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Short communication

Bimetallic cis-dioxomolybdenum(VI) complex containing hydrazone ligand: Syntheses, crystal structure and catalytic studies

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ABSTRACT

Bimetallic molybdenum(VI) complex [$(MoO_2)_2$(slsch)$(H_2O)_2$] containing dihydrazone ligand was synthesized by reaction of ligand with $MoO_2(acac)_2$ in 1:2 M ratio in methanol. The bimetallic complex obtained was characterized by various spectroscopic studies. The structure of complex was assigned using Single Crystal X-ray Crystallography and DFT method. We have also explored the catalytic behavior of complex for oxidation of primary benzylic, aliphatic, allylic, and propargylic alcohols.

1. Introduction

Molybdenum complexes are of considerable interest, especially those featuring high valent oxidation states are used as catalysts for oxidation reactions in recent years [1–4]. In biological systems, molybdenum has been found in many enzymes such as oxotransferases [5], sulfite oxidase [6], aldehyde oxidase [7], nitrate reductase [8], and xanthine oxidase/dehydrogenase [9]. Molybdenum ions when coordinate to protein usually exist in +4, +5 and +6 oxidation states [10,11]. Oxotransferases are a broad class of enzymes which are involved in oxygen atom transfer processes and are often referred as oxomolybdenum enzymes [12]. The active site in these enzymes usually consists of a cis-dioxo molybdenum(VI) cation with one oxo group and one or two molybdopterin ligands [13,14]. In order to mimic the activity of these enzymes, the search for new model compounds containing high valent $[MoO_2]^{2+}$ core have been synthesized [15,16].

So, in this communication we have described the synthesis of bimetallic molybdenum complex containing multi-dentate hydrazone ligand [17]. The structure of [$(MoO_2)_2$(slsch)$(H_2O)_2$] was established with the help of single X-ray crystallography. We also report the catalytic oxidation of alcohols to their corresponding aldehyde using H_2O_2 as the terminal oxidant.

Complex was synthesized following the standard reported literature [10]. The single crystal of the complex were grown by a slow evaporation of water/acetonitrile solution (3:2, v/v), at room temperature. The crystal structure of the complex and optimized geometry are shown in Fig. 1. Complex crystallized in monoclinic $P2_1/n$ space group. Crystal data and structure refinement for complex are given in Table 1, selected bond length and bond angles are presented in Table S1. The ligand coordinate to the metal ions in tridentate fashion with O1, O2, N1 and O4 at the equatorial position, whereas the axial position are occupied by O3 and O5 forming six coordinate octahedral geometry around molybdenum(VI) ions.

The M—O bond lengths of the complex are 1.909(7) Å (Mo—O1), 1.967(7) Å (Mo—O2), 1.698(7) Å (Mo—O3), 1.708(6) Å (Mo—O4) and 2.272(8) Å (Mo—O5), whereas Mo1—N1 bond distance is 2.271(9) Å. The equatorial and axial bond angles are 151.6(3)^0, 155.6(3)^0 and 171.3(3)^0, respectively. Crystal packing diagram of the complex (Fig. S1) shows O—H…O hydrogen bond interaction between O5—H(A)…O3 and O5—H(B)…O4 with geometrical hydrogen bond length of 2.714(13) Å and 2.698(13) Å, whereas the hydrogen bond angles are 122^0 and 159^0, respectively. The metal…metal distance is 9.566 Å while the packing efficiency is 68.37% (Table 2).

The gas phase optimized geometry of the complex were performed using density functional theory (DFT) with hybrid functional B3LYP with 6-31 + G(d,p) basis set for carbon, hydrogen, oxygen, nitrogen and bromine atoms and LANL2DZ [18] for molybdenum ions implemented in Gaussian 09 program [19]. The optimized geometrical bond lengths and bond angles of the complex are comparable with experimental solid state structure, slight difference being observed between these two because geometrical optimization are carried out in gas

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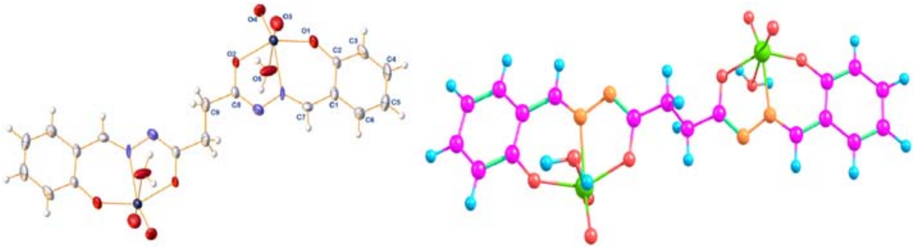


Fig. 1. (a) Molecular structure of bimetallic complex and (b) optimized geometrical structure.

Table 1
Crystal data and structure refinement for complex.

Empirical formula	$C_9H_9MoN_2O_5$
Formula weight	321.12
Temperature/K	294.11(10)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	8.7716(11)
b/Å	11.5108(13)
c/Å	11.4795(17)
α/°	90
β/°	109.170(16)
γ/°	90
Volume/Å^3	1094.8(3)
Z	4
μ/mm^{-1}	1.210
Reflections collected	3503
Data/restraints/parameters	2240/0/155
Goodness-of-fit on F^2	1.195
Final R indexes [I > = 2σ (I)]	$R_1 = 0.0751$, $wR_2 = 0.2098$
Final R indexes [all data]	$R_1 = 0.0829$, $wR_2 = 0.2147$

Table 2
Represents hydrogen bond parameters of the complex.

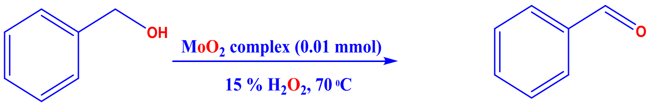
Donor – H...Acceptor →	D - H	H...A	D...A	D - H...A
O(5) –H(5A)...O(4)#1	0.86	1.88	2.698(13)	159
O(5) –H(5B)...O(3)#2	0.86	2.16	→ 2.714(13)	122

#1: -x, 1 − y,-z; #2: 1/2 − x, -1/2 + y,1/2 − z

phase in which intermolecular interactions are absent and moreover its structure is more extended compared to solid state structure, in which intermolecular interactions become prominent (Fig. 2).

The use of molybdenum complexes as catalysts for the oxidation reaction has become a topical research area in recent years. Thus, having synthesized homobimetallic molybdenum(VI) complex, we investigated the catalytic activity in the oxidation reaction of alcohols using hydrogen peroxide as a mild oxidant. In order to achieve the best catalytic performance, we carried out the oxidation of benzyl alcohol as a standard substrate [20] (Scheme 1).

The catalytic studies were carried out using different amount of catalyst and found that 0.01 mmol gave the best results at a temperature of 70 °C (Figs. 3 & 4) with 49% of the oxidized product. Different solvent were tested under similar condition and was found that acetonitrile (Fig. 5) gave best yield. In order to improve the catalytic studies and selectivity of the product, we also introduced some base in the reaction medium and it seems that addition of a base decrease the reaction rate. The catalytic oxidation of benzyl alcohol were also tested using different metal sources such as, MoO_3, $Mo_2(OAC)_4$ and $MoO_2(acac)_2$ but it was found that the catalytic activity of complex is superior giving high yield. Additionally, the reaction was also carried out under dinitrogen atmosphere but only a trace amount of the product was observed, hence the catalytic oxidation reaction proceed solely with air.



Scheme 1. Oxidation of benzyl alcohol using synthesized complex.

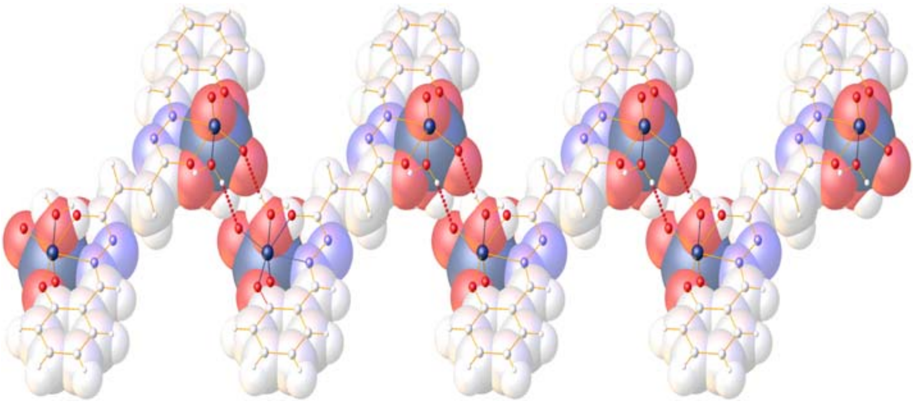


Fig. 2. Overlay structure of space fill model with zigzag one dimensional hydrogen bonding.

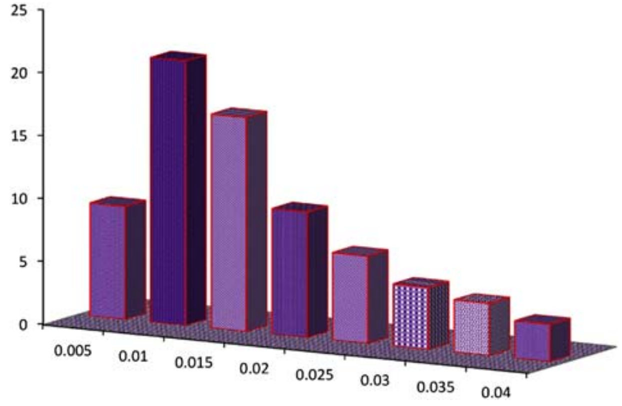


Fig. 3. Effect of concentration of catalyst on oxidation of benzyl alcohol.

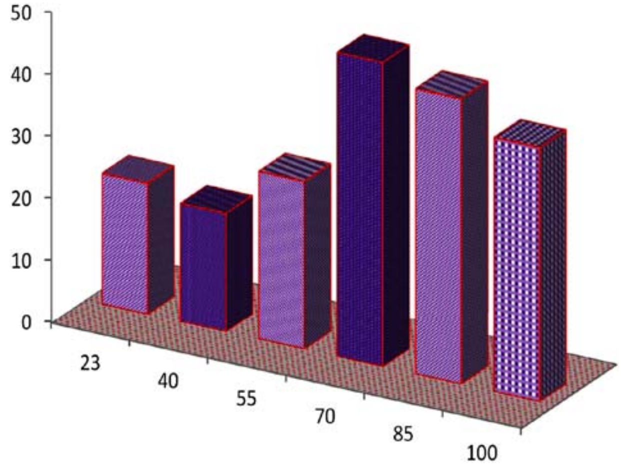


Fig. 4. Effect of temperature on oxidation of benzyl alcohol.

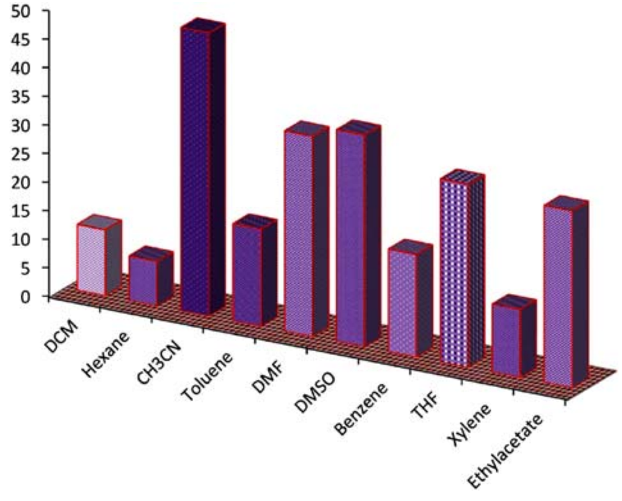


Fig. 5. Effect of solvent on oxidation of benzyl alcohol.

The catalytic study of complex was applied to diverse substrates by oxidizing various benzylic, allylic and propargylic alcohols (Table 3) using the optimization method to assess the reaction scope and limitation. Both primary and secondary benzyl alcohols were reacted to afford corresponding aldehydes and ketones in good to excellent yields (Table 3, Entry 1–4, 6–12). Primary benzyl alcohols bearing electron donating groups such as, p-methoxy benzyl alcohol gave 90% isolated yield of p-methoxy benzaldehyde (GC: 94%), *p*-methyl benzyl alcohol yields 88% of *p*-methyl benzaldehyde, whereas 3,4,5-trimethoxy benzyl alcohol gave 90% of isolated yield within 3 h. Electron donating group present at the ortho and para position of the benzene ring such as, *o*-methyl benzyl alcohol gave 79% of *o*-methyl benzaldehyde and *m*-methyl benzyl alcohol gave 78% of *m*-methyl benzaldehyde. Electron withdrawing groups such as p-nitro benzyl alcohol and m-chloro benzyl alcohol gave 81% (Table 3, Entry 3) and 78.4% (Table 3, Entry 8) isolated yield lower to that of electron donating groups present in para position of the benzene ring. Benzyl alcohol containing double bond functional groups, such as cinnamyl alcohol was also oxidized to cinnamaldehyde with selectively 87% conversion without oxidation of double bond. 2-hydroxy-1,2-diphenylethan-1-one was also oxidized to benzil with 85% yield within 2 h. Secondary benzyl alcohols such as phenyl ethanol (entry 6), phenyl propanol (entry 7), cyclohexanol (entry 5) and cycloheptanol (entry 13) were either not react or only poorly oxidized to their corresponding ketone 0.7%, not reactive, not reactive and 0.5% yield, respectively. On the other hand, hetero-aryl alcohols like furan-2-yl-methanol, pyridine-2-yl methanol and thiophene methanol (entries 14, 15, 16) gave 88%, 89% and 77.9% of their corresponding aldehydes. In case of aliphatic alcohols such as n-propanol (entry 20), n-butanol (entry 18), and n-octanol (entry 21) were also oxidized for a period of 48 h, and gave moderate to excellent yields of 69%, 78%, and 35.3%, respectively. Propargylic alcohols such as 2-hexyne-1-ol, were also oxidized to 2-hexyne-1-al with lower yield 17% (entry 19) (Scheme 2).

The result above shows that homobinuclear molybdenum(VI) complex containing hydrazone ligand can be used as a model catalyst for oxidation of wide range of benzylic alcohol, hetero-aryl alcohols, aliphatic alcohols and propargylic alcohols using H_2O_2 as terminal oxidant. The catalytic behavior of the binuclear molybdenum(VI) complexes are comparable to that of the reported complexes containing molybdenum ions [21]. The process is efficient and the catalyst can be recovered without any appreciable loss in the catalytic process (Fig. S11).

In conclusion, binuclear complex $[MoO_2)_2(slsch)(H_2O)_2]$ has been prepared and well characterized. Crystal structure shows that ligand coordinates to metal ion in bis-(tridentates) fashion in tetra-deprotonated form. The crystal structure of complex (water coordinated) confirmed the distorted octahedral geometry on each metal ion. The complex can be used as a model catalyst for oxidation of primary benzylic alcohols, aliphatic, allylic, and propargylic alcohols in the present of 15% H_2O_2. The process went on smoothly and moreover the complexes can be easily recovered without any decrease in percentage yield in the next cycles.

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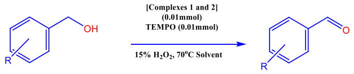
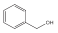
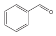
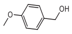
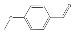
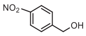
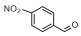
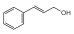
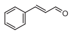
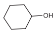
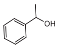
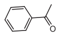
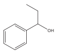
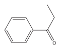
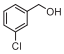
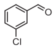
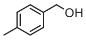
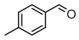
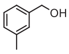
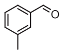
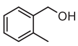
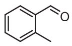
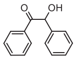
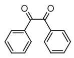
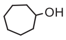
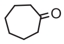
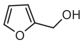
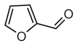
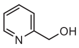
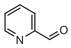
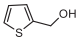
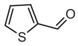
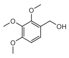
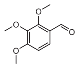
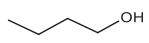
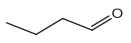
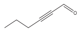
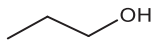
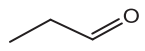
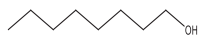
Appendix A. Supplementary material

The crystallographic data (CCDC number: **1566197**), can be obtained via https://summary.ccdc.cam.ac.uk/structure-summary-form, from Cambridge Crystallographic Data Centre. Supplementary data associated with this article can be found online at. https://doi.org/10.1016/j.inoche.2017.09.018.

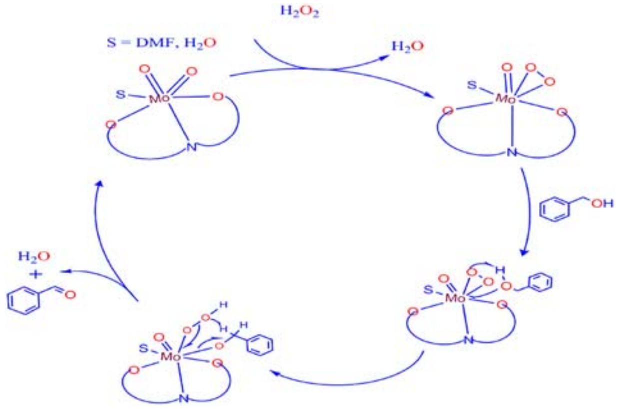
Table 3
Oxidation of alcohols catalyzed by $[(MoO_2)_2slsch(H_2O)_2]$ under mild condition[a].



R=Cl, Br, NO_2, OMe, Me

Sl. no	Alcohol	Product	Time (h)	Yield (%) (isolated)[b] R-CHO	Yield (%) (GC %)[c] R-CHO
1			3	89	90
2			3	90	94
3			3	81	85.8
4			3	87	90
5			3	–	0.7
6			5	No reaction	No reaction
7			5	No reaction	No reaction
8			4	78.4	80.6
9			4	88	89
10			3	78	82.8
11			3	79	87.7
12			2	85	89.7
13			3	No reaction	0.5
14			3	88	90
15			3	89	91
16			2	77.9	83
17			3	90	91
18			48	78	81.7
19			14	–	17
20			48	69	75.7
21			48	32	35

[a] Reaction condition: catalyst (0.010 mmol); 15% H_2O_2 (4.85 mmol); alcohol (4.84 mmol).
[b] Yield.
[c] GC yield.



Scheme 2. Bimetallic complex as precatalyst for the catalytic oxidation alcohol (only one unit of complex is shown).

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(c) $[MoO_2)_2(slsch)(H_2O)_2]$. To a solution of molybdenum acetylacetonate (0.326 g, 1mmol) in methanol (20 mL), H_4slsch (0.175 g, 0.5 mmol) was added with

constant stirring and reflux for 20 minutes. The reaction mixture was cool to room temperature and evaporated under vacuum to obtain the desired complex. The single light yellow crystals suitable for X-ray analysis were obtained by a slow evaporation of their CH_3CN/water solutions (2:1, v/v), in air at room temperature. Anal (%): Calcd for $C_{24}\ H_{28}\ N_6\ O_{10}\ Mo_2$: C, 38.31; H, 3.75; N, 11.17; Found: C, 38.72; H, 3.71; N, 11.60. IR data (cm^{-1}, KBr): 3400 (sbr) ν(OH), 1621 (s) ν(C=N), 1558 (s) Amide II + (C-O) (Phenyl), 1545 (vs) ν(NCO-), 1341 (m), 1270 (m) ν(C-O), 1017 (w) ν(N-N), 925 (s), 907 (s), ν(M=O), 578 (w) (Mo-O) (phenolic), 466 (w) (M-O)(carbonyl). ^{1}H NMR (400 MHz, DMSO-d_6, Me_4Si): δ (ppm): 7.94 (s, 1H, H-C=O), 6.88–7.94 (m, 8H, Ar-H), 8.28–8.76 (s, 2H, C(H)=N), 2.5 (s, 4H, ($-CH_2$)). Electronic spectrum CH_3CN Solution, λ_{max}: 310, 384.

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[20] Benzyl alcohol (0.05 g, 0.5 mmol), was added to a mixture of 15% H_2O_2 (0.3 g, 8.83 mmol), complex $[MoO_2)_2(slsch)(H_2O)_2]$ (0.01 g, 0.017 mmol) in acetonitrile solution in 50 mL round bottom flask. The mixture was first stirred at ambient temperature for 20 mins and then the temperature was raised to 70 °C for 2 h. The crude product was separated by a separating funnel and dried over anhydrous sodium sulfate. The oxidized product was purified by column chromatography to afford benzaldehyde. The isolated product was ascertained by comparison with the authentic sample using ^{1}H and ^{13}C NMR spectroscopies.

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