

View Article Online View Journal

# **NJC** Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. R. Maurya, L.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



## rsc.li/njc

### Molybdednum complexes having $\mu$ -O{MoO<sub>2</sub>}<sub>2</sub> core: Synthesis<sub>OF</sub> crystal JO3162E structure and application as catalyst for the oxidation of bicyclic alcohols using N-based additives

M.R. Maurya, L. Rana and F. Avecilla

Binuclear molybdenum(VI) complexes having  $\mu$ -O{MoO<sub>2</sub>}<sub>2</sub> core as catalyst for the oxidation of bicyclic alcohols (fenchyl alcohol and isoborneol) using 30% H<sub>2</sub>O<sub>2</sub> as oxidant in the presence of NEt<sub>3</sub> as additive are reported.



New Journal of Chemistry Accepted Manuscript

Molybdednum complexes having  $\mu$ -O{MoO<sub>2</sub>}<sub>2</sub> core: Synthesis, crystal  $\lambda$  and  $\lambda$  core structure and application as catalyst for the oxidation of bicyclic alcohols using N-based additives<sup>†</sup>

Mannar R. Maurya,<sup>a</sup>\* Lata Rana<sup>a</sup> and Fernando Avecilla<sup>b</sup>

<sup>a</sup>Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India.
E-mail: rkmanfcy@iitr.ac.in; Fax: +91 1332 273560; Tel: +91 1332 285327
<sup>b</sup>Departamento de Química Fundamental, Universidade da Coruña, Campus de A Zapateira, 15071 A Coruña, Spain

<sup>†</sup> Electronic supplementary information (ESI) available: CCDC 1508583 for complex **2a** and 1508582 for **3a**. Spectral data and representative <sup>1</sup>H NMR spectra of ligand and complex. For ESI and crystallographic data in CIF or other electronic format see DOI: xxxxxxx

#### ((Abstract))

Published on 30 November 2016. Downloaded by UNIVERSITY OF OTAGO on 13/12/2016 15:52:07

µ-oxidobis{dioxidomolybdenum(VI)} Three binuclear complexes, [(µ- $O{Mo^{VI}O_2(MeOH)}_2(L^1)$  $[(\mu-O){Mo^{VI}O_2(MeOH)}_2(L^2)]$ 1, 2. and [(µ-O){Mo<sup>VI</sup>O<sub>2</sub>(MeOH)}<sub>2</sub>(L<sup>3</sup>)] **3** with potential dibasic tetradentate azine ligands [H<sub>2</sub>L<sup>1</sup> = azine of salicyaldehyde,  $H_2L^2$  = azine of 3-methoxysalicyaldehyde and  $H_2L^3$  = azine of 3,5ditertiarybutylsalicylaldehyde] are reported. The complexes are characterized by elemental analysis, various spectroscopic techniques (FT-IR, UV-Vis, <sup>1</sup>H and <sup>13</sup>C NMR), thermogravimetric and by single-crystal X-ray diffraction (2 and 3) studies. These complexes are binuclear having  $\mu$ -O{MoO<sub>2</sub>}<sub>2</sub> core where ligands coordinate through a set of phenolic oxygen and azine nitrogen to each molybdenum, thus behave as bis (bidentate). These complexes are investigated as catalyst for the oxidation of two bicyclic alcohols (fenchyl alcohol and isoborneol) using 30% H<sub>2</sub>O<sub>2</sub> as oxidant in the presence of NEt<sub>3</sub> as additive. The conversion of bicyclic alcohols within the additives follows the order:  $NEt_3 > py > NH_3 >$  $K_2CO_3 > KOH$ . In the presence of N-based additive, fenchyl alcohol and isoborneol selectively gives high yield of fenchone and camphor, respectively while in the absence of additive the conversion is relatively low.

#### Introduction

### Dioxomolybdenum(VI) complexes with cis-[Mo<sup>VI</sup>O<sub>2</sub>] core exhibit high catalytic performance towards the epoxidation / oxidation of various substrates viz. olefins,<sup>1</sup> sulphides,<sup>2,3</sup> phenol,<sup>4</sup> phosphine,<sup>5</sup> alcohols,<sup>6,7</sup> hydrocarbons,<sup>8</sup> and oxidative bromination of salicylaldehyde, styrene and thymol,<sup>9</sup> Such complexes also exhibit oxygen atom transfer properties and thus act as functional mimics of molybdenum transferase enzymes which have active *cis*-[Mo<sup>VI</sup>O<sub>2</sub>] core.<sup>10</sup> During past few years high nuclearity oxidomolybdenum complexes containing (a) $\mu$ -O{MoO}<sub>2</sub>,<sup>11</sup> (b) ( $\mu$ -O)<sub>2</sub>{MoO}<sub>2</sub>,<sup>12</sup> (c) $\mu$ -O{MoO<sub>2</sub>},<sup>13-15</sup> and (d) ( $\mu$ -O)<sub>2</sub>{MoO<sub>2</sub>},<sup>16,17</sup> cores (Scheme 1), and of other high nuclearity with no systematic patterns<sup>18,19</sup> have been reported in the literature. Modec et. al. have reported oxidomolybdenum(V) complexes with a basic building unit of ( $\mu$ -O)<sub>2</sub>{OMo-MoO} having one terminal and one bridged oxygen on each molybdenum along with molybdenum-molybdenum bond.<sup>12(c),20</sup> All these complexes are effective catalysts for the epoxidation of olefins.



#### Scheme 1 Possible metal-oxido cores present in molybdenum complexes.

Recently our attention was drawn on dinuclear vanadium complex with azine ligand where two vanadium ions are connected by rigid azine nitrogen  $atoms^{21}$  while ONO dibasic tridentate behaviour of azines has earlier been inferred in dioxidomolybdenum(VI) complex<sup>22</sup> and in oxidoperoxido complexes of molybdenum(VI), tungsten(VI), uranium(VI), zirconium(IV) and thorium(IV) on the basis of spectroscopic studies.<sup>23</sup> This prompted us to re-consider azine ligands, **I–III** (Scheme 2) and prepare their molybdenum complexes. Gonçalves *et al.* have observed that complexes of the type [MoO<sub>2</sub>Cl<sub>2</sub>L] (where L = mono or bidentate ligands) having chloride ions coordinated to the molybdenum are potential precursors to design a molybdenum complex of higher nuclearity.<sup>18,19</sup> However, in the present study, we have used [Mo<sup>VI</sup>O<sub>2</sub>(acac)<sub>2</sub>] precursor to prepare molybdenum complexes and report their complete characterization along with single crystal X-ray study of the two complexes. In these complexes potential dibasic tetradentate ligands behave as bridging

View Article Online DOI: 10.1039/C6NJ03162E bis(monobasic ON bidenate) leading to hitherto rare binucleating molybdenum  $\mu$   $MoO_2$  core.

Catalytic potential of these complexes towards the oxidation of bicyclic alcohols (fenchyl alcohol and isoborneol) with aqueous 30% H<sub>2</sub>O<sub>2</sub> has also been explored. Camphor (1,7,7-trimethylbicyclo[2.2.1]heptan-2-one), an important bio product is obtained upon oxidation of isoborneol (1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol), while fenchone (1,3,3-trimethylbicyclo[2.2.1]heptan-2-one), a main component of absinthe and the essential oil of fennel is obtained upon oxidation of fenchyl alcohol (1,3,3-trimethylbicyclo[2.2.1]heptan-2-one). Catalytic oxidation of isoborneol and fenchyl alcohol (1,3,3-trimethylbicyclo[2.2.1]heptan-2-one). Catalytic oxidation of isoborneol and fenchyl alcohol have been studied<sup>7</sup> earlier using dioxidomolybdenum(VI) and other complexes as catalysts. The catalytic efficiency of these catalysts could be increased by using N-based additive i.e. NEt<sub>3</sub>.<sup>7</sup>



Scheme 2 Azine ligands used in the present study.

#### **Experimental Section**

#### **Materials**

Published on 30 November 2016. Downloaded by UNIVERSITY OF OTAGO on 13/12/2016 15:52:07

Analytical reagent grade hydrazine hydrate, triethylamine (Rankem, India), ammonium molybdate, salicylaldehyde (Loba Chemie India), 2-hydroxy-3,5-ditertbutylsalicylaldehyde, *o*-vanillin, fenchyl alcohol, isoborneol (Aldrich, USA) and 30% H<sub>2</sub>O<sub>2</sub> (Qualizens, India) were used as obtained. All other chemicals and solvents were of reagent grade and used without purification. Metal precursor [Mo<sup>VI</sup>O<sub>2</sub>(acac)<sub>2</sub>] was prepared as reported in the literature.<sup>24</sup> Ligands H<sub>2</sub>L<sup>1</sup> (**I**), H<sub>2</sub>L<sup>2</sup> (**II**) and H<sub>2</sub>L<sup>3</sup> (**III**) (Scheme 2) were synthesized following the procedure described by Tarafder *et al.*<sup>23</sup>

#### Instrumentation and characterization procedures

Element analysis (C, H and N) of ligands and their complexes was performed on an Elementar model Vario-EL-III. IR spectra were recorded on a Nicolet NEXUS Aligent 1100 FT-IR spectrometer. Electronic spectra were obtained in DMSO using a Shimadzu 1601 UV-Vis spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained in DMSO-d<sub>6</sub> using TMS as an internal standard on JEOL 400 MHz spectrometer. Thermogravimatric analysis of complexes was performed using oxygen environment on TG Stanton Redcroft STA 780. All catalytic reactions were analysed using 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. The product identity was confirmed by a GC-MS Perkin-Elmer, model Clarus 500 and comparing the obtained data with electronic library.

#### Synthetic of complexes

 $[(\mu-O){Mo^{VI}O_2(MeOH)}_2(L^1)]$  **1.** A suspension of  $H_2L^1$  (0.30 g, 1 mmol) in methanol (10 mL) was added to a filtered solution of  $[Mo^{VI}O_2(acac)_2]$  (0.652 g, 2 mmol) in same solvent (10 mL) and stirred initially at room temperature for 1 h and then refluxed on a water bath for 6 h where yellow solid slowly separated out. This was filtered washed with methanol and dried in desiccator over silica gel. Yield 0.378 g (66%). (Found: C, 33.79; H, 3.14; N, 4.78%. Calc'd. for  $C_{16}H_{18}N_2O_9Mo_2$  (574): C, 33.47; H, 3.16; N, 4.88).

 $[(\mu-O){Mo^{VI}O_2(MeOH)}_2(L^2)]$  2. A light brown complex 2 was prepared following the procedure described for 1 using H<sub>2</sub>L<sup>2</sup> (0.240 g, 1 mmol) and  $[Mo^{VI}O_2(acac)_2]$  (0.652 g, 2 mmol). Yield 0.408 g (65%) (Found: C, 33.99; H, 3.45; N, 4.38 %. Calc'd. for C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>11</sub>Mo<sub>2</sub> (634): C, 34.08; H, 3.50; N, 4.42). Single crystals of 2 suitable for X-ray analysis were grown from DMSO. Crystal of complex 2 is now formulated as  $[(\mu-O){MoO_2(DMSO)}_2(L^2)]$  2a.

 $[(\mu-O){Mo^{VI}O_2(MeOH)}_2(L^3)]$  3. Complex 3 as light brown solid was prepared similarly as described for 1 using H<sub>2</sub>L<sup>3</sup> (0.46 g, 1 mmol) and  $[Mo^{VI}O_2(acac)_2]$  (0.652 g, 2 mmol). Yield 0.602 g (75%) (Found: C, 47.82; H, 6.30; N, 3.49 %. Calc'd. for C<sub>32</sub>H<sub>50</sub>N<sub>2</sub>O<sub>9</sub>Mo<sub>2</sub> (798): C, 48.12; H, 6.31; N, 3.51). Single crystals of 3 suitable for X-ray analysis were grown from DMF. Crystal of complex 3 is now formulated as  $[(\mu-O){Mo^{VI}O_2(DMF)}_2(L^3)]$ ·3DMF 3a.

New Journal of Chemistry Accepted Manuscript

View Article Online DOI: 10.1039/C6NJ03162E

# Catalytic oxidation of bicyclic alcohols (fenchyl alcohol and isoborneol) with aqueous $30\%~H_2O_2$

Catalytic oxidation of bicyclic alcohols (fenchyl alcohol and isoborneol) with aqueous 30% H<sub>2</sub>O<sub>2</sub> were performed in a 50 mL two necked round bottom flask fitted with a reflux condenser and constant stirring at oil bath.

#### **Oxidation of fenchyl alcohol**

In a typical reaction, fenchyl alcohol (0.308 g, 2 mmol), aqueous 30%  $H_2O_2(0.678 g, 6 mmol)$ , and catalyst (0.002 g) were mixed in a reaction flask containing 7 mL of MeCN and reaction mixture was stirred at 80 °C for 6 h. The oxidation of fenchyl alcohol was studied both in the absence and in the presence of additive i.e. NEt<sub>3</sub> (0.005 g, 0.05 mmol). The progress of the reaction was examined by withdrawing small aliquot of the reaction mixture at every 1.5 h interval, extracting sample with hexane and analysing quantitatively by gas chromatograph equipped with a FID detector. The identity of products was confirmed by GC-MS.

#### **Oxidation of isoborneol**

Isoborneol (0.308 g, 2 mmol), aqueous 30%  $H_2O_2$  (0.904 g, 8 mmol), and catalyst (0.002 g) were mixed in a flask containing 7 mL of MeCN and the reaction mixture was stirred at 80 °C for 6 h. Again, the reaction was performed both in the absence and in the presence of additive i.e. NEt<sub>3</sub> (0.005 g, 0.05 mmol). The reaction progress was monitored by withdrawing small aliquot of the reaction mixture at every 1.5 h interval, extracting sample with hexane, analysing quantitatively and identifying the products as mentioned above.

#### X-Ray crystal structure determination

Three-dimensional X-ray data were collected on a Bruker Kappa Apex CCD diffractometer at low temperature for **2a** and at room temperature for **3a** by the  $\phi$ - $\omega$  scan method. Reflections were measured from a hemisphere of data collected from frames, each of them covering 0.3° in  $\omega$ . A total of 113501 for **2a** and 37100 for **3a** reflections measured were corrected for Lorentz and polarization effects and for absorption by multi-scan methods based on symmetry-equivalent and repeated reflections. Of the total, 9313 for **2a** and 9719 for **3a**, independent reflections exceeded the significance level  $(|F|/\sigma|F|) > 4.0$ . After data

collection, in each case an multi-scan absorption correction (SADABS) <sup>25</sup> was applied variables of the structure was solved by direct methods and refined by full matrix least-squares on  $F^2$  data using SHELX suite of programs.<sup>26</sup> Hydrogen atoms were included in calculation position and refined in the riding mode in the two structures. Refinements were done with allowance for thermal anisotropy of all non-hydrogen atoms. The crystal of **2a** presents a disorder on sulphur atom of one coordinated DMSO molecule. The disorder has been refined and two atomic sites have been observed and refined with the anisotropic atomic displacement parameters. The site occupancy factor was 0.78964 for S (1A). A final difference Fourier map showed a residual density outside: 1.237 and  $-1.152 \text{ e.Å}^{-3}$  for **2a**, due to the disorder around sulphur atom of DMSO molecule and 1.669 and  $-1.753 \text{ e.Å}^{-3}$  for **3a**, next to Mo atoms, which cannot be refined. A weighting scheme w =  $1/[\sigma^2(F_0^2) + (0.035000P)^2 + 19.977900 P]$  for **2a** and w =  $1/[\sigma^2(F_0^2) + (0.163300 P)^2 + 5.708200 P]$  for **3a**, where P =  $(|F_0|^2 + 2|F_c|^2)/3$ , were used in the latter stages of refinement. Further details of the crystal structures determination are given in Table 1.

~ .	
8	
ä	
ŝ	
15	
9	
01	
õ	
5	
3	
-	
on	
0	
Ū,	
2	
5	
ſT.	
ō	
Я.	
É-	
SI	
Ř	
۳.	
E	
E.	
2	
by (	
ed by I	
ided by I	
oaded by I	
nloaded by I	
wnloaded by U	
Downloaded by I	
6. Downloaded by U	
16. Downloaded by U	
2016. Downloaded by U	
er 2016. Downloaded by U	
ber 2016. Downloaded by U	
ember 2016. Downloaded by U	
vember 2016. Downloaded by U	
November 2016. Downloaded by I	
0 November 2016. Downloaded by I	
30 November 2016. Downloaded by I	
on 30 November 2016. Downloaded by I	
d on 30 November 2016. Downloaded by I	
hed on 30 November 2016. Downloaded by I	
ished on 30 November 2016. Downloaded by U	
blished on 30 November 2016. Downloaded by U	
Published on 30 November 2016. Downloaded by U	

	2a	3a
Formula	$C_{20}H_{26}Mo_2N_2O_{11}S_2$	$C_{45} H_{77} Mo_2 N_7 O_{12}$
Formula weight	726.43	1100.01
Τ, Κ	100(2)	296.0(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P 1 6
a/Å	11.6534(3)	10.510(5)
<i>b</i> /Å	39.0383(12)	15.733(7)
c/Å	12.9675(4)	18.670(8)
$\alpha'^{o}$	90	79.12(2)
β/°	116.5241(13)	74.44(2)
γ/°	90	77.50(2)
$V/\text{\AA}^3$	5278.4(3)	2875(2)
Ζ	8	2
F <sub>000</sub>	2912	1152
$D_{\rm calc}/{\rm g~cm}^{-3}$	1.828	1.271
$\mu/\mathrm{mm}^{-1}$	1.168	0.493
<i>θ</i> ∕ (°)	1.04 to 26.44	1.34 to 28.46
<i>R</i> <sub>int</sub>	0.0764	0.0322
Crystal size/ mm <sup>3</sup>	$0.30 \times 0.28 \times 0.08$	$0.22 \times 0.18 \times 0.10$
Goodness-of-fit on F <sup>2</sup>	1.097	1.067
$R_1[I > 2\sigma(I)]^a$	0.0431	0.0584
$wR_2$ (all data) <sup>b</sup>	0.0985	0.2634
Largest differences peak and	1.237 and -1.152	1.669 and –1.753
hole (eÅ <sup>-3</sup> )		2

 ${}^{a}\mathbf{R}_{1} = \Sigma \left[ \left| \mathbf{F}_{o} \right| - \left| \mathbf{F}_{c} \right| \right] / \Sigma \left| \mathbf{F}_{o} \right| . {}^{b}w\mathbf{R}_{2} = \left\{ \Sigma \left[ w \left( \left| \left| \mathbf{F}_{o} \right|^{2} - \left| \mathbf{F}_{c} \right|^{2} \right| \right)^{2} \right] \right] / \Sigma \left[ w \left( \mathbf{F}_{o}^{2} \right)^{2} \right] \right\}^{1/2}$ 

New Journal of Chemistry Accepted Manuscript

#### **Result and discussion**

The dinuclear complexes **1–3** of general formula  $[(\mu-O){Mo^{VI}O_2(MeOH)}_2(L^n)]$  (Scheme 3,  $H_2L^n = ligands I$ , II and III) having  $\mu$ -O{MoO<sub>2</sub>}<sub>2</sub> core are practicable by the reaction of ligands with  $[Mo^{VI}O_2(acac)_2]$  (in 1 : 2 molar ratio) in refluxing methanol. Among these, complexes **1** and **2** are only soluble in DMF and DMSO while complex **3** is additionally soluble in MeOH and MeCN. These complexes are characterized by elemental, spectroscopic (viz. FT-IR, UV-Vis , <sup>1</sup>H and <sup>13</sup>C NMR) and thermogravimetric analyses, and single crystal X-ray diffraction study of complexes **2** and **3**.



Scheme 3 Structure of complexes 1–3.

#### Solid state characterizations

ORTEP diagrams of  $[(\mu-O){Mo^{VI}O_2(DMSO)}_2(L^2)]$  **2a** and  $[(\mu-O){Mo^{VI}O_2(DMF)}_2(L^3)]$  **3a** are shown in Figs. 1 and 2, respectively. The asymmetric unit of **3a** also contains three DMF molecules. The asymmetric unit of **2a** contains two dinuclear complexes (we only discuss the structure around Mo(1) and Mo(2) atoms for simplicity). Selected bond distances and angles are given in Table 2. These dinuclear complexes present {Mo<sub>2</sub>N<sub>2</sub>O<sub>9</sub>} cores. The two Mo(VI) centers in each complex, exhibit highly distorted octahedral coordination environments. The  $\mu_2$ -bridging oxido group is responsible for the conformation of dinuclear cores, which are formed by two octahedra, with {MoNO<sub>5</sub>} cores, they share a corner.

The equatorial planes are occupied by the one terminal oxido group [O(2) in Mo(1) and O(6) in Mo(2)],  $\mu_2$ -bridging oxido group [O(4)], one phenolic oxygen atom [O(3) in Mo(1) and O(7) in Mo(2)] and one oxygen atom from DMSO molecule in **2a** and from DMF molecule in **3a**. The apical positions are occupied by the other terminal oxido group [O(1) in Mo(1) and O(5) in Mo(2)] and by N<sub>azine</sub> nitrogen atoms. These latter groups present a well-known trans effect [Mo-N<sub>azine</sub> distances, 2.337(4) Å for Mo(1) and 2.363(4) Å for Mo(2) in **2a** and 2.367(4) Å for Mo(1) and 2.331(4) Å for Mo(2) in **3a**,], with the Mo(1) and Mo(2) centers displaced by *ca*. 0.29 Å from the plane described for the equatorial atoms in the two

compounds. The two equatorial planes in each compound form a dihedral angle of 60.377 (MAGRICONJOSIGEE and 59.29(11)°, respectively. The separation between Mo atoms in dinuclear cores are: 3.628(4) Å in **2a** and 3.563(3) Å in **3a**, and is shorter than in other similar complexes,<sup>27</sup> due to the conformation of the ligand and to closer  $\mu_2$ -bridging oxido, which imposes a Mo-O-Mo "kink" angle of 146.18(17)° in **2a** and 138.5(2)° in **3a**.

Intermolecular hydrogen bonds and  $\pi$ - $\pi$  interactions do not appear in the crystal packing of the compounds **2a** and **3a**.

Table 2 Bond lengths [Å] and angles [°] for  $[(\mu-O){Mo^{VI}O_2(DMSO)}_2(L^2)]$  2a and  $[(\mu-O){Mo^{VI}O_2(DMF)}_2(L^3)] \cdot 3DMF$  3a

Bond lengths	2a		3a
Mo(1)-O(1)	1.700(3)		1.733(4)
Mo(1)-O(2)	1.702(3)		1.683(4)
Mo(1)-O(3)	1.969(3)		1.967(4)
Mo(1)-O(4)	1.909(3)		1.883(4)
Mo(1)-N(1)	2.337(3)		2.367(4)
Mo(1)-O(1D)			2.303(4)
Mo(1)-O(8)	2.265(3)		
N(1)-N(2)	1.414(5)		1.424(6)
Mo(2)-O(4)	1.883(3)		1.927(4)
Mo(2)-O(5)	1.715(3)		1.702(4)
Mo(2)-O(6)	1.699(3)		1.684(4)
Mo(2)-O(7)	1.986(3)		1.986(4)
Mo(2)-N(2)	2.363(3)		2.331(4)
Mo(2)-O(2D)			2.290(4)
Mo(2)-O(9)	2.251(3)		
Angles	2a		<b>3</b> a
O(2)-Mo(1)-O(1)	105.41(14)		105.3(2)
O(2)-Mo(1)-O(4)	97.99(14)		99.0(2)
O(1)-Mo(1)-O(4)	98.68(13)		100.9(2)
O(2)-Mo(1)-O(3)	94.53(14)		97.29(19)
O(1)-Mo(1)-O(3)	98.99(13)		98.37(19)
O(4)-Mo(1)-O(3)	154.76(12)		150.37(16)
O(2)-Mo(1)-O(8)	165.16(13)	O(2)-Mo(1)-O(1D)	167.5(2)
O(1)-Mo(1)-O(8)	88.69(13)	O(1)-Mo(1)-O(1D)	86.98(19)
O(4)-Mo(1)-O(8)	84.13(12)	O(4)-Mo(1)-O(1D)	80.57(17)
O(3)-Mo(1)-O(8)	78.41(12)	O(3)-Mo(1)-O(1D)	78.22(16)
O(2)-Mo(1)-N(1)	90.72(13)		92.20(19)
O(1)-Mo(1)-N(1)	163.84(13)		162.35(18)
O(4)-Mo(1)-N(1)	79.59(12)		77.89(16)
O(3)-Mo(1)-N(1)	78.41(12)		76.91(15)
O(8)-Mo(1)-N(1)	75.15(12)	O(1D)-Mo(1)-N(1)	75.43(15)
Mo(1)-O(4)-Mo(2)	146.18(17)		138.5(2)

Published on 30 November 2016. Downloaded by UNIVERSITY OF OTAGO on 13/12/2016 15:52:07.



Fig. 1 ORTEP plot of the complex  $[(\mu-O){Mo^{VI}O_2(DMSO)}_2(L^2)]$  2a. All the non-hydrogen atoms are presented by their 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.



Fig. 2 ORTEP plot of the complex  $[(\mu-O){Mo^{VI}O_2(DMF)}_2(L^3)]$  3a. All the non-hydrogen atoms are presented by their 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

View Article Online

The thermal study of all binuclear molybdenum complexes were studied wirderice Online oxygen environment at a temperature increment rate of 10 °C/ min. These symmetric complexes lose mass exothermically between 195-300 °C equivalents to loss of one methanol molecule from each metal center. Increasing temperature further, the methanol free complexes decompose in two-three exothermic overlapping steps, and finally form MoO<sub>3</sub> above 400 °C.

#### **Spectroscopic studies**

All complexes exhibits two characteristic IR bands at 889-915 and 933-950 cm<sup>-1</sup> assignable to the symmetric and asymmetric stretching modes, respectively, for *cis*-[MoO<sub>2</sub>] core.<sup>28</sup> An additional band centred at 767-773 cm<sup>-1</sup> is attributable to a v(Mo-O-Mo) stretching mode. The IR spectra of ligands exhibit two intense bands at 1572-1591 and 963-974 cm<sup>-1</sup>due to  $v(C=N)_{azomethine}$  and  $v(N-N)_{azine}$  stretches, respectively (Table S1).

Upon complexation  $v(C=N)_{azomethine}$  band shifted to lower frequency<sup>23</sup> while a positive shift occurred in  $v(N-N)_{azine}$  stretch, revealing that both nitrogen atoms participate in coordination to the metal center.<sup>29</sup> A broad band covering the area 3040–3150 cm<sup>-1</sup> is assigned to intramolecular hydrogen bonded v(OH) mode. Absent of this band in complexes indicates the breaking of the hydrogen bond. However, the unequivocal identification of the coordination of the phenolic oxygen atom could not be established due to a distinct peak at 3422-3431 cm<sup>-1</sup> in the IR spectra of all complexes which is assignable to v(OH) stretch possibly due to the presence of coordinated MeOH.

Fig. S1 replicates the UV-visible spectra of complexes and complete spectral data of ligands and their complexes are presents in Table S2. Two spectral bands exhibited at 297-308 nm and 358-376 nm in the UV region are assigned due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively. Both bands shift to higher wave lengths and appear at 320-323 and 363-371 nm; the latter one merges with a new band appearing at ca. 410-416 nm and makes the overall appearance as broad. The characteristic band at ca. 410-416 nm is assigned due to the ligand to metal charge transfer transition.

Table 3 presents the <sup>1</sup>H NMR spectral data of ligands and the corresponding complexes. The <sup>1</sup>H NMR spectra of H<sub>2</sub>L<sup>3</sup> **III** and its complex **3** are shown in Fig. S2. Due to centre of symmetry, one singlet each due to phenolic protons at  $\delta = 11.12$ -11.50 ppm and azomethine protons at  $\delta = 8.77$ -9.96 ppm appears in the <sup>1</sup>H NMR spectra of ligands. The

#### New Journal of Chemistry

absence of phenolic protons in complexes suggests the replacement of protons by the metalicle online atom during complexation. All aromatic protons in ligands as well as in complexes appear in the expected region with slight variations. Tertiary butyl groups give two intense peaks at  $\delta =$ 1.40 and 1.30 ppm in complex **3**. In addition, the spectra of the complexes also display a peak at  $\delta = 3.18-3.22$  ppm equivalent to six methyl protons which confirm that each molybdenum is coordinated to one methanol. This is further supported by the appearance of a broad peak at  $\delta=4.09-4.12$  ppm due to methanolic OH.

Further, endorsement of the coordination modes of the ligands to the metal complexes are obtained by recording the <sup>13</sup>C NMR spectra of ligands and complexes. The <sup>13</sup>C NMR spectra of a representative ligand (H<sub>2</sub>L<sup>1</sup>) and its complex **1** are depicted in Fig. 3 while Table 4 provides all spectral data. All binuclear complexes unveil a distinct peak at  $\delta = 47.0-48.88$ ppm which corresponds to the carbon of coordinated methanol. A considerable change in the chemical shifts [ $\Delta \delta = \delta$  (complex) –  $\delta$  (free ligand)] of the carbon atoms present in the vicinity [i.e. C1/C1', C2/C2', and C7/C7' in Table 4] of the coordinating atoms (i.e. O<sub>phenolic</sub> and N<sub>azine</sub>) has been observed due to coordination of these functionalities with the molybdenum. The carbon atoms of the tertiary butyl groups in H<sub>2</sub>L<sup>3</sup> and its complex **3**, and methoxy carbon in H<sub>2</sub>L<sup>2</sup> and its complex **2** appear well within the expected region. Signals for other aromatic carbon atoms of the ligands and complexes also appear in the expected region.

Table 3	H NMR	chemical	shifts (	δin	ppm)	of the	ligands	and	their	complexes	recorded	1 in
DMSO-d	6											

Compound	-OH (phenolic/ methanol	Tert-butyl	OCH <sub>3</sub>	-OCH <sub>3</sub> (Methanol)	-CH=N-	Aromatic protons
I	11.12 (br, 2H)	-	-	-	8.96 (s, 2H)	7.42-7.69 (q, 2H), 7.38-7.40 (q, 2H), 6.96 (d, 2H), 6.95 (d, 2H)
1	4.10 (br, 2H)	-	-	3.15 (s, 6H)	8.99 (s, 2H)	7.28-7.30 (q, 2H), 7.26 (m, 2H), 7.20 (m, 2H), 7.12-7.14 (m, 2H)
п	11.10 (br, 2H)	-	3.83 (s, 6H)	-	8.99 (s, 2H)	7.27-7.30 (q, 2H), 7.12-7.14 (m, 2H), 6.89-6.93 (m, 2H)
2	4.12 (br, 2H)	-	3.83 (s, 6H)	3.12 (s, 6H)	8.99 (s, 2H)	7.28-7.30 (q, 2H), 7.20-7.26 (m, 2H), 6.88-7.14 (m, 2H)
III	11.50 (br. 2H)	1.37 (s, 36 H),		-	9.96 (s. 2H)	7.63-7.62 (m, 2H), 7.56-7.55 (m, 2H)
3	(br, 211) 4.10 (br,2H)	1.20 (s, 36 H) 1.40 (s, 36 H), 1.30 (s, 36 H)	-	3.16 (s, 6H)	(s, 2H) 8.79 (s, 2H)	7.54-7.55 (m, 2H), 7.52-7.53 (m, 2H)

New Journal of Chemistry Accepted Manuscript



Fig. 3  $^{13}$ C NMR spectra of ligand  $H_2L^1$  (I) and complex 1 recorded in DMSO-d<sub>6</sub>.

Table 4<sup>13</sup>C NMR spectral data of ligands and complexes

8'

View Article Online DOI: 10.1039/C6NJ03162E

I	$ \overset{\text{Me}}{\underset{\text{H}}{}} \overset{\text{O}}{\underset{\text{H}}{}} \overset{\text{O}}{\overset{\text{O}}} \overset{\text{O}}{\underset{\text{H}}{}} \overset{\text{O}}{\underset{\text{H}}{}} \overset{\text{O}}{\overset{\text{O}}} \overset{\text{O}}{\underset{\text{H}}} \overset{\text{O}}{\overset{\text{O}}} \overset{\text{O}}{\overset{\text{O}}} \overset{\text{O}}{\underset{\text{H}}} \overset{\text{O}}{\overset{\text{O}}} \overset{\text{O}} \overset{\text{O}} \overset{\text{O}}{\overset{\text{O}}} \overset{\text{O}}{\overset{\text{O}}} \overset{\text{O}}{\overset{\text{O}}} \overset{\text{O}}{\overset{\text{O}}} \overset{\text{O}} \overset{\text{O}}{\overset{\text{O}}} \overset{\text{O}}{\overset{\text{O}}} \overset{\text{O}} \overset{\text{O}}} \overset{\text{O}} \overset{\text{O}}} \overset{\text{O}} \overset{\text{O}} \overset{\text{O}} \overset{\text{O}}} $		Me $2'$ $R_1$ 3' 4' $5'$ $R_2$	$R_1 = -H,$ $R_2 = -H,$ comp. 1	-OCH <sub>3</sub> , te -H, te <b>2</b>	rt butyl rt butyl 3				
Compo nd <sup>a</sup>	ou C1/C1	C2/C2	C7/C7	C5/C5	C3/C3'	C4/C4	C6/C6	C8/C8'(m ethanol)	C ( <i>t</i> -but.)	C (methoxy)
I	118.24	163.05	158.71	119.92	116.55	132.84	130.95	-	-	-
1	120.63	155.33	162.62	147.77	118.34	149.39	148.31	47.95	-	-
$(\Delta\delta)$	(2.39)	(-7.72)	(3.91)							
Π	121.47	162.32	162.88	118.32	147.81	115.78	122.47	-	-	55.46
2	125.48	155.40	165.84	125.25	157.66	120.60	149.48	48.48	-	55.83
$(\Delta\delta)$	(4.01)	(-6.92)	(2.96)							
III	117.33	154.20	158.84	140.55	137.35	129.55	127.84	-	34.51,3 3.31	-
<b>3</b>	119.85 (2.52)	145.57 (-8.63)	161.45 (2.61)	138.53	129.42	128.77	119.81	48.46	34.90, 33.95	-

<sup>a</sup>[ $\Delta \delta = [\delta \text{ (complex)} - \delta \text{ (free ligand)}]$ 

#### Catalytic activity studies: Oxidation of fenchyl Alcohol and isoborneol

The oxidative conversion of bicyclic alcohols eg. fenchyl alcohol and isoborneol catalysed by dinuclear molybdenum complexes in the presence of  $H_2O_2$  and additive (NEt<sub>3</sub>) in MeCN led to the formation of fenchone and camphor, selectively (Scheme 4).



Scheme 4 Oxidation products of fenchyl alcohol and isoborneol.

Considering  $[(\mu-O){Mo^{VI}O_2(MeOH)}_2(L^3)]$  **3** as a representative catalyst precursor for the oxidation of fenchyl alcohol, parameters, like amounts of catalyst, 30 % aqueous  $H_2O_2$ 

solvent and temperature of the catalytic reaction have been studied for obtaining/vertaticle Online maximum conversion of fenchyl alcohol.

Thus, for 2 mmol (0.308 g) of fenchyl alcohol, three different amounts of catalyst precursor **3** ( $1.25 \times 10^{-3}$ ,  $1.87 \times 10^{-3}$  and  $2.5 \times 10^{-3}$  mmol) and 30 % aqueous H<sub>2</sub>O<sub>2</sub> (2, 4 and 6 mmol) were taken in three different volumes of solvent MeCN (5, 7 and 9 mL) and reaction was carried out at three different temperatures (60, 70 and 80 °C) in the presence of NEt<sub>3</sub> (0.05 g, 0.05 mmol). About 6 h was required to achieve the equilibrium. Fig. 4 presents conversion profiles under different reaction conditions and Table 5 summarises conversion of fenchyl alcohol under a particular set of conditions. It is clear from the data of the table that the optimized reaction conditions for the conversion of 2 mmol (0.308 g) of fenchyl alcohol are those using substrate to catalyst molar ratio of 1 :  $2.5 \times 10^{-3}$  and substrate : H<sub>2</sub>O<sub>2</sub> : NEt<sub>3</sub> molar ratios of 1 : 3 : 0.025 in 7 mL of MeCN at 80 °C (i.e. entry 9 of Table 5). Under these conditions 82 % conversion was achieved in 6 h of reaction time. In the absence of additive not only enhances the conversion, it helped in reducing the reaction time. Only 16 % conversion was obtained in the absence of catalyst but in presence of NEt<sub>3</sub>, while in the absence of catalyst as well as NEt<sub>3</sub> both only 4 % conversion was obtained.

**Table 5** Conversion of fenchyl alcohol (0.308 g, 2 mmol) using  $[(\mu - O){Mo^{VI}O_2(MeOH)}_2(L^3)]$  **3** as catalyst precursor in the presence of NEt<sub>3</sub> (0.05 g, 0.05 mmol) in 6 h of reaction time under reaction different parameters

Entry	Catalyst	H <sub>2</sub> O <sub>2</sub>	MeCN	Temp.	Conv.
No.	[g (mmol)]	[g (mmol)]	[mL]	[°C]	[%]
1	$0.0010~(1.25 \times 10^{-3})$	0.226 (2)	5	60	42
2	$0.0015~(1.87  imes 10^{-3})$	0.226 (2)	5	60	48
3	$0.0020~(2.50  imes 10^{-3})$	0.226 (2)	5	60	52
4	$0.0020(2.50 \times 10^{-3})$	0.452 (4)	5	60	73
5	$0.0020~(2.50  imes 10^{-3})$	0.672 (6)	5	60	80
6	$0.0020~(2.50  imes 10^{-3})$	0.672 (6)	7	60	81
7	$0.0020~(2.50  imes 10^{-3})$	0.672 (6)	9	60	74
8	$0.0020~(2.50  imes 10^{-3})$	0.672 (6)	7	70	72
9	$0.0020\;(2.50\times 10^{-3})$	0.672 (6)	7	80	82



**Fig. 4** (a) Effect of amount of catalyst variation (0.0010, 0.0015 and 0.0020 g) on the oxidation of fenchyl alcohol. Reaction conditions : fenchyl alcohol (0.308 g, 2 mmol), Catalyst **3**, 30 % aqueous  $H_2O_2$  (0.226 g, 2 mmol), MeCN (5 mL), NEt<sub>3</sub> (0.05 g, 0.05 mmol) and reaction temp (60 °C) for 6 h. (b) Effect of amount of oxidant variation (30 %  $H_2O_2$ ) (substrate to oxidant ratio: 1:1, 1:2 and 1:3) on the oxidation of fenchyl alcohol. Reaction conditions : fenchyl alcohol (0.308 g, 2 mmol), Catalyst **3** (0.002 g), MeCN (5 mL), NEt<sub>3</sub> (0.05 g, 0.05 mmol) and reaction temp (60 °C) for 6 h. (c) Effect of amount of solvent variation (5, 7 and 9 mL) on the oxidation of fenchyl alcohol. Reaction conditions : fenchyl alcohol (0.308 g, 2 mmol), Catalyst **3** (0.0020 g), 30 % aqueous  $H_2O_2$  (0.672 g, 6 mmol), NEt<sub>3</sub> (0.05 g, 0.05 mmol) and reaction temp (60 °C) for 6 h. (d) Effect of temperature variation (60, 70 and 80 °C) on the oxidation of fenchyl alcohol. Reaction conditions : fenchyl alcohol (0.308 g, 2 mmol), Catalyst **3** (0.0020 g), 30 % aqueous  $H_2O_2$  (0.672 g, 6 mmol), MeCN (7 mL), NEt<sub>3</sub> (0.05 g, 0.05 mmol) for 6 h.

Catalyst precursor **3** was also used to optimise the reaction conditions  $1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1005_{91}(1$ 

Catalytic potential of other complex precursors i.e. complexes 1 and 2 under specified conditions for fenchyl alcohol as well as for isoborneol have also been tested, and results are summarised in Table 7. Their catalytic potentials are equally good (84-89%) for both substrates in the presence of additive. Under similar reaction conditions  $[Mo^{VI}O_2(acac)_2](6.13 \times 10^{-3} \text{ mmol})$  and  $MoO_3(13.8 \times 10^{-3} \text{ mmol})$  give 66-70% conversion. Along with lower conversion (73-81 %), reaction again required 24 h in the absence of additive (NEt<sub>3</sub>) to achieve equilibrium Thus, additive helps in reducing the reaction time from 24 h to 6 h and improving the potential of catalysts in the oxidation of fenchyl alcohol and isoborneol.

Published on 30 November 2016. Downloaded by UNIVERSITY OF OTAGO on 13/12/2016 15:52:07

**Table 6** Conversion of isoborneol (0.308 g, 2 mmol) using  $[(\mu-O){Mo^{VI}O_2(MeOH)}_2(L^3)]$  as catalyst precursor in the presence of NEt<sub>3</sub> (0.05 g, 0.05 mmol) in 6 h reaction time under different reaction parameters

Entry No.	Catalyst [g (mmol)]	$H_2O_2$ [g (mmol)]	MeCN [mL]	Temp. [°C]	Conv. [%]
1	$0.0010 (1.25 \times 10^{-3})$	0.226 (2)	5	60	51
2	$0.0015~(1.87  imes 10^{-3})$	0.226 (2)	5	60	54
3	$0.0020~(2.50  imes 10^{-3})$	0.226 (2)	5	60	60
4	$0.0020~(2.50  imes 10^{-3})$	0.452 (4)	5	60	70
5	$0.0020~(2.50  imes 10^{-3})$	0.672 (6)	5	60	71
6	$0.0020~(2.50  imes 10^{-3})$	0.452 (4)	7	60	76
7	$0.0020~(2.50  imes 10^{-3})$	0.452 (4)	9	60	72
8	$0.0020~(2.50\times 10^{-3})$	0.452 (4)	7	70	79
9	<b>0.0020</b> (2.50×10 <sup>-3</sup> )	0.452 (4)	7	80	84



**Fig. 5** (a) Effect of amount of catalyst variation (0.0010 g, 0.0015 and 0.0020 g) on the oxidation of isoborneol. Reaction conditions : isoborneol (0.308 g, 2 mmol), Catalyst **3**, 30 % aqueous  $H_2O_2$  (0.226 g, 2 mmol), MeCN (5 mL), NEt<sub>3</sub> (0.05 g, 0.05 mmol) and reaction temp (60 °C) for 6 h. (b) Effect of amount of oxidant variation (30 %  $H_2O_2$ ) (substrate to oxidant ratio: 1:1, 1:2 and 1:3) on the oxidation of isoborneol. Reaction conditions: isoborneol (0.308 g, 2 mmol), Catalyst **3** (0.0020 g), MeCN (5 mL), NEt<sub>3</sub> (0.05 g, 0.05 mmol) and reaction temp (60 °C) for 6 h. (c) Effect of amount of solvent variation (5, 7 and 9 mL) on the oxidation of isoborneol. Reaction conditions: isoborneol (0.308 g, 2 mmol), Catalyst **3** (0.0020 g), 30 % aqueous  $H_2O_2$  (0.452 g, 4 mmol), NEt<sub>3</sub> (0.05 g, 0.05 mmol) and reaction temp (60 °C) for 6 h. (d) Effect of temperature variation (60, 70 and 80 °C) on the oxidation of isoborneol. Reaction conditions: isoborneol temp (60 °C) for 6 h. (d) Effect of temperature variation (60, 70 and 80 °C) on the oxidation of isoborneol. Reaction conditions: isoborneol (0.308 g, 2 mmol), Catalyst **3** (0.0020 g), 30 % aqueous  $H_2O_2$  (0.452 g, 4 mmol), NEt<sub>3</sub> (0.05 g, 0.05 mmol) for 6 h.

**New Journal of Chemistry Accepted Manuscri** 

ò	
· · ·	
0	
ŝ	
-	
9	
-	
0	
2	
2	
- 24	
ŝ	
1	
_	
- =	
0	
$\sim$	
2	
C	
7	
~	
E	
0	
~	
ГĽ	
$\sim$	
5	
5	
H	
$\sim$	
~	
Ē	
-	
~	
Z	
5	
$\mathbf{r}$	
2	
bv L	•
l by L	,
d by L	,
led by I	•
aded by I	•
paded by I	•
loaded by L	•
nloaded by I	•
wnloaded by I	
wnloaded by I	•
Downloaded by L	•
Downloaded by I	
. Downloaded by I	
6. Downloaded by I	•
16. Downloaded by U	
016. Downloaded by I	•
2016. Downloaded by U	•
r 2016. Downloaded by I	•
er 2016. Downloaded by U	
ber 2016. Downloaded by U	
nber 2016. Downloaded by I	•
smber 2016. Downloaded by I	•
rember 2016. Downloaded by U	•
vember 2016. Downloaded by I	•
Jovember 2016. Downloaded by I	•
November 2016. Downloaded by I	•
) November 2016. Downloaded by I	
30 November 2016. Downloaded by U	
30 November 2016. Downloaded by L	•
n 30 November 2016. Downloaded by I	•
on 30 November 2016. Downloaded by I	
1 on 30 November 2016. Downloaded by U	
ed on 30 November 2016. Downloaded by U	•
ned on 30 November 2016. Downloaded by I	•
shed on 30 November 2016. Downloaded by I	•
ished on 30 November 2016. Downloaded by U	
blished on 30 November 2016. Downloaded by U	
iblished on 30 November 2016. Downloaded by U	

**Table 7** Conversion of bicylic alcohol (0.308 g, 2 mmol) and TOF calculated with Vieth dicle Online without additive

Catalyst	With additive <sup>a</sup>		Without additive	
(conc. in mmol)	Conv.[%] TOF	[h <sup>-1</sup> ] <sup>b</sup>	Conv. [%] TO	$F[h^{-1}]^c$
$1(3.48 \times 10^{-3})$	89	85	81	19
<b>2</b> (3.15×10 <sup>-3</sup> )	84	89	75	20
<b>3</b> (2.50×10 <sup>-3</sup> )	85	113	78	26
$[MoO_2(acac)_2](6.13 \times 10^{-3})$	70	38	67	36
MoO <sub>3</sub> (13.8×10 <sup>-3</sup> )	66	16	63	15
Blank	16	-	4	-
<b>1</b> (2.50×10 <sup>-3</sup> )	82	109	69	23
<b>2</b> (3.48×10 <sup>-3</sup> )	89	85	75	18
<b>3</b> (3.15×10 <sup>-3</sup> )	85	90	73	19
$[MoO_2(acac)_2](6.13 \times 10^{-3})$	69	38	65	35
MoO <sub>3</sub> (13.8×10 <sup>-3</sup> )	67	16	64	15
Blank	12	-	7	-
	Catalyst (conc. in mmol) $1 (3.48 \times 10^{-3})$ $2 (3.15 \times 10^{-3})$ $3 (2.50 \times 10^{-3})$ $[MoO_2(acac)_2](6.13 \times 10^{-3})$ $MoO_3(13.8 \times 10^{-3})$ Blank $1 (2.50 \times 10^{-3})$ $2 (3.48 \times 10^{-3})$ $3 (3.15 \times 10^{-3})$ $[MoO_2(acac)_2](6.13 \times 10^{-3})$ $MoO_3(13.8 \times 10^{-3})$ Blank	CatalystWith additivea(conc. in mmol)Conv.[%] TOF $1 (3.48 \times 10^{-3})$ 89 $2 (3.15 \times 10^{-3})$ 84 $3 (2.50 \times 10^{-3})$ 85 $[MoO_2(acac)_2](6.13 \times 10^{-3})$ 70 $MoO_3(13.8 \times 10^{-3})$ 66Blank16 $1 (2.50 \times 10^{-3})$ 82 $2 (3.48 \times 10^{-3})$ 89 $3 (3.15 \times 10^{-3})$ 85 $[MoO_2(acac)_2](6.13 \times 10^{-3})$ 69 $MoO_3(13.8 \times 10^{-3})$ 67Blank12	CatalystWith additivea(conc. in mmol) $Conv.[\%] TOF[h^{-1}]^b$ $1 (3.48 \times 10^{-3})$ $89$ $2 (3.15 \times 10^{-3})$ $84$ $3 (2.50 \times 10^{-3})$ $85$ $3 (2.50 \times 10^{-3})$ $85$ $[MoO_2(acac)_2](6.13 \times 10^{-3})$ $70$ $Blank$ $16$ $1 (2.50 \times 10^{-3})$ $82$ $1 (2.50 \times 10^{-3})$ $89$ $2 (3.48 \times 10^{-3})$ $89$ $3 (3.15 \times 10^{-3})$ $85$ $3 (3.15 \times 10^{-3})$ $69$ $16$ $90$ $[MoO_2(acac)_2](6.13 \times 10^{-3})$ $69$ $81ank$ $16$ $16$ $38$ $MoO_3(13.8 \times 10^{-3})$ $67$ $16$ $16$ $Mandana = 12$ $-$	CatalystWith additiveaWithout additivea(conc. in mmol) $Conv.[\%] TOF[h^{-1}]^b$ $Conv. [\%] TOP[h^{-1}]^b$ 1 ( $3.48 \times 10^{-3}$ )8985812 ( $3.15 \times 10^{-3}$ )8489753 ( $2.50 \times 10^{-3}$ )8511378[MoO_2(acac)_2]( $6.13 \times 10^{-3}$ )703867MoO_3( $13.8 \times 10^{-3}$ )661663Blank16-41 ( $2.50 \times 10^{-3}$ )82109692 ( $3.48 \times 10^{-3}$ )8985753 ( $3.15 \times 10^{-3}$ )693865MoO_3( $13.8 \times 10^{-3}$ )671664Blank12-7

<sup>a</sup> NEt<sub>3</sub> = 0.05 mmol

<sup>b</sup>TOF values calculated at 6 h of reaction time for both alcohols.

<sup>c</sup>TOF values calculated at 24 h of reaction time.

We have also studied the effect of different additives on the conversion of fenchyl alcohol and isoborneol under above optimised reaction conditions and results are summarised in Table 8. Overall conversions for both substrates are poor using pyridine, NH<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> and KOH than those obtained using NEt<sub>3</sub>. However, conversion within the additives follows the order: NEt<sub>3</sub>> py> NH<sub>3</sub>> K<sub>2</sub>CO<sub>3</sub>> KOH. This observation possibly suggests that only mild base is required to accelerate the conversion rate.

	ŝ		_
	ļ		
	1	_	
	ļ	L	
	1		
	ĺ	2	1
	1		
	į	11	
			Ч
	į		-
	Ĵ		
	1		
	l	F	
	ì		
	ļ		
-			_
	ġ	2	
		2	
	(		
			1
			D
	ļ	1	2
×.		h	
	ĵ		
	1		
	l		1
	1	ų,	2
	I	P.	
	1		
	ļ	í.	-
			2
	i		
	1		
	1		>
	į		
		L	
	ļ		
			-
	į	11	
	l		R
į,	į	-	-
1	Ĵ		
	(		
	į		
	į		
	1		
	,		
1			
	6		
1			
ĸ.	ļ		
		۲	
	į	P	
			_
1			
	l		
	l		Y
	į		
	ì		
	į		
	ļ		C
		-	
	Ī	C	
	(		
	(		
	(		
	(		
	(		

Additive	Fenchy	Fenchyl alcohol		rneol
	Conv. [%]	TOF [h <sup>-1</sup> ]	Conv. [%]	TOF [h <sup>-1</sup> ]
Pyridine	49 65		46	61
NH <sub>3</sub>	38 50		37	49
K <sub>2</sub> CO <sub>3</sub>	21 28		25	33
КОН	1925		21	28

**Table 8** Oxidation of bicylic alcohol and % conversion with different additives in presenver of the Online Conjugation of bicylic alcohol and % conversion with different additives in presenver of the Conjugation of the Co

# Reactivity of molybdenum complexes with $H_2O_2$ and possible reaction intermediate for the oxidation of bicyclic alcohols

The cis-[Mo<sup>VI</sup>O<sub>2</sub>]<sup>2+</sup> complexes are known to undergo transformation into  $[Mo^{VI}O(O_2)]^{2+}$  upon reaction with  $H_2O_2$  in suitable solvent and in some cases solid peroxido complexes have also been isolated.<sup>30</sup> The in situ formation of such peroxido species has also been established spectrophotometrically by reacting complex 3 with  $H_2O_2$  in DMSO. In a typical reaction, 25 mL of  $1.24 \times 10^{-6}$  M solution of **3** in DMSO was treated with one drop portions of 30 % aqueous H<sub>2</sub>O<sub>2</sub> (0.096 g, 5 mmol) dissolve in 5 mL of DMSO and the obtained spectral changes are shown in Fig 6 (a). Thus, the band at 320 nm shifted to 305 nm along with increase in intensity while 270 nm band showed only increase in intensity. The intensity of the band at 371 remained almost unchanged. Simultaneously, the intensity of the weak and broad charge transfer band appearing at 416 nm slowly decreased along with further broadening and shifting to 420 nm [inset of Fig 6 (a)]. These changes along with the generation of an isosbestic point at 396 nm indicate the interaction of 3 with H<sub>2</sub>O<sub>2</sub> and the plausible formation of the corresponding peroxido complex in DMSO. Very similar spectral changes were obtained after adding only few drops of a mixture of NaHCO3 and H2O2 which indicates the quick formation of oxidoperoxido species. As reported, NaHCO3 reacts with  $H_2O_2$  instantly and produces  $HCO_4^-$  (peroxymonocarbonate)<sup>31, 2(b)</sup> which actually reacts with dioxidomolybdenum(VI) complex to give oxidoperoxidomolybdenum(VI) intermediate more rapidly as compared to  $H_2O_2$  alone. Similar changes have also been noted for complexes 1 and 2; Figs. 6 (b) and 6 (c). Thus, the catalytic reaction is likely to proceed through the  $[Mo^{VI}O(O_2)]^{2+}$  intermediate formed upon reaction of  $H_2O_2$  with complexes which may transfer oxygen to the substrates during the catalytic oxidation.

View Article Online DOI: 10.1039/C6NJ03162E



Published on 30 November 2016. Downloaded by UNIVERSITY OF OTAGO on 13/12/2016 15:52:07

**Fig. 6** (a) Plots representing the spectral changes during the titration of  $[(\mu - O){Mo^{VI}O_2(MeOH)}_2(L^3)]$  **3** with H<sub>2</sub>O<sub>2</sub>. Spectra recorded after successive addition of one drop portions of 30% aqueous H<sub>2</sub>O<sub>2</sub> (0.096 g, 0.50 mmol) dissolved in 5 mL DMSO to 25 mL of  $1.24 \times 10^{-6}$  M solution of **3** in DMSO. Inset shows expanded region (375 - 500 nm). (b) Spectral changes during the titration of  $[(\mu - O){Mo^{VI}O_2(MeOH)}_2(L^1)]$  **1** with H<sub>2</sub>O<sub>2</sub>. Spectra observed after successive addition of one drop portion of 30 % aqueous H<sub>2</sub>O<sub>2</sub> (0.076 g, 3.3 mmol) dissolved in 5 mL DMSO to 25 mL of  $1.25 \times 10^{-6}$  M solution of **1** in DMSO. Inset shows the expanded (300-500 nm) region. (c) Spectral changes during the titration of  $[(\mu - O){Mo^{VI}O_2(MeOH)}_2(L^2)]$  **2** with H<sub>2</sub>O<sub>2</sub>. Spectra recorded after successive addition of one drop portion of 30 % aqueous H<sub>2</sub>O<sub>2</sub> (0.102 g, 3.6 mmol), dissolved in 5 mL DMSO to 25 mL of  $1.25 \times 10^{-6}$  M solution of **2** in DMSO. Inset shows the expanded (320-500 nm) region.

#### Conclusions

Three binuclear molybdenum (VI) complexes,  $[(\mu-O){Mo^{VI}O_2(MeOH)}_2(L^1)]$  **1**,  $[(\mu-O){Mo^{VI}O_2(MeOH)}_2(L^2)]$  **2** and  $[(\mu-O){Mo^{VI}O_2(MeOH)}_2(L^3)]$  **3** with  $\mu$ -O{MoO<sub>2</sub>}<sub>2</sub> core have been prepared from dibasic ONNO tetradentate ligands. The X-ray crystal structures of **2** (DMSO solvated) and **3** (DMF solvated) confirm the distorted octahedral environment on each molybdenum center and the bis (monobasic ON bidentate) behaviour of ligands. Each cis-[MoO<sub>2</sub>] unit is linked through bridged-oxygen. These complexes are good catalyst precursors for the oxidation of bicyclic alcohols (fenchyl alcohol and isoborneol)in the presence of 30 % aqueous H<sub>2</sub>O<sub>2</sub> and a range of N-base additives to give bio-active product fenchone and camphor, respectively. The N-base additive plays an important role in abstracting hydrogen from H<sub>2</sub>O<sub>2</sub> and generate the oxidoperoxidomolybdenum(VI) species which easily facilitate the transfer of oxygen to the substrate resulting in good yield of oxidised product. However, conversion of bicyclic alcohols within the additives follows the order: NEt<sub>3</sub>> py > NH<sub>3</sub>> K<sub>2</sub>CO<sub>3</sub>> KOH. Much poor conversion of substrates in the absence of additive was noted which demonstrate the importance of additive for such a catalysts.

#### Acknowledgements

L.R. thank the Council of Scientific and Industrial Research, New Delhi for financial support. Gas chromatograph used in this study was procured from the grant of Department of Science and Technology (SR/S1/IC-32/2010), Government of India, New Delhi.

#### References

- [1] (a) J. Pisk, D. Agustin, V. Vrdoljak and R. Poli, *Adv. Synth. Catal.*, 2011, 353, 2910–2914; (b) M. R. Maurya, *Curr. Org. Chem.* 2012, 16, 73–88; (c) J. Pisk, B. Prugovečki, D. Matković-Čalogović, R. Poli, D. Agustin and V. Vrdoljak, *Polyhedron*, 2012, 33, 441–449.
- (a) N. Gharah, S. Chakraborty, A. K. Mukherjee and R. Bhattacharyya, *Inorg. Chim. Acta*, 2009, 362, 1089–1100; (b) M. Bagherzadeh, M. Amini, H. Parastar, M. Jalali-Heravi, A. Ellern and L. K. Woo, *Inorg. Chem. Commun.*, 2012, 20, 86–89.
- [3] (a) F. Batigalhia, M. Zaldini-Hernandes, A. G. Ferreira, I. Malvestiti and Q. B. Cass, *Tetrahedron*, 2001, 57, 9669–9676; (b) M. M. Javadi, M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, H. Kargar and M. N. Tahir, *Polyhedron*, 2014, 72, 19–26.

- [4] Z. Wang, C. W. Kee, S. Li, T. A. Hor and J. Zhao, *Appl. Catal. A: Gen.* 2011 V393 ticle Online 269–274.
- [5] (a) B. L. Tran, A. Arita, A. L. Cooksy and C. J. Carrano, *Inorg. Chim. Acta*, 2016, 447, 45–51; (b) M. Volpe and N. C. Mösch-Zanetti, *Inorg. Chem.*, 2012, 51, 1440–1449.
- [6] (a) M. R. Maurya, N. Saini and F. Avecilla, *Inorg. Chim. Acta*, 2015, **438**, 168–178.
- [7] (a) M. T. Räisänen, A. Al-Hunaiti, E. Atosuo, M. Kemell, M. Leskelä and T. Repo, *Catal. Sci. Technol.*, 2014, 4, 2564–2573; (b) M. R. Maurya, N. Saini and F. Avecilla, *RSC Adv.*, 2015, 5, 101076–101088.
- [8] X. Liu, N. Xing, J. Song, Q. Wu, Z. Yan, Y. Zhang and Y. Xing, *Polyhedron*, 2015, 102, 386–393.
- [9] (a) M. R. Maurya, U. Kumar and P. Manikandan, *Dalton Trans.*, 2006, 3561–2575; (b)
  P. Adão, J. Costa Pessoa, R. T. Henriques, M. L. Kuznetsov, F. Avecilla, M. R. Maurya, U. Kumar and I. Correia, *Inorg. Chem.*, 2009, 48, 3542–3561; (c) M. R. Maurya, S. Dhaka and F. Avecilla, *Polyhedron*, 2014, 67, 145–159; (d) M. R. Maurya, S. Dhaka and F. Avecilla, *Polyhedron*, 2015, 96, 79–87; (e) S. Pasayat, S. P. Dash, S. Roy, R. Dinda, S. Dhaka, M. R. Maurya, W. Kaminsky, Y. P. Patil and M. Nethaji, *Polyhedron*, 2014, 67, 1–10; (f) S. K. Kurapati, S. Maloth and S. Pal, *Inorg. Chim. Acta*, 2015, 430, 66–73.

- [10] (a) D. Biswal, N. R. Pramanik, S. Chakrabarti, M. G. B. Drew, P. Mitra, K. Acharya, S. Biswas and T. P. Monldal, *New J. Chem.*, 2015, **39**, 8681–8694; (b) S. S. Paul, Md. Selim, A. Saha and K. K. Mukherjea, *Dalton Trans.*, 2014, **43**, 2835–2848; (c) A. Majumdar, *Dalton Trans.*, 2014, **43**, 8990–9003; (d) A. Ducrot, B. Scattergood, B. Coulson, R. N. Perutz and A. K. Duhme-Klair, *Eur. J. Inorg. Chem.*, 2015, 3562–357; (e) J. Leppin, C. Förster and K. Heinze, *Inorg. Chem.*, 2014, **53**, 12416–12427; (f) H. Sugimoto, M. Sato, K. Asano, T. Suzuki, K. Mieda, T. Ogura, T. Matsumoto, L. J. Giles, A. Pokhrel, M. L. Kirk and S. Itoh, *Inorg. Chem.*, 2016, **55**, 1542–1550; (g) D. Biswal, N.R. Pramanik, S. Chakrabarti, N. Chakraborty , K. Acharya, S. S. Mandal, S. Ghosh, M. G. B. Drew, T. K. Mondal and S. Biswas, *New J. Chem.*, 2015, **39**, 2778–2794.
- [11] (a) M. Nakamoto, K. Tanaka and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 1985, 58, 1816–1820; (b)L. Awwal, J. E. Drake, M. B. Hursthouse, R. Kumar, M. E. Light, R. Ratnani and K. Saraswat, *Polyhedron*, 2007, 26, 3973–3979; (c) C. Knobler, B. R. Penfold, W. T. Robinson, C. J. Wilkins and S. H. Yong, *J. Chem. Soc.*, *Dalton Trans.*, 1980, 248–

#### New Journal of Chemistry

252; (d) S. Gupta, S. Roy, T. N. Mandal, K. Das, S. Ray, R. J. Butcher and S. K. VKWArticle Online J. Chem. Sci., 2010, **122**, 239–245; (e) R. Ratnani, G. Srivastava and R. C. Mehrotra, *Inorg. Chimi. Acta.*, 1989, **161**, 253–259.

- [12] (a) J. M. Sobczak, T. Glowiak and J. J. Ziólkowski, *Trans. Met. Chem.*, 1990, 15, 208–211; (b) M. Cindrić, V. Vadoljak, N. Strukan, P. Tepeš, P. Novak, A. Brbot-Šaranović, G. Giester and B. Kamenar, *Eur.J. Inorg. Chem.*, 2002, 2128–2137; (c) B. Modec and J. V. Brenčič, *Eur. J. Inorg. Chem.*, 2005, 1698–1709; (d) E. Kahrović, Krešimir Molčanov, L. Tušek-Božić and B. K.-Prodić , *Polyhedron*, 2006, 25, 2459–2464; (e) X. Ma, C. Schulzke, H-G. Schmidt and M. Noltemeyer, *Dalton Trans.* 2007, 1773–1780; (f) M. Tašner , B. Prugovečki, ŽeljkaSoldin , S. Prugovečki , L. Rukavina and D. Matković-Čalogović, *Polyhedron*, 2013, 52, 268–275.
- (a) H. Arzoumanian, R. Bakhtchadjian, G. Agrifoglio, H. Krentzien and Jean-Claude. Daran, *Eur.J. Inorg. Chem.*, 1999, 2255–2259; (b) H. Arzoumanian, R. Bakhtchadjian, G. Agrifoglio, R. Atencio and A. Briceño, *Transition. Met. Chem.*, 2006, **31**, 681–689;
  (c) A. C. Coelho, M. Nolasco, S. S. Balula, M. M. Antunes, C. C. L. Pereira, F. A. A. Paz, A. A. Valente, M. Pillinger, P. Ribeiro-Claro, J. Klinowski, and I. S. Gonçalves, *Inorg. Chem.*, 2011, **50**, 525–538 ; (d) T. R. Amarante, A. C. Gomes, P. Neves, F. A. A. Paz, A. A. Valente, M. Pillinger and I. S. Gonçalves, *Inorg. Chem. Commun.*, 2013, **32**, 59–63; (e) M. B. Pereira, C. R. Kopp, L. A. Fontana, G. M. de Oliveira, D. F. Back, P. C. Piquini and M. A. Villetti, *New J. Chem.*, 2014, **38**, 3092–3101.
- [14] (a)S. Gago, P. Neves, B. Monteiro, M. Pessêgo, A. D. Lopes, A. A. Valente, F. A. Paz, M. Pillinger, J. Moreira, C. M. Silva and I. S. Goncalves, *Eur.J. Inorg. Chem.*, 2009, 4528–4537; (b) J. A. Brito, M. Gómez, G. Muller, H. Teruel, Jean-Claude Clinet, E. Duñach and M. A. Maestro, *Eur. J. Inorg. Chem.*, 2004, 4278–4285; (c) M. E. Judmaier, C. H. Sala, F. Belaj, M. Volpe and N. C. Mösch-Zanetti, *New J. Chem.*, 2013, **37**, 2139–2149.
- [15] N. Kitanovski, A. Golobič and B. Čeh, Inorg. Chem. comm., 2006, 9, 296–299.
- [16] (a) S. M. O. Quintal, H. I. S. Nogueira, H. M. Carapuca, V. Félix and M. G. B. Drew, J. Chem. Soc. Dalton Trans., 2001, 3196–3201; (b) T. R. Amarante, P. Neves, F. A. A. Paz, M. Pillinger, A. A. Valente and I. S. Goncalves, *Inorg. Chem. Commun.*, 2012, 20, 147–150.
- [17] S. Figueiredo, A. C. Gomes, P. Neves, T. R. Amarante, F. A. A. Paz, R. Soares, A. D. Lopes, A. A. Valente, M. Pillinger, and I. S. Gonçalves, *Inorg. Chem.*, 2012, 51, 8629–8635.

- [18] T. R. Amarante, P. Neves, A. C. Coelho, S. Gago, A. A. Valente, F. A. A. Particle Online Pillinger and I. S. Gonçalves, *Organometallics*, 2010, **29**, 883–892.
- [19] T. R. Amarante, P. Neves, C. Tomé, M. Abrantes, A. A. Valente, F. A. A. Paz, M. Pillinger and I. S. Gonçalves, *Inorg. Chem.*, 2012, **51**, 3666–3676,
- [20] B. Modec, D. Dolenc and J.V. Brenčič, *Inorg. Chim. Acta*, 2007, **360**, 663–678.
- [21] N. Noshiranzadeh, R. Bikas, M. Emami, M. Siczek, T. Lis, *Polyhedron*, 2016, **111**, 167–172.
- [22] T. Gündüj, Communication de la Faculte des Science De I' Universite d' Ankara, SerieB: Chemie, 1964, 11, 21.
- [23] M. T. H. Tarafder and A. R. Khan, *Polyhedron*, 1991, **10**, 819–822.

- [24] G. J. Chen, J. W. McDonald and W. E. Newton, *Inorg. Chem.*, 1976, 15, 2612–2615.
- [25] G. M. Sheldrick, SADABS, version 2.10, University of Göttingen, Germany, (2004).
- [26] (a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann,
   J. Appl. Cryst., 2009, 42, 339–341; (b) G. M. Sheldrick, SHELX, Acta Crystallogr.,
   Sect. A, 2008, 64, 112–122.
- [27] T. R. Amarante, A. C. Gomes, P. Neves, F. A. Almeida Paz, A. A. Valente, M. Pillinger and I. S. Gonçalves, *Inorg. Chem. Commun.*, 2013, 32, 59–63.
- [28] A. Syamal and M. R. Maurya, *Coord. Chem. Rev.*, 1989, **95**, 183-238.
- [29] R. C. Aggarwal, N. K. Singh and R. P. Singh, *J. Indian Chem. Soc.*, 1986, 63, 466–468.
- [30] M. R. Maurya, N. Saini and F. Avecilla, *RSC Adv.*, 2016, 6, 12993–13009.
- [31] S. K. Maiti, S. Dinda, S. Banerjee, A.K. Mukherjee and R. Bhattacharyya, *Eur. J. Inorg. Chem.*, 2008, 2038–2051.