



Synthesis, characterization and anticandidal activity of dioxomolybdenum(VI) complexes of the type $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{Ar}\}_2]$ and $[\text{MoO}_2\{\text{OC}(\text{R})\text{CHC}(\text{R}')=\text{NC}_6\text{H}_5\}_2]$



Purnima Nag^{*}, Deepankar Sharma

Department of Chemistry, Jaipur National University, Jaipur, 302017, India

ARTICLE INFO

Keywords:

Organic chemistry
Inorganic chemistry
Dioxomolybdenum(VI) complexes
Internally functionalized oximes
Schiff's bases derived from β -diketones

ABSTRACT

Interaction of $[\text{MoO}_2(\text{acac})_2]$ with internally functionalized oximes like $\text{HON}=\text{C}(\text{CH}_3)\text{Ar}$ ($\text{Ar} = \text{C}_4\text{H}_3\text{S}$, $\text{C}_4\text{H}_3\text{O}$ or $\text{C}_5\text{H}_4\text{N}$) and Schiff's Bases derived from β -diketones like $\text{HOC}(\text{R})\text{CHC}(\text{R}')=\text{NC}_6\text{H}_5$ ($\text{R} = \text{R}' = \text{CH}_3$ or C_6H_5 ; $\text{R} = \text{CH}_3$ and $\text{R}' = \text{C}_6\text{H}_5$) led to the formation of yellow dioxomolybdenum(VI) complexes of the type $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{Ar}\}_2]$ and $[\text{MoO}_2\{\text{OC}(\text{R})\text{CHC}(\text{R}')=\text{NC}_6\text{H}_5\}_2]$. Oximes were synthesized by green methodology. The newly synthesized complexes were characterized on basis of elemental analysis and various spectral findings.

Anticandidal activity of $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_6\text{H}_4\text{N}\}_2]$ clearly reveals that the complex is biologically active against fungal diseases.

1. Introduction

Molybdenum has been an important metal due to its capability of forming complexes with variety of ligands [1, 2, 3, 4], it is an essential constituent of recognized enzymes that catalyzes reduction of molecular nitrogen and nitrates in plants and oxidation (hydroxylation) of Xanthine and other Purines as well as aldehydes in animals [5]. Oxo- and dioxo-molybdenum complexes have been generously studied as catalysts for variety of organic transformations, commonly for sulfoxidation of sulfides [5], oxygen atom transfer (OAT) reactions [6, 7, 8, 9, 10, 11, 12]; antioxidant activities [13], and also as neutral esterification agents [14].

The variety of transition metal complexes with wide choice of oximes and schiff's bases ligand system and coordination environment have instigated us to undertake research in this area [15]. Complexes with Schiff base ligand systems have showed significant applications in many organic transformations as homogeneous and heterogeneous catalysts [16] such as in reduction of ketones to alcohols [17] and alkylation of allylic substrates [18, 19, 20]. Oxime metal chelates exhibit higher biological activity than corresponding free ligands [21]. Varied metallic complexes of oximes exhibited cytotoxicity in murine and human tissue cultured cell lines [22].

In continuation to our previous work [14, 23, 24, 25, 26] and to further study the chemistry of oxomolybdenum complexes incorporating

oxygen, nitrogen and sulphur donor atoms; the synthesis of dioxomolybdenum(VI) complexes with internally functionalized oximes and Schiff's bases derived from β -diketones is reported in present work.

2. Experimental

2.1. Materials and methods

2-acetyl thiophene, 2-acetyl furan, 2-acetyl pyridine, pentane 2,4 dione, 1-phenyl butane-1,3 dione, 1,3 diphenyl, propane-1,3 dione, acetylacetone and aniline (from Merck) were used as such. Hydroxylamine hydrochloride, sodium hydroxide and sodium acetate (from E. Merck) were used after drying at reduced pressure for 4–5 hours to ensure the complete removal of absorbed moisture. Precursor $[\text{MoO}_2(\text{acac})_2]$ was synthesized according to the literature method [27]. Oximes were synthesized by novel green methodology without using any organic solvent. Schiff bases of β -diketones were synthesized by literature method [28]. Molybdenum was estimated gravimetrically as oxinate. C and H were analyzed on a Perkin-Elmer C, H, N and S II series 2400 analyzer. Sulphur and nitrogen were estimated by standard methods. FT-IR spectra were recorded on a Perkin-Elmer spectrophotometer in the $4000\text{--}400\text{ cm}^{-1}$ range using KBr pellets. $^1\text{H-NMR}$ spectra were recorded in CDCl_3 and $d_6\text{-DMSO}$ using TMS as an internal reference on a JEOL

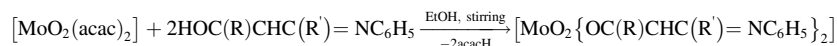
^{*} Corresponding author.

E-mail address: purnima_nag007@yahoo.com (P. Nag).

FX90Q spectrometer. UV spectra were measured using a copy- 50 Bio (Varian) UV-visible spectrophotometer. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/Data system using Ar/Xe (6kv, 10mA) as the FAB gas, *m*-nitrobenzyl alcohol was used as the matrix.

2.2. Synthesis of oximes by green method

A solution of 2- acetyl thiophene (1.0g, 7.926 mmol) and hydroxylamine hydrochloride (0.55g, 7.926 mmol) in 10–12 ml water was stirred at 40–50 °C for half an hour. To this solution, sodium hydroxide pellets (0.32g, 7.926 mmol) were added portion wise and contents were stirred



for another 2 hours at room temperature. The precipitate was collected by filtration, washed with water and dried in vacuum to obtain white solid product. A similar procedure was used to prepare compounds $\text{HON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{O}$ and $\text{HON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}$.

2.3. Synthesis of $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}\}_2]$

A solution of $[\text{MoO}_2(\text{acac})_2]$ (2.41g, 7.40 mmol) and $\text{HON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}$ (2.09g, 14.81 mmol) in ethanol was stirred at room temperature for 2 hours. After stripping off the solvent from yellow colored solution under reduced pressure the product was isolated as yellow solid.

A similar procedure was used to prepare compounds $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{O}\}_2]$, $[\text{MoO}_2\{\text{OC}(\text{CH}_3)\text{CHC}(\text{CH}_3)=\text{NC}_6\text{H}_5\}_2]$, $[\text{MoO}_2\{\text{OC}(\text{CH}_3)\text{CHC}(\text{C}_6\text{H}_5)\text{N}=\text{C}_6\text{H}_5\}_2]$ and $[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)\text{N}=\text{C}_6\text{H}_5\}_2]$. Physical data for these newly synthesized complexes are provided as supplementary material (Table S2).

2.4. Synthesis of $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$

To the ethanolic solution of $[\text{MoO}_2(\text{acac})_2]$ (2.08g, 6.38 mmol), ethanolic solution of $\text{HON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}$ (1.74g, 12.78 mmol) was added. Yellow precipitate was immediately obtained. The mixture was stirred for 2 hours. The precipitate was collected by filtration, washed with ethanol and dried in vacuum.

The compound $[\text{MoO}_2\{\text{ON}=\text{C}(\text{C}_5\text{H}_4\text{N})\}_2]$ may also be synthesized by the following procedure:

To an aqueous solution of sodium molybdate (2.41g, 9.26 mmol) an ethanolic solution of 2-acetyl pyridyl oxime (2.52g, 18.53 mmol) was added. 5% solution of sulfuric acid was added to it. This mixture was stirred for 2 hours. Yellow precipitate, so obtained (at pH 5.2) was collected through filtration, washed with distilled water and dried over P_4O_{10} in vacuum.

The analytical results of both types of complexes are summarized in Table 1.

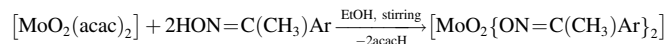
Table 1

Elemental Analysis and m.p. of $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{Ar}\}_2]$ and $[\text{MoO}_2\{\text{OC}(\text{R})\text{CHC}(\text{R}')=\text{NC}_6\text{H}_5\}_2]$.

S. No.	Complex	Elemental Analysis (%) Found (Calcd.)					M.P. (°C) ^d
		C	H	N	S	Mo	
1	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}\}_2]$	34.52 (34.91)	2.80 (2.88)	6.63 (6.82)	15.48 (15.73)	23.33 (23.52)	205
2	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{O}\}_2]$	37.98 (38.27)	3.02 (3.19)	7.18 (7.43)	-	25.91 (25.48)	200
3	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$	42.84 (42.23)	3.61 (3.49)	14.13 (14.04)	-	24.05 (24.09)	210
4	$[\text{MoO}_2\{\text{OC}(\text{CH}_3)\text{CHC}(\text{CH}_3)=\text{NC}_6\text{H}_5\}_2]$	55.03 (55.48)	4.83 (4.91)	5.82 (5.88)	-	20.31 (20.24)	173
5	$[\text{MoO}_2\{\text{OC}(\text{CH}_3)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2]$	63.74 (64.04)	4.63 (4.68)	2.15 (2.28)	-	16.14 (15.98)	175
6	$[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2]$	69.14 (69.58)	4.17 (4.35)	3.47 (3.88)	-	13.01 (13.18)	180

3. Results and discussion

The interaction of $[\text{MoO}_2(\text{acac})_2]$ with internally functionalized oximes like $\text{HON}=\text{C}(\text{CH}_3)\text{Ar}$ ($\text{Ar}=\text{C}_4\text{H}_3\text{S}$, $\text{C}_4\text{H}_3\text{O}$ or $\text{C}_5\text{H}_4\text{N}$) and Schiff bases derived from β -diketones like $\text{HOC}(\text{R})\text{CHC}(\text{R}')=\text{NC}_6\text{H}_5$ ($\text{R} = \text{R}' = \text{CH}_3$ or C_6H_5 , $\text{R} = \text{CH}_3$ and $\text{R}' = \text{C}_6\text{H}_5$) in 1:2 molar ratio in CH_3OH has led to the formation of yellow dioxomolybdenum(VI) complexes of the types, $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{Ar}\}_2]$ and $[\text{MoO}_2\{\text{OC}(\text{R})\text{CHC}(\text{R}')=\text{NC}_6\text{H}_5\}_2]$.



All these products are yellow colored solids and are soluble in polar solvents like CH_3OH , CH_3CN , THF etc. except $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$ which remain sparingly soluble even in coordinating solvents like DMF and DMSO. Elemental analysis and m.p. of all the complexes have been summarized in Table 1.

3.1. IR Spectra

Some important IR spectral bands of complexes are summarized in Table 2. IR spectra of a representative complex $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$ and its parent ligand are provided as supplementary material (Figs. S1 and S2).

The absence of a signal in the spectra of the complexes, $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{Ar}\}_2]$ and $[\text{MoO}_2\{\text{OC}(\text{R})\text{CHC}(\text{R}')=\text{NC}_6\text{H}_5\}_2]$ due to

Table 2

Some characteristic IR spectral data of $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{Ar}\}_2]$ and $[\text{MoO}_2\{\text{OC}(\text{R})\text{CHC}(\text{R}')=\text{NC}_6\text{H}_5\}_2]$.

S. No.	Complex	$\nu(\text{C}=\text{N})$ in cm^{-1}	$\nu(\text{C} = \text{X}; \text{aromatic ring})$ or $\nu(\text{C}=\text{C}; \beta\text{-diketone})$ in cm^{-1}	$\nu(\text{Mo}=\text{O})$ in cm^{-1}
1	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}\}_2]$	1515 (m)	1390 (w)	900 (s) 920 (s)
2	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{O}\}_2]$	1500 (m)	1410 (w)	905 (s) 920 (s)
3	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$	1490 (m)	1450 (w)	890 (s) 910 (s)
4	$[\text{MoO}_2\{\text{OC}(\text{CH}_3)\text{CHC}(\text{CH}_3)=\text{NC}_6\text{H}_5\}_2]$	1620 (s)	1400 (m)	915 (s) 925 (s)
5	$[\text{MoO}_2\{\text{OC}(\text{CH}_3)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2]$	1610 (s)	1380 (m)	900 (s) 925 (s)
6	$[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2]$	1605 (s)	1370 (m)	890 (s) 910 (s)

ν (OH) in the 3600–3200 cm^{-1} region suggests that ligands are bonded to molybdenum through the oxygen atom *via* deprotonation [28] (for IR details of ligands, refer Table S1 in supplementary data). This is further supported by two strong bands in the region 890–935 cm^{-1} assigned to *cis* (Mo=O) symmetric and antisymmetric stretching vibrations [27, 29].

A weak band is observed in the free oximes in the range 1690–1640 cm^{-1} , characteristic of the azomethine (>C=N) group has shifted to lower frequencies (1515–1490 cm^{-1}) in the spectra of the complexes of the type $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{Ar}\}_2]$. Additionally, ν (C = X) (X = S, O or N) of aromatic ring in complexes were observed in the range 1450–1390 cm^{-1} in IR spectrum. These values are lower than that observed for related free oximes in range 1490–1405 cm^{-1} [30,31]; suggesting the bidentate behavior of the ligands.

The bands of ν (C=N) in the spectra of the complexes $[\text{MoO}_2\{\text{OC}(\text{R})\text{CHC}(\text{R}')=\text{NC}_6\text{H}_5\}_2]$ were observed in the region 1620–1605 cm^{-1} indicating the formation of a coordinate bond through nitrogen to molybdenum atom [32]. These values are lower than that of free Schiff bases in region 1630–1620 cm^{-1} ; characteristic of the azomethine (>C=N) group [33]. Bidentate behavior of Schiff bases is further supported by bands of C=C (of β -diketone) observed in the region 1400–1370 cm^{-1} for the respective complexes; which is lower in comparison to that of free Schiff bases (1460–1405 cm^{-1}).

3.2. Electronic Absorption Spectra

The important electron absorption bands in the spectra of all these derivatives are compiled in Table 3.

Dioxomolybdenum(VI) complexes of oxime derivatives $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{Ar}\}_2]$ exhibit bands in 273–300 nm ranges which may be attributed to intraligand transitions [34]. Similarly, Schiff base derivatives, $[\text{MoO}_2\{\text{OC}(\text{R})\text{CHC}(\text{R}')=\text{NC}_6\text{H}_5\}_2]$ show such transitions at 307–317 nm [35].

Bands at 320–333 nm are characteristics of ligand to molybdenum(VI) charge transfer transitions in both types of complexes [27]. The absence of bands due to d-d transition in the range 650–420 nm supports the presence of molybdenum in +6 oxidation state.

3.3. ^1H NMR Spectra

The proton chemical shifts of these derivatives are summarized in Table 4.

The OH signals present in the spectra of the free oximes and Schiff bases are found to be absent in the spectra of the above complexes showing deprotonation of the ligands, resulting in the formation of the desired products [28]. A comparison of peak positions in these complexes with those of their corresponding positions in the spectra of the free ligands [28, 30, 31, 32] reveals their high field shifting (*ca* 0.2–0.4 δ ppm), indicating bonding of the ligand moieties to the molybdenum atom.

Table 3

Some Relevant Electronic Absorption Spectral Data [λ_{max} in nm] for $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{Ar}\}_2]$ and $[\text{MoO}_2\{\text{OC}(\text{R})\text{CHC}(\text{R}')=\text{NC}_6\text{H}_5\}_2]$.

S. No.	Complex	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$O_t \rightarrow \text{Mo}^{\text{VI}}$
1	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}\}_2]$	365 (1.59)	210 (0.39)	318 (1.67)
2	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{O}\}_2]$	353 (1.66)	218 (0.77)	325 (1.56)
3	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$	375 (1.57)	213 (0.91)	315 (1.13)
4	$[\text{MoO}_2\{\text{OC}(\text{CH}_3)\text{CHC}(\text{CH}_3)=\text{NC}_6\text{H}_5\}_2]$	369 (1.37)	217 (-0.60)	319 (1.01)
5	$[\text{MoO}_2\{\text{OC}(\text{CH}_3)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2]$	370 (1.33)	215 (-0.69)	315 (0.63)
6	$[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2]$	371 (1.32)	216 (-0.68)	309 (0.63)

Table 4

^1H -NMR Spectral Data (δ p.p.m.) of $(\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{Ar}\}_2)$ and $[\text{MoO}_2\{\text{OC}(\text{R})\text{CHC}(\text{R}')=\text{NC}_6\text{H}_5\}_2]$.

S. No.	Complex	^1H Chemical Shift
1	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}\}_2]$	2.24(s,6H CH ₃); 7.02(dd, 2H,H-4)C; 7.11 (d, 2H, H-3); 7.24 (d, 2H, H-5)
2	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{O}\}_2]$	2.15(s,6H CH ₃); 6.40(dd, 2H,H-4)C; 6.43 (d, 2H, H-3); 7.33 (d, 2H, H-5)
3	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$	2.19(s,6H CH ₃); 7.15(dd, 2H,H-4)C; 7.60 (dd, 2H, H-5); 7.85 (d, 2H, H-3); 8.43(d,2H,H-6)
4	$[\text{MoO}_2\{\text{OC}(\text{CH}_3)\text{CHC}(\text{CH}_3)=\text{NC}_6\text{H}_5\}_2]$	2.17(s,6H, CH ₃ CN); 2.21 (s,6H, CH ₃ CO), 5.87 (s,2H, CH); 6.51–7.45 (m, 10H, C ₆ H ₅)
5	$[\text{MoO}_2\{\text{OC}(\text{CH}_3)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2]$	2.34 (s,6H, CH ₃ CO); 5.91(s,2H, CH); 7.01–7.57 (m,20H, C ₆ H ₅)
6	$[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2]$	3.81 (s, 2H, CH); 7.01–7.78 (m, 30H, C ₆ H ₅)

Table 5

^{13}C $\{^1\text{H}\}$ NMR Spectral Data (δ ppm) of $(\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{Ar}\}_2)$ and $[\text{MoO}_2\{\text{OC}(\text{R})\text{CHC}(\text{R}')=\text{NC}_6\text{H}_5\}_2]$.

S. No.	Complex	^{13}C $\{^1\text{H}\}$ Chemical Shift
1	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}\}_2]$	11.9 (CH ₃); 125.3(C-4); 125.9(C-3); 127.5(C-5); 143.4(C-2); 152.5(C-N)
2	$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{O}\}_2]$	10.8(CH ₃); 104.9(C-4), 110.3(C-3); 142.0 (C-5); 148.4(C-2); 153.3 (C-N)
3	$[\text{MoO}_2\{\text{OC}(\text{CH}_3)\text{CHC}(\text{CH}_3)=\text{NC}_6\text{H}_5\}_2]$	20.4 (CH ₃ CN), 25.1(CH ₃ CO), 48.4 (C ₆ H ₅), 159.4 (C=N), 196.5(CO)
4	$[\text{MoO}_2\{\text{OC}(\text{CH}_3)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2]$	19.3 (CH ₃ CN), 97.3(CH), 123–128.8 (C ₆ H ₅), 120.4–127.9 (C=N), 194.6(CO)
5	$[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2]$	92.6(CH), 112.7–128.2 (C ₆ H ₅), 163.8 (C=N), 185.0 194.6(CO)

Shifting of aromatic protons of the oxime moiety as well as of phenyl protons of the Schiff base to lower ppm value indicate bidentate behaviour of these ligands towards molybdenum(VI) moiety.

3.4. ^{13}C $\{^1\text{H}\}$ NMR Spectra

The ^{13}C $\{^1\text{H}\}$ NMR spectra of these complexes exhibit characteristic peaks for ligand carbon atoms. The data are summarized in Table 5. Down field shifting of C=N, C-2 and C-5 aryl carbon signals of the oxime group as well as C=N and phenyl carbon signals of the Schiff base in ^{13}C $\{^1\text{H}\}$ NMR Spectra of these complexes as compared to the free ligands [30, 31] suggest bidentate behaviour of the ligands.

3.5. FAB Mass Spectra

Some of the most important mass spectral ion peaks of a typical oxime as well as a Schiff base derivative of dioxomolybdenum(VI), $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$ and $[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2]$, with their tentative assignments are compiled in Tables 6 and 7. FAB mass spectrum of the $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$ exhibits the highest ion peak at $m/z = 447$, suggesting monomeric behavior of the complex with association of (CH_3NOH^+) moiety.

Similarly the complex $[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2]$ shows the highest ion peak at $m/z = 899$, indicating the presence of monomeric unit of the complex associated with ($\text{C}_6\text{H}_5\text{COC}_5\text{H}_8$) moiety.

3.6. Anticandidal Activity

The *in vitro* evaluation of anticandidal activity for $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$ was carried out against *Candida albicans* in Dr. B. Lal Clinical Laboratory Pvt. Ltd. - Centre for Innovation, Research and Development (CIRD), Jaipur using Kirby-Bauer well diffusion method [36]. Compound was dissolved in DMSO at concentrations C1 = 10

Table 6FAB mass spectral data of $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$.

m/e	Assignment
447	$[\text{MoO}_2\{\text{ONC}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2\text{CH}_3\text{NOH}]^+$
440	$[\text{MoO}_2\{\text{ONC}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$
371	$[\text{MoO}_2\{\text{ONC}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}(\text{COC}_5\text{H}_4\text{N})]$
339	$[\text{MoO}_2\{\text{CH}=\text{CC}_5\text{H}_4\text{N}\}(\text{COC}_5\text{H}_4\text{N})]$
289	$[\text{MoO}_2(\text{C}_3\text{H}_3\text{N})(\text{COC}_5\text{H}_4\text{N})]$
261	$[\text{MoO}_2(\text{C}_3\text{H}_3\text{N})(\text{C}_5\text{H}_4\text{N})]$
232	$[\text{MoO}_2(\text{C}_6\text{H}_4\text{CN})]^+$
206	$[\text{MoO}_2(\text{C}_6\text{H}_4)]^+$
192	$[\text{MoO}_2(\text{C}_5\text{H}_2)]$
149	$[\text{Mo}(\text{OH})_3]$
137	$[\text{Mo}(\text{C}_3\text{H}_3)]$

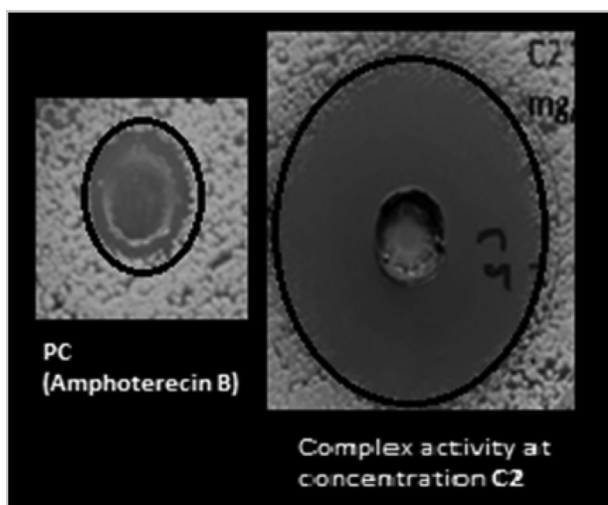
Table 7FAB mass spectral data of $[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2]$.

m/e	Assignment
899	$[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)=\text{NC}_6\text{H}_5\}_2] \text{C}_6\text{H}_5\text{COC}_5\text{H}_8$
752	$[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)\text{NC}_6\text{H}_5\}_2] \text{C}_2\text{H}_2$
712	$[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)\text{NC}_6\text{H}_5\}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)\text{NC}_6\text{H}_5\}]$
688	$[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)\text{NC}_3\text{H}_3\}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)\text{NC}_6\text{H}_5\}]$
609	$[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_4\text{H}_3)\text{NC}_3\text{H}_3\}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)\text{NC}_6\text{H}_5\}]$
560	$[\text{MoO}_2\{\text{OC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)\text{NC}_6\text{H}_5\}_2\text{C}_6\text{H}_5\text{CHO} \cdot \text{C}_2\text{H}_2]$
473	$[\text{MoO}_2\{\text{OCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{NHC}_6\text{H}_5\}_2\text{C}_6\text{H}_5\text{CHO} \cdot \text{C}_2\text{H}_2]$
396	$[\text{MoO}_2\{\text{OCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{NHC}_6\text{H}_5\}_2\text{C}_3\text{H}_3\text{O}]$
351	$[\text{MoO}_2\{\text{OCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{NHC}_6\text{H}_5\}_2\text{C}_3\text{H}_3\text{O}]$
225	$[\text{MoO}_2\text{C}_6\text{H}_5\text{C}_2\text{H}_6]$
154	$[\text{MoO}(\text{C}_3\text{H}_4)]$
136	$[\text{Mo}(\text{C}_3\text{H}_2)]$

Table 8Anticandidal activity of $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$.

Compound	Zone of Inhibition (mm)
	<i>Candida albicans</i>
NC – DMSO	NZI
$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$ at C1	NZI
$[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$ at C2	14
PC - Amphotericin B (50 µg)	2

NZI - No zone of inhibition.

**Fig. 1.** Anticandidal activity of $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}\}_2]$.

mg mL^{-1} and C2 = 100 mg mL^{-1} concentrations; Amphotericin B was used as PC- positive control at 50 µg/ml concentration and DMSO was used as NC- negative control. Results of anticandidal activity are listed in

Table 8 (also see Fig. 1).

4. Conclusion

In absence of crystal structure which may be due to the amorphous nature of the synthesized novel molecules, we cannot put forward the exact structures of the respective compounds; but in view of the above elemental and spectral studies, we may propose that all the complexes synthesized can be represented as $[\text{MoO}_2\text{L}_2]$ (where L = corresponding ligand; oxime/schiff base). Anticandidal activity has been carried out on $[\text{MoO}_2\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_6\text{H}_4\text{N}\}_2]$ which clearly reveals that the complex is biologically active.

Declarations

Author contribution statement

Deepankar Sharma: Performed the experiments; Wrote the paper.
Purnima Nag: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at <https://doi.org/10.1016/j.heliyon.2019.e01729>.

References

- [1] V.S. Sergienko, V.L. Abramenco, Y.E. Gorbunova, Dioxomolybdenum(VI) Complexes with R1-Substituted Salicylidene Allylimines ($\text{H}^{\text{I}^{\text{a}}}$): Synthesis and Structure. Crystal Structure of $[\text{MoO}_2(\text{L}^{\text{I}^{\text{a}}})_2]$ ($\text{R}^1 = \text{H}$), Russ. J. Inorg. Chem. 63 (2018) 28.
- [2] L. Wang, Y.J. Han, Q.B. Li, Synthesis, crystal structures, and catalytic property of dioxomolybdenum(VI) complexes with hydrazone ligands derived from 3,5-di-tert-butylsalicylaldehyde, Russ. J. Coord. Chem. 43 (2017) 389.
- [3] Z. Asgharpour, F. Farzaneh, A. Abbasi, M. Ghiasi, Synthesis, crystal structure and DFT studies of a new dioxomolybdenum(VI) Schiff base complex as an olefin epoxidation catalyst, Polyhedron 101 (2015) 282.
- [4] R.C. Maurya, J. Chourasia, M.H. Martin, S. Roy, A.K. Sharma, P. Vishwakarma, Dioxomolybdenum(VI) chelates of bioinorganic, catalytic, and medicinal relevance: Studies on some cis-dioxomolybdenum(VI) complexes involving O, N-donor 4-oximino-2-pyrazoline-5-one derivatives, Arab J Chem 8 (2015) 293.
- [5] (a) R.R. Mendel, Molybdenum: biological activity and metabolism, Dalton Trans. 21 (2005) 3404;
(b) S. Rayati, N. Rafiee, A. Wojtczak, Cis-Dioxo-molybdenum(VI) Schiff base complexes: Synthesis, crystal structure and catalytic performance for homogeneous oxidation of olefins, Inorg. Chim. Acta 386 (2012) 27.
- [6] M. Bagherzadeh, M. Amini, H. Parastar, Synthesis, X-ray structure and oxidation catalysis of an oxido-peroxido molybdenum(VI) complex with a tridentate Schiff base ligand, Inorg. Chem. Commun. 20 (2012) 86.
- [7] M. Mirzaee, B. Bahramian, A. Amoli, Schiff base-functionalized boehmite nanoparticle-supported molybdenum and vanadium complexes: efficient catalysts for the epoxidation of alkenes, Appl. Organomet. Chem. 29 (2015) 593.
- [8] I. Abdalghani, L. Biancalana, Dioxomolybdenum(VI) compounds with α -amino acid donor ligands as catalytic precursors for the selective oxyfunctionalization of olefins, Mol Cat 446 (2018) 39.
- [9] W.G. Zhang, J.H. Liang, Synthesis, characterization, and crystal structures of dioxomolybdenum(VI) complexes with O,N,N type tridentate hydrazone ligands as catalyst for oxidation of olefins, Russ. J. Coord. Chem. 43 (2017) 411.
- [10] M.K. Hossain, M. Haukka, R. Sillanpää, Syntheses and catalytic oxotransfer activities of oxo molybdenum(VI) complexes of a new aminoalcohol phenolate ligand, Dalton Trans. 46 (2017) 7051.

- [11] S. Ghosh, S.K. Kurapati, S. Pal, Complexes of cis-dioxomolybdenum(VI) with a chiral tetradentate tripodal-like ligand system: Syntheses, structures and catalytic activities, *Polyhedron* 125 (2017) 26.
- [12] R.H. Holm, Metal-centered oxygen atom transfer reactions, *Chem. Rev.* 87 (1987) 1401.
- [13] S. Eglence, M. Sahin, M. Özyürek, R. Apak, B. Ülküseven, Dioxomolybdenum(VI) complexes of S-methyl-5-bromosalicylidene-N-alkyl substituted thiosemicarbazones: Synthesis, catalase inhibition and antioxidant activities, *Inorg. Chim. Acta* 469 (2018) p. 495.
- [14] P. Nag, R. Bohra, R.C. Mehrotra, Dioxomolybdenum(VI) complexes as catalytic neutral esterification agents, *J Chem Res(S)* 2 (2002) 86.
- [15] A. Majumder, G.M. Rosair, A. Mallick, N. Chattopadhyay, S. Mitra, Synthesis, structures and fluorescence of nickel, zinc and cadmium complexes with the N,N,O-tridentate Schiff base N-2-pyridylmethylidene-2-hydroxy-phenylamine, *Polyhedron* 25 (2006) 1753.
- [16] K.C. Gupta, A.K. Sutar, Catalytic activities of Schiff base transition metal complexes, *Coord. Chem. Rev.* 252 (2008) 1420.
- [17] W.S. Kim, Y.K. Choi, Electrocatalytic effects of thionyl chloride reduction by polymeric Schiff base transition metal(II) complexes, *Appl. Catal. Gen.* 252 (2003) 163.
- [18] T. Hayashi, Catalytic asymmetric reactions via π -allylpalladium complexes coordinated with chiral monophosphine ligands, *J. Organomet. Chem.* 576 (1999) 195.
- [19] G. Helm chen, Enantioselective palladium-catalyzed allylic substitutions with asymmetric chiral ligands, *J. Organomet. Chem.* 576 (1999) 203.
- [20] H. Brunner, I. Demi, W. Dimberger, B. Number, W. Reiber, Enantioselective palladium-catalysed allylation of 1,5-dimethylbarbituric acid, *Eur. J. Inorg. Chem.* 1 (1998) 43.
- [21] B.H. Mehta, B. Nagarkoti, Synthesis and characterization of some transition metal complexes of 2-naphthoin oxime, *Asian J. Chem.* 14 (2002) 103.
- [22] I.H. Hall, C.C. Lee, G. Ibrahim, M.A. Khan, G. Bouet, Cytotoxicity of metallic complexes of furan oximes in murine and human tissue cultured cell lines, *Appl. Organomet. Chem.* 11 (1997) 565.
- [23] P. Nag, Semiempirical calculations of some internally functionalized oximes, *Inroads (Special Issue)* 3 (2014) 385.
- [24] P. Nag, R. Bohra, A semiempirical MO study on the cause of different acidic behaviour of some aromatic chelating ligands towards Mo(VI) entity, *Inroads* 1 (2012) 47.
- [25] P. Nag, R. Bohra, R.C. Mehrotra, Chemistry of oxomolybdenum(V) and (VI) complexes incorporating oxygen, nitrogen and/or sulfur donor atoms. Part I. Synthesis and characterization of $[\text{Mo}_2\text{O}_3\text{L}_4]$ (LH = $\text{HSCH}_2\text{CH}_2\text{CO}_2\text{H}$, $\text{HSCH}_2\text{CO}_2\text{Me}$ or $\text{HSCH}_2\text{CH}_2\text{CO}_2\text{Me}$) and $[\text{MoO}_2\text{L}'_2]$ (L'H = $\text{HOC}_6\text{H}_4\text{NH}_2$, $\text{HOCH}_2\text{C}_6\text{H}_4\text{NH}_2$, $\text{HOC}_6\text{H}_4\text{CHO}$ or $\text{HOC}_{10}\text{H}_8\text{N}$), *Trans. Met. Chem.* 27 (2002) 321.
- [26] P. Nag, R. Bohra, R.C. Mehrotra, Chemistry of oxomolybdenum(V) and (VI) complexes incorporating oxygen, nitrogen and/or sulphur donor atoms. Part II. Synthesis and characterization of some heteroleptic Dioxomolybdenum(VI) complexes of the type, $[\text{MoO}_2\text{Cl}(\text{L})\text{L}']$ (L=Dithiocarbamates or Xanthates and $\text{L}'=\text{OPPh}_3$ and DMSO), *Synth. React. Inorg. Met. Org. Chem.* 32 (2002) 1549.
- [27] H. Gehrke Jr., J. Veal, Acetylacetonate complexes of molybdenum(V) and molybdenum(VI). I. *Inorg. Chim. Acta* 3 (1969) 623.
- [28] N. Sharma, R.K. Sharma, R. Bohra, Syntheses and structural elucidations of some novel heterocyclic compounds containing aluminium(III) atoms at bridge-head positions. L. Reactions of bis(acetylacetonato)aluminium(III)-di- μ -isopropoxo-diisopropoxo aluminium(III) with simple and internally functionalized oximes, *Main Group Met Chem* 24 (2001) 781.
- [29] Y.L. Wong, L.H. Tong, J.R. Dilworth, D.K.P. Ng, H.K. Lee, New dioxo-molybdenum(VI) and -tungsten(VI) complexes with N-capped tripodal N_2O_2 tetradentate ligands: Synthesis, structures and catalytic activities towards olefin epoxidation, *Dalton Trans.* 39 (2010) 4602.
- [30] A. Gupta, R.K. Sharma, R. Bohra, V.K. Jain, J.E. Drake, M.B. Hursthouse, M.E. Light, Triorganoantimony(V) complexes with internally functionalized oximes: synthetic, spectroscopic and structural aspects of $[\text{R}_3\text{Sb}(\text{Br})\text{L}]$, $[\text{R}_3\text{Sb}(\text{OH})\text{L}]$ and $[\text{R}_3\text{SbL}_2]$, crystal and molecular structures of $[\text{Me}_3\text{Sb}\{\text{ON}=\text{C}(\text{Me})\text{C}_4\text{H}_9\text{O}\}_2]$, $[\text{Me}_3\text{Sb}\{\text{ON}=\text{C}(\text{Me})\text{C}_4\text{H}_9\text{S}\}_2]$, $2\text{-OC}_4\text{H}_9\text{C}(\text{Me})=\text{NOH}$ and $2\text{-SC}_4\text{H}_9\text{C}(\text{Me})=\text{NOH}$, *J. Org. Chem.* 645 (2002) 118.
- [31] V. Sharma, R.K. Sharma, R. Bohra, R. Ratnani, V.K. Jain, J.E. Drake, M.B. Hursthouse, M.E. Light, Synthesis, spectroscopic and structural aspects of some tetraorganodistannoxanes with internally functionalized oxime: crystal and molecular structures of $[\{\text{R}_2\text{Sn}(\text{ON}=\text{C}(\text{Me})\text{py})\}_2\text{O}]_2$ (R=Buⁿ and Et) and $2\text{-NC}_5\text{H}_4\text{C}(\text{Me})=\text{NOH}$, *J. Org. Chem.* 651 (2002) 98.
- [32] N. Sharma, R.K. Sharma, R. Bohra, J.E. Drake, M.B. Hursthouse, M.E. Light, Molecular structure of bis(N-phenylsalicylideneiminato)aluminiumdi(μ -isopropoxy)di(isopropoxo)aluminium(III) and its reactions with alkoxyalkanols, *J. Chem. Soc. Dalton Trans.* 1631 (2002).
- [33] B. Khera, A.K. Sharma, N.K. Kaushik, Bis(indenyl)titanium(IV) and zirconium(IV) complexes of monofunctional bidentate salicylidimines, *Polyhedron* 2 (1983) 1177.
- [34] (a) K. Serbest, I. Degirmencioglu, S. Karaböcek, S. Güner, A new binucleating ligand incorporating four oxime groups and its copper(II), manganese(II) and cobalt(III) complexes, *Trans Met Chem* 26 (2001) 232; (b) N.S. Rao, D.D. Mishra, R.C. Maurya, N.N. Rao, Novel 8-coordinate cis-MoO₂(VI) complexes with some 4-aminoantipyrene schiff base derivatives, *Bull. Chem. Soc. Jpn.* 68 (1995) 1589.
- [35] N.A. Nawar, A.M. Shallaby, N.M. Hosny, M.M. Mostafa, Mono- and binuclear Schiff base complexes derived from glycine, 3-acetylpyridine and transition metal ions, *Trans Met Chem* 26 (2001) 180.
- [36] D.F.J. Brown, D. Kothari, Comparison of antibiotic discs from different sources, *J. Clin. Pathol. (Lond.)* 28 (1975) 779.