ^{1}H NMR spectra of a representative ligand **I** and its complex. The entire spectral data presented in Table S1 (See SI section) confirms the coordination of ligands as dianionic (ONO(2−)) only.

The ^{13}C NMR spectra of a representative ligand **I** and its complex **1** are presented in Fig. S2 while Table **6** provides entire spectral data. Assignments of the peaks are based on the chemical shift obtained for various carbons and on the coordination-induced shifts ($\Delta\delta$) of the signals for carbon atoms in the vicinity of the coordinating atoms.[36] These data supplement the inference obtained from IR studies.

Table 6 ^{13}C NMR spectral data of ligand and complexes



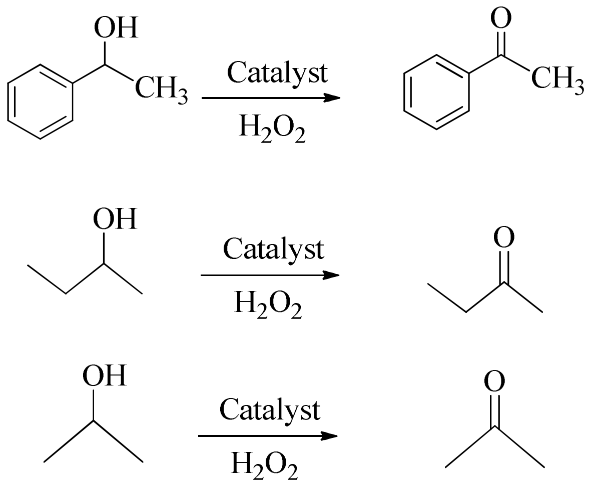
Compound	C1	C2	C3/C4	C5/C6	C7	C8/C8'	C9/C9'	C10	R
I	20.38	129.03	132.47	120.37	155.18	146.63	163.48		133.35, 130.88, 128.73, 128.15
1	19.94	130.70	132.14	120.92	142.23	163.01,136.34	168.90,155.98	48.63	128.88, 133.20, 129.83, 131.85, 127.69,
($\Delta\delta$)					(-12.95)	(16.38)	(5.42)		128.04, 128.50, 123.92
II	20.35	128.91	131.32	120.17	155.37	147.73	161.94		140.41, 150.85, 123.25
2	20.35	131.36	131.98	121.22	156.34	163.20,143.52	167.32,158.41	48.70	138.20,140.46,152.02,152.58,129.42,
($\Delta\delta$)					(0.97)	(15.47)	(5.38)		125.80

III	20.32	129.07	131.18	120.14	155.25	147.32	162.11		128.86, 148.99, 124.18, 152.88, 136.02
3	20.35	131.37	131.69	121.27	156.55	162.11,143.32	167.84,157.12	48.52	124.48,126.51,152.8,149.07,123.52,124.08, 149.25,135.95,152.95,137.16
(Δ*δ*)					(1.3)	(14.79)	(5.73)		

Catalytic activity studies

Conventional liquid phase method for the oxidation of secondary alcohols

Oxidation of alcohols catalyzed by molybdenum (VI) complexes has been studied using TBHP as well as H_2O_2 as an oxidant. [8, 9] All new molybdenum complexes reported here have ability to catalyze secondary alcohols *viz*. 1-phenyl ethanol, 2-butanol and 2-propanol to acetophenone, 2-butanone and acetone, respectively (Scheme 3), with a remarkable yield as well as turn over frequency.



Scheme 3 Oxidation of secondary alcohols.

We have selected **1** as a representative catalyst and 1-phenyl ethanol as a representative secondary alcohol and optimized reaction conditions for the maximum oxidation of 1-phenyl ethanol by studying four different reaction parameters *viz.* the effect of amounts of catalyst, oxidant, solvent and temperature of the reaction mixture in detail. The effect of amount of catalyst was studied considering three different amounts: 0.001, 0.002 and 0.003 g of catalyst for 1-phenyl ethanol (0.610 g, 5 mmol) and aqueous 30% H_2O_2 (1.70 g , 15 mmol) in 5 ml of CH_3CN and the reaction was carried out at 80 ^{o}C. As illustrated in entries no. 1, 2 and 3 of Table 7, the percent conversion of 1-phenyl ethanol improved from 77% to 91% on increasing the amount of catalyst, from 0.001 g to 0.002 g, while 0.003 g catalyst improved the conversion only 3%, suggesting that 0.002 g of catalyst is sufficient enough to perform the reaction with good conversion. Similarly, three different molar ratios of 1-phenyl ethanol to H_2O_2 were considered under above conditions (entries no. 4 and 5 of Table **7**) and out of these 1:3 was the suitable one for the maximum conversion. Amongst three different temperatures of 60, 70 and 80 ^oC (entries no. 1, 8 and 9 of Table **7**) for the fixed operating conditions of 1-phenyl ethanol (0.610 g, 5 mmol), H_2O_2 (1.70 g, 15 mmol), **1** (0.002 g) and CH_3CN (5 ml), running the reaction at 80 ^oC gave much better conversion. Variation in the volume of CH_3CN (5, 10 and 15 ml) was also studied (entries no. 1, 6 and 7 of Table **7**) and it was observed that 5 ml of CH_3CN was sufficient enough to get good transformation of 1-phenyl ethanol. Thus, all reaction conditions as concluded above for 5 mmol 1-phenyl ethanol [i.e. H_2O_2 (1.70 g, 15 mmol), **1** (0.002 g), CH_3CN (5 ml) and reaction temperature 80 ^oC] were considered essential and applied for the maximum transformation of 91% with 66 TOF of 1-phenyl ethanol into oxidation product. About 20 h was required to attain the equilibrium. Fig. 4 and Table 7 summarize all the conditions and conversions obtained under a particular set of conditions.

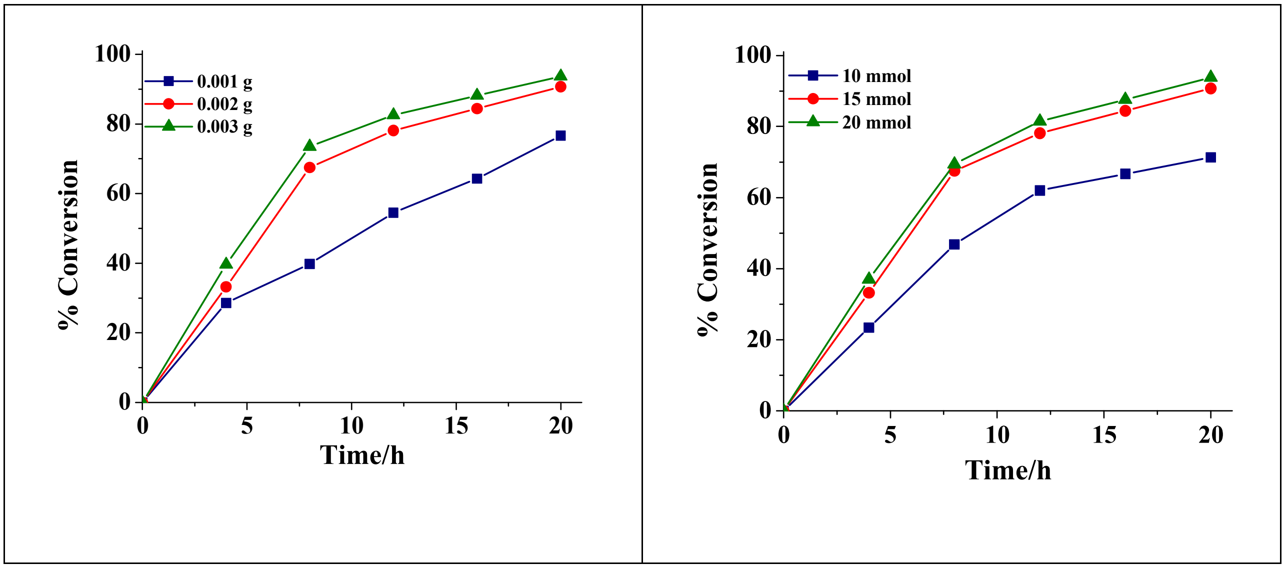
Table 7 Conversion of 1-phenyl ethanol (0.61 g, 5 mmol), using **1** as catalyst precursor in 20 h of reaction time under different reaction conditions

Entry No.	Catalyst [g (mmol)]	H_2O_2 [g (mmol)]	CH_3CN [mL]	Temp. [^oC]	Conversion [%]
1	0.001 (1.8×10^{-3})	1.70 (15)	5	80	77
2	0.002 (3.5×10^{-3})	1.70 (15)	5	80	91
3	0.003 (5.3×10^{-3})	1.70 (15)	5	80	94
4	0.002 (3.5×10^{-3})	1.14 (10)	5	80	71
5	0.002 (3.5×10^{-3})	2.27 (20)	5	80	94
6	0.002 (3.5×10^{-3})	1.70 (15)	10	80	84
7	0.002 (3.5×10^{-3})	1.70 (15)	15	80	81
8	0.002 (3.5×10^{-3})	1.70 (15)	5	70	80
9	0.002 (3.5×10^{-3})	1.70 (15)	5	60	69

Under the optimized reaction conditions other catalysts precursors have also been tested and their catalytic potentials are equally good. The oxidation of other two alcohols, 2-butanol and 2-propanol using catalysts **1**, **2** and **3** under above optimized reaction conditions gave 86-87% conversion in 8 h with TOF of ca. 150 and 90-94% conversion in 6 h with TOF of ca. 210.

The addition of N-based additive like NEt_3,[7] accelerates the reaction with equally good conversion and reduces the equilibrium attainment time from 20 h to 8 h, 8 h to 3 h and 6 h to 2 h for the substrate 1-phenyl ethanol, 2-butanol and 2-propanol, respectively.

Blank reaction (i.e. in absence of catalyst) under above reaction conditions gave 28% conversion for 1-phenylethanol, 32% conversion for 2-butanol and 38% conversion for 2-propanol.



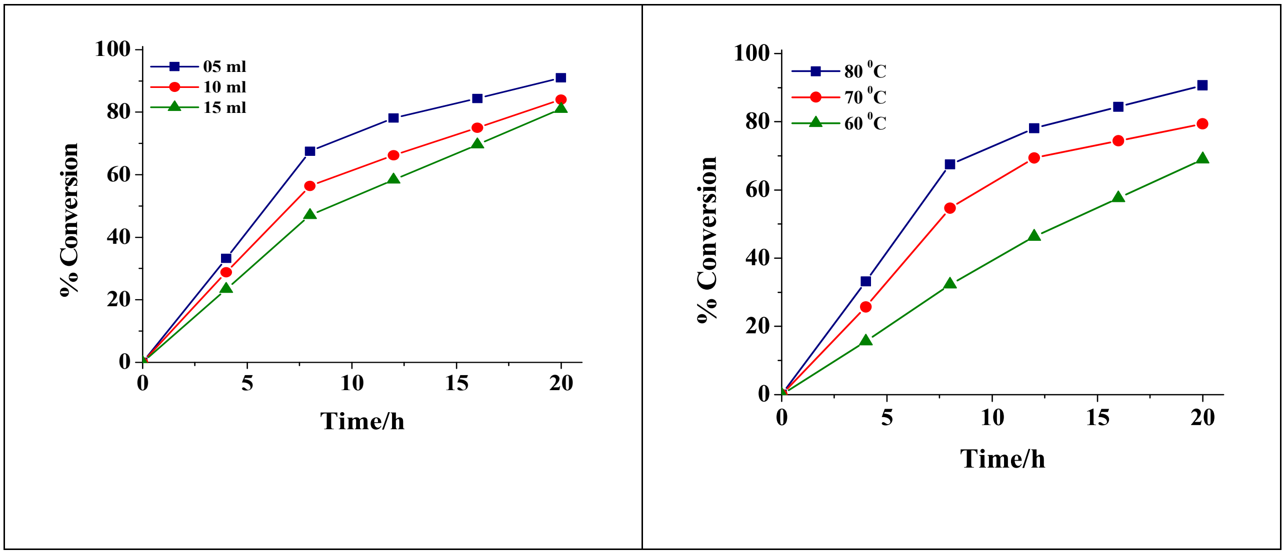


Fig. 4 (a) Effect of catalyst amount on the oxidation of 5 mmol of 1-phenyl ethanol. Other reaction conditions: 30 % H_2O_2 (1.70 g, 15 mmol), temperature (80 °C) and acetonitrile (5 ml). (b) Effect of oxidant amount on the oxidation of 5 mmol of 1-phenyl ethanol. Other reaction conditions: catalyst (0.002 g), temperature (80 °C) and acetonitrile (5 ml). (c) Effect of solvent amount on the oxidation of 5 mmol of 1-phenyl ethanol. Other reaction conditions: catalyst (0.002 g), 30 % H_2O_2 (1.70 g, 15 mmol) and temperature (80 °C) (d) Effect of temperature variation on the oxidation of 5 mmol of 1-phenyl ethanol. Other reaction conditions: catalyst (0.002 g), 30 % H_2O_2 (1.70 g, 15 mmol) and acetonitrile (5 ml).

Microwave assisted oxidation of secondary alcohols

Oxidation of secondary alcohols, catalyzed by copper complexes, by Microwave-assisted method has been reported in the literature.[7,37] Complexes **1**, **2** and **3** were also tested as catalyst precursor for the oxidation of 1-phenyl ethanol to acetophenone using aqueous 30 % H_2O_2 as oxidizing agent, under typical conditions of 80 °C in acetonitrile with low power (25 W) microwave irradiation (MW) for 30-120 min reaction time. The catalytic reactions in microwave were carried out under the same optimized reaction conditions as concluded for conventional method and the obtained results are summarized in Table 8 and compared with the results obtained by conventional method. It is clear from the data of table that reaction completes within 2 h compared to 20 h by conventional method. This time was further reduced to 1 h when additive NEt_3 (0.250 g) was used. Under the same reaction conditions other secondary alcohols, 2-butanol and 2-propanol were also tested and similar proportionate reduction in reaction time was noted (Table 8). Apart from the respective ketone, GC and GC–MS analyses of the final reaction mixtures show no traces of by-product except the unreacted substrate. Thus, catalytic efficiency as well as selectivity of catalysts by microwave assisted method is comparable to conventional liquid phase oxidation method.

Control experiments (blank tests) were also carried out using microwave irradiation method and obtained conversions are 17% for 1-phenylethanol, 31% for 2-butanol and 23% for 2-propanol under the same experimental conditions.

Table 8 Oxidation of alcohols by both conventional and microwave assisted method using molybdenum complexes as catalyst.

Catalyst	Conventional method				Microwave method			
	Without additive		With additive [a]		Without additive		With additive [a]	
	Conv. %	Time (h)	Conv. %	Time (h)	Conv. %	Time (h)	Conv. %	Time (h)
1- phenyl ethanol								
1	91	20	90	8	82	2	91	1
2	93	20	93	8	77	2	94	1
3	92	20	93	8	80	2	93	1
2-butanol								
1	86	8	91	3	81	1	91	0.5
2	87	8	92	3	85	1	92	0.5
3	87	8	95	3	84	1	89	0.5
2-propanol								
1	94	6	95	2	92	1	93	0.5
2	92	6	93	2	89	1	94	0.5
3	90	6	94	2	90	1	94	0.5

[a] additive NEt_3 (0.250 g)

Reactivity of dioxidomolybdenum(VI) complexes and possible mechanism for catalytic oxidation of substrates.

As observed earlier, the dioxidomolybdenum(VI) complexes react with H_2O_2 to give the corresponding $[Mo^{VI}O(O_2)]^{2+}$ complexes.[38] The generation of such species has been established here in methanol by electronic absorption spectroscopy. In a typical reaction, 20 mL of 2.6×10^{-5} M solution of **1** was treated drop wise with a solution prepared by dissolving 30% aqueous H_2O_2 (0.715 g, 6.3 mmol) in 5 mL of methanol and the resultant spectroscopic changes are presented in Fig. **5**. Thus 358 nm band shifts to 363 nm along with only marginal change in the intensity while the 299 nm band increases its intensity considerably and finally disappears. The broad charge transfer band appearing at 430 nm slowly decreases in intensity (Fig. **5**(**a**)) along with further broadening and finally disappears. Simultaneously, a new shoulder band appears at ca. 380 nm. These changes indicate the interaction of **1** with H_2O_2 and the plausible formation of $[Mo^{VI}O(O_2)\{Hdfmp(bhz)_2\}(MeOH)]$ in methanol; Eq. (3). Similar spectral changes have also been noted for other complexes; Fig. **5**(**b**) and **5**(**c**). Thus, the reaction of H_2O_2 with complexes during catalytic reaction is likely to proceed through the $[Mo^{VI}O(O_2)]^{2+}$ intermediate which may transfer oxygen to the substrates during the catalytic oxidation.

$$[Mo^{VI}O_2\{Hdfmp(bhz)_2\}(MeOH)] + H_2O_2 \rightarrow [Mo^{VI}O(O_2)\{Hdfmp(bhz)_2\}(MeOH)] + H_2O \quad (3)$$

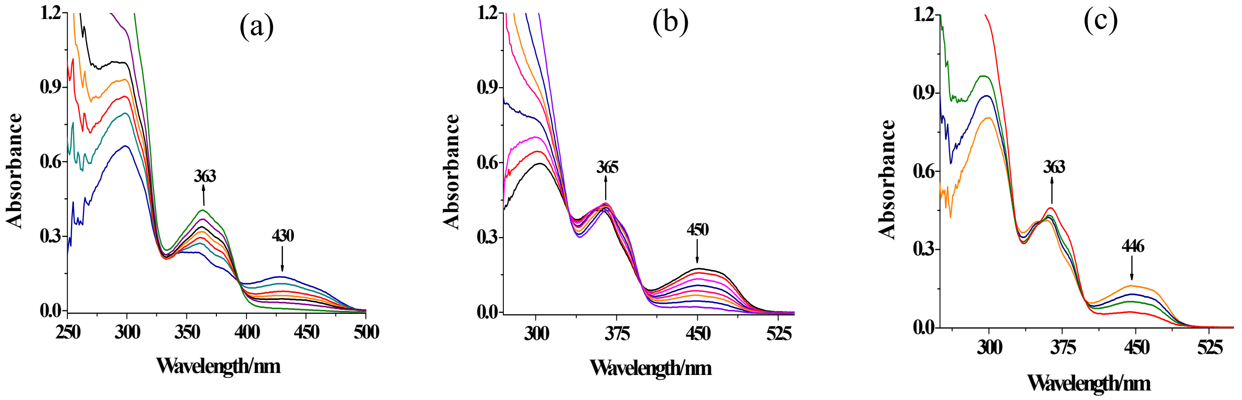


Fig. 5 Spectral changes observed during the titration of dioxidomolybdenum(VI) complexes. (a) The spectra were recorded after successive addition of one drop portion of H_2O_2 [30% H_2O_2 (0.715 g, 6.3 mmol) dissolved in 5 mL of MeOH; final concentration of H_2O_2 = 1.26 M)] to 20 mL of 2.6×10^{-5} M solution of $[Mo^{VI}O_2\{Hdfmp(bhz)_2\}(MeOH)]$. (b) The spectra were recorded after successive addition of one drop portion of H_2O_2 [30% H_2O_2 (0.910 g, 8.0 mmol) dissolved in 5 mL of MeOH; final concentration of H_2O_2 = 1.60 M)] to 20 mL of 3.2×10^{-5} M solution of $[Mo^{VI}O_2\{Hdfmp(inh)_2\}(MeOH)]$. (c) The spectra were recorded after successive addition of one

drop portion of H_2O_2 [30% H_2O_2 (0.845 g, 7.5 mmol) dissolved in 5 mL of MeOH; final concentration of H_2O_2 = 1.48 M] to 20 of mL of 2.4 × 10^{-5} M solution of $[Mo^{VI}O_2\{Hdfmp(nah)_2\}(MeOH)]$.

Conclusions

The dioxidomolybdenum(VI) complexes $[Mo^{VI}O_2\{Hdfmp(bhz)_2\}(MeOH)]$ **1**, $[Mo^{VI}O_2\{Hdfmp(inh)_2\}(MeOH)]$ **2** and $[Mo^{VI}O_2\{Hdfmp(nah)_2\}(MeOH)]$ **3** have been prepared from potential tribasic pentadentate $O(NO)_2$ type ligands $H_3dfmp(bhz)_2$ **I**, $H_3dfmp(inh)_2$ **II** and $H_3dfmp(nah)_2$ **III**, respectively but they behave as dibasic tridentate and other coordinating atoms remain free. All these complexes have fully been characterized by employing various spectroscopic techniques and two of them by single crystal X-ray study. The single crystal X-ray analysis of complexes **1** and **3** confirms the coordination of the ligands in the dianionic (ONO^{2-}) enolate-tautomeric form leaving one of the hydrazide moieties non-coordinated.

These complexes are good catalyst precursors for the oxidation of secondary alcohols, 1-phenylethaol, 2-butanol and 2-propanol in acetonitrile. In the presence of 30 % H_2O_2 as oxidant these secondary alcohols gave corresponding ketones with high yield ca. 90-95% under optimized reaction conditions. Microwave assisted catalytic oxidation technique reduces time considerably and also shows equally good conversion In fact, this technique emerges out as a highly time efficient system over conventional liquid phase oxidation method. Addition of N-based additive assists both catalytic systems in reducing time without posing any side effect on the oxidation of secondary alcohols. The $[Mo^{VI}O_2]^{2+}$ complexes upon treatment H_2O_2 in methanol instantly generate $[Mo^{VI}O(O_2)]^{2+}$species in solution which is considered to be the intermediate species responsible for the transfer of oxygen to the substrates during catalytic oxidation.

Acknowledgments

Gas chromatograph used in this study was procured from the grant given by Department of Science and Technology (DST), Government of India, New Delhi, (SR/S1/IC-32/2010) India to MRM. S.D. acknowledges the University Grant Commission, New Delhi, India for a Senior Research fellowship.

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