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*cis*-Dioxomolybdenum(VI) complexes with symmetrical tetradentate Schiff bases and their antibacterial activityDevendra P. Rao<sup>1,\*</sup>, Hardeo S. Yadav<sup>2</sup>, Anita Srivastava<sup>1</sup>

## ABSTRACT

Five new dioxomolybdenum(VI) complexes, [MoO<sub>2</sub>(L)](acac)<sub>2</sub>, [MoO<sub>2</sub>(mac1)](acac)<sub>2</sub>, [MoO<sub>2</sub>(mac2)](acac)<sub>2</sub>, [MoO<sub>2</sub>(mac3)](acac)<sub>2</sub> and [MoO<sub>2</sub>(mac4)](acac)<sub>2</sub>, (where mac1, mac2, mac3 and mac4 are ligands derived from condensation of thenil with 2,3 - diamino - 5 - bromopyridine and their cyclization with β-diketones) have been synthesized. The complexes have been characterized by elemental analyses, molar conductance data, UV - Vis, IR and spectra. The probable coordination number of molybdenum is six. Molybdenum has octahedral geometry in each complex. All tested complexes showed low to moderate activity against *S. aureus*, while the [MoO<sub>2</sub>(mac1)](acac)<sub>2</sub> complex showed moderate activity against *E. aerogenes* and *B. subtilis*. The slight increment in the antibacterial activity of dioxomolybdenum(VI) complexes can be explained on the basis of chelation theory.

**Keywords:** *dioxomolybdenum(VI)*, *thenil*, *β-diketones*, *macrocylic complexes*.

## 1. INTRODUCTION

The physiological importance of molybdenum is due to its ability to provide facile electron-transfer pathways. Mostly Mo(VI) complexes contain the *cis*-MoO<sub>2</sub><sup>2+</sup> cation, and participate in many oxygen atom transfer reactions [1,2]. The *cis*-dioxomolybdenum(VI) complexes with Schiff bases influence coordination chemistry of molybdenum(VI) [3]. The molybdenum complexes have played an important role as molybdoenzymes due to their preparative accessibility [4-6]. The coordination chemistry of molybdenum has received great attention to researchers due to the chemistry of its coordination number, oxidation state, ligating atom, their structure, reactivity and potential applications of molybdenum complexes [7-9]. A number of planner tetradentate ligands are capable to forming six coordinated complexes [10]. In the second row of transition series, only molybdenum is important as micronutrients for plants, animals and microorganisms. There are many reports on the use of *cis* - dioxomolybdenum(VI) complexes-, which act as catalysts in some physiological processes [10,12]. Thenil is a versatile in nature, having two reactive carbonyl groups capable of undergoing Schiff base condensation with di - and polyamines. Thus, thenil has played a significant role in the designing of macrocyclic ligands and such ligands form macrocyclic complexes with molybdenum [13]. With the significance of dioxomolybdenum(VI) cations in oxygen transfer reactions, a new series of dioxomolybdenum(VI) macrocyclic complexes with new denticity ligands derived from condensation of thenil with 2,3 - diamino - 5 - bromopyridine capable of undergoing

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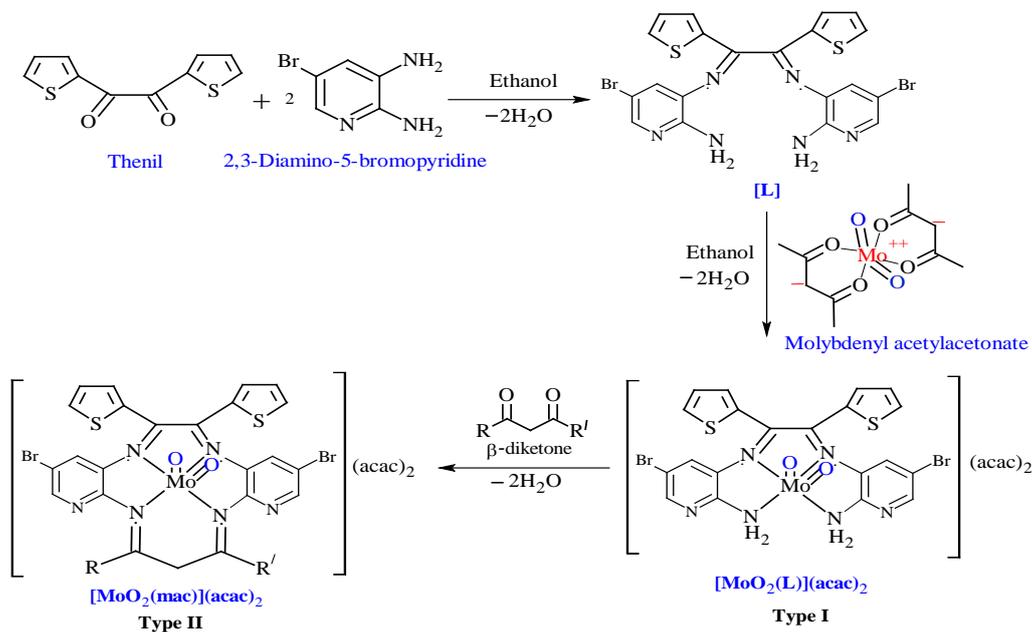
cyclization with  $\beta$ -diketones via the metal template effect have been prepared. Herein, the synthesis of these dioxomolybdenum(VI) complexes and their tentative structures, based on molar conductivity, elemental analyses, UV – VIS and IR are reported.

## 2. EXPERIMENTAL SECTION

**2.1. Reagents and Chemicals.** All the chemicals provided by Aldrich were used without any further purification. All the chemicals and solvents were of analytical reagent grade. Molybdenyl acetylacetonate, diamine, thenil and  $\beta$  - diketones, namely acetylacetonate, benzoylacetonate, thenoyltrifluoroacetone, and dibenzoylmethane were provided by Aldrich.

**2.2. Analytical Methods and Physical Measurements.** The elemental analyses, IR and TG/DTA were performed at SAIF, IIT Bombay, India. Microanalysis of carbon, hydrogen and nitrogen for the complexes were performed by using Flash EA 1112 Series. The nitrogen estimation of the complexes was done by Kjeldahl's method. Molybdenum was estimated gravimetrically after decomposing the complex with concentrated nitric acid using standard method [14]. Sulfur was estimated as barium sulfate [15]. The determination of melting point (uncorrected) using standard technique with sulfuric acid bath was employed. The UV spectra of the complexes were recorded by using methanol as solvent by UV - 1800, Shimadzu instrument in the ranges 1100 - 220 nm at D.A-V. P.G. College, Kanpur, India. The IR spectra of the complexes ( $4000 - 50 \text{ cm}^{-1}$ ) were recorded in CsI pellets on Nicolet Instruments Corporation, USA model no. Magna 550 spectrophotometer.

**2.3. In-situ preparation of dioxomolybdenum(VI) complexes with ligands derived by condensation of thenil with 2,3-diamino-5-bromopyridine and their reactions with  $\beta$ -diketones.** Scheme shows the preparation procedure of  $[\text{MoO}_2(\text{mac})](\text{acac})_2$ .



Where, L = thenil+ 2,3-diamino-5-bromopyridine; mac = macrocyclic ligands carried out from condensation of L with  $\beta$ -diketones in presence of dioxomolybdenum(VI) cation; R =  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$ ,  $\text{C}_4\text{H}_9$ ,  $\text{C}_6\text{H}_5$ ; R' =  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CF}_3$ ,  $\text{C}_6\text{H}_5$ ; respective  $\beta$ -diketone = (i) acetylacetonate, (ii) benzoylacetonate, (iii) thenoyltrifluoroacetone, (iv) dibenzoylmethane.

**Figure 1:** *In-situ* preparation of macrocyclic complexes of *cis*-dioxomolybdenum(VI)

Molybdenyl acetylacetonate (5 mmol, 0.8153g) dissolved in ethanol (25 ml) was added dropwise to a refluxing solution of thenil (5 mmol, 0.4753g) and 2,3 - diamino - 5 - bromopyridine (10 mmol, 0.9401g) in ethanol (30 mL) in RB flask. The resulting reaction mixture was mild refluxed for 4h on heating mantel. The color of the mixture turned into pale yellow. The solid residue was filtered off,

washed with ethanol, and isolated under *in vacuo* over silica gel. TLC was applied for checking the purity of the complex. Yields:75 % (type I). The reaction mixture of type I suspended in ethanol further reacted for 3h with  $\beta$ -diketones such as acetylacetone or benzoylacetone or thenoyltrifluoroacetone or dibenzolymethane (1:1) to give macrocyclic products (type II). The purities of the macrocyclic complexes were checked by TLC (yield 70 %). Elemental analyses (table 1) of the complexes showed 1:1 metal to ligand stoichiometry.

**Table 1:** Physical and analytical data of the complexes

Complex	Empirical Formula	F.W.	Yield (%)	m.p. ( $^{\circ}$ C)	C % Calcd. (found)	H % Calcd. (found)	N % Calcd. (found)	Mo % Calcd. (found)	S % Calcd. (found)
[MoO <sub>2</sub> (L)] (acac) <sub>2</sub>	C <sub>30</sub> H <sub>28</sub> N <sub>6</sub> MoS <sub>2</sub> O <sub>6</sub> Br <sub>2</sub>	888.69	65	125	40.55 (41.95)	3.17 (2.80)	9.45 (9.15)	10.79 (10.20)	7.2 (6.95)
[MoO <sub>2</sub> (mac <sup>1</sup> )] (acac) <sub>2</sub>	C <sub>35</sub> H <sub>32</sub> N <sub>6</sub> MoS <sub>2</sub> O <sub>6</sub> Br <sub>2</sub>	952.55	60	114	44.13 (42.23)	3.38 (3.15)	8.82 (8.23)	10.07 (9.35)	6.73 (6.65)
[MoO <sub>2</sub> (mac <sup>2</sup> )] (acac) <sub>2</sub>	C <sub>40</sub> H <sub>34</sub> N <sub>6</sub> MoS <sub>2</sub> O <sub>6</sub> Br <sub>2</sub>	1014.63	55	120	47.35 (46.50)	3.37 (3.85)	8.28 (8.0)	9.45 (9.12)	6.32 (5.90)
[MoO <sub>2</sub> (mac <sup>3</sup> )] (acac) <sub>2</sub>	C <sub>38</sub> H <sub>29</sub> N <sub>6</sub> MoO <sub>6</sub> S <sub>3</sub> Br <sub>2</sub> F <sub>3</sub>	1074.63	63	125	42.47 (42.85)	2.72 (2.35)	7.82 (7.10)	8.92 (8.55)	8.95 (8.55)
[MoO <sub>2</sub> (mac <sup>4</sup> )] (acac) <sub>2</sub>	C <sub>45</sub> H <sub>36</sub> N <sub>6</sub> MoS <sub>2</sub> O <sub>6</sub> Br <sub>2</sub>	1076.70	52	115	50.19 (49.75)	3.37 (3.0)	7.80 (8.50)	8.91 (8.44)	5.95 (5.42)

**2.4 Antibacterial activity assay.** The antibacterial activity of the synthesized dioxomolybdenum(VI) complexes were evaluated *in vitro* against four bacterial strain viz. *Staphylococcus aureus*, *Enterobacter aerogenes*, *Salmonella typhi* and *Bacillus subtilis* using cup and agar-well diffusion method [16-18]. Doxycycline was used as the standard antibacterial agent and wells having size of 6 mm in diameter were dug in the agar media with the help of metallic borer. The concentration of each strain in each well was adjusted to  $3 \times 10^5$  colony-forming units (CFU) mL<sup>-1</sup> were spread on the surface of the agar. The synthesized complexes were dissolved in 1 % DMSO and concentration of the test sample (was 300  $\mu$ g mL<sup>-1</sup> in DMSO). The test samples were introduced in the own wells. Other wells were supplied with DMSO and antibacterial agent doxycycline (0.05 %). Growth inhibition evaluation was carried out after 28 h incubation at 35  $^{\circ}$ C.

### 3. RESULTS SECTION

The dioxomolybdenum(VI) complexes with Schiff base were synthesized using an *in-situ* method by refluxing the reaction mixture of thenil, diamines and molybdenyl acetylacetonate in 1:2:1 molar ratio in aqueous ethanol, which results in macrocyclic complexes according to scheme.

**3.1. Infrared spectra.** The infrared bands of all the complexes and their tentative assignments are given in table 2. The coordination of nitrogen atoms of azomethine groups to the molybdenum were evidenced by the shift of  $\nu_{C=N}$  to lower frequency [19-22] in all macrocyclic complexes. The band region 1665- 1625 cm<sup>-1</sup> is associated with  $>C=N$  absorption, which normally appears at 1690 cm<sup>-1</sup> in isolated ligands [19-21]. Absorption band at around 475 - 485 cm<sup>-1</sup> may be assigned to  $\nu_{Mo-N}$  vibration [23], which is absent in free ligands. The coordination of two keto groups of thenil through carbonyl oxygen with diamines was evidenced by the appearance of  $>C=N$  band and the absence of the  $>C=O$  band around 1710 cm<sup>-1</sup> [24,25]. The asymmetrical and symmetrical N-H stretching frequencies of the coordinated terminal amino group observed at 3350 and 3215 cm<sup>-1</sup> [24]. The dioxomolybdenum(VI) complexes to form prefer a cis-dioxo group due to the maximum utilization of the d-orbital for bonding. The dioxomolybdenum(VI) complexes showed two Mo=O

stretching modes at 890 - 905 cm<sup>-1</sup> and 940 - 995 cm<sup>-1</sup> due to asymmetric and symmetric stretching of the *cis*-[MoO<sub>2</sub>]<sup>2+</sup> core in C<sub>2v</sub> symmetry [26]. These two infrared spectral bands are referred to V<sub>asym(O=Mo=O)</sub> and V<sub>sym(O=Mo=O)</sub> vibrations respectively [27-30]. Usually, the frequencies of V<sub>asym(O=Mo=O)</sub> vibrations are lower than those of V<sub>sym(O=Mo=O)</sub> [31,32]. The presence of acetylacetonate group present in outer to coordination sphere is confirmed by the bands appearing around 1545 - 1560 cm<sup>-1</sup> and 1455 - 1472 cm<sup>-1</sup> are assigned to V<sub>C=O</sub> and V<sub>C=C</sub> vibrations [33]. Infrared bands of the macrocyclic complexes of type - IIa and IIb show the same pattern of spectral bands. The asymmetrical and symmetrical N-H stretching bands of terminal amino groups disappear due to coordination of these amino groups with carbonyl group of β-diketones in cyclization reactions [33,34].

**Table 2:** Infrared spectral bands (ν / cm<sup>-1</sup>) of molybdenum complexes. All spectra were recorded using CsI in the range 4000 - 50 cm<sup>-1</sup>.

Complex	V <sub>C=N</sub>	V <sub>Mo-N</sub>	V <sub>C=O</sub> of acetylacetonate	V <sub>C=C</sub> of acetylacetonate	V <sub>asym</sub> (O=Mo=O)	V <sub>sym</sub> (O=Mo=O)	V <sub>asym</sub> (N-H)	V <sub>sym</sub> (N-H)
[MoO <sub>2</sub> (L)](acac) <sub>2</sub>	1655s	475m	1560s	1472m	890s	995m	3350s	3215m
[MoO <sub>2</sub> (mac <sup>1</sup> )](acac) <sub>2</sub>	1645s	485s	1555m	1470m	895w	940s		
[MoO <sub>2</sub> (mac <sup>2</sup> )](acac) <sub>2</sub>	1665m	482s	1548s	1455m	900s	975s		
[MoO <sub>2</sub> (mac <sup>3</sup> )](acac) <sub>2</sub>	1625s	482m	1560s	1465m	905s	950m		
[MoO <sub>2</sub> (mac <sup>4</sup> )](acac) <sub>2</sub>	1648m	480m	1545m	1472m	899m	965s		

**3.2. UV - Visible spectra.** The absorptions bands appearing in UV-Vis spectra of the dioxomolybdenum(VI) complexes were carried out in 10<sup>-3</sup> mol L<sup>-1</sup> DMF solution and these spectral bands are interpreted according to reported energy level scheme [35,36]. The UV - Vis spectra are like to other dioxomolybdenum(VI) complexes having nitrogen donor atoms. The UV - Vis spectra of synthesized complexes are characterized by strong absorption bands in the UV region at ≈ 320 nm and at ≈ 376 nm seem to be due to charge transfer and intraligand n → π\* / π → π\* transitions.

In some complexes, a medium intense bands appearing in the region at ≈ 355 nm and at ≈ 415 nm may be reported for L → M charge - transfer transition between the lowest unoccupied molybdenum d-orbital and highest occupied ligand molecular orbital [37,38]. Ballhausen - Gray energy level scheme have applied for these complexes. The electronic spectra indicate a distorted octahedral geometry for all these complexes [39].

**3.3. Magnetic and molar conductance measurements.** The dioxomolybdenum(VI) complexes are diamagnetic in nature, as expected for d<sup>0</sup> configuration. Since there is no electron present in d-orbital, therefore, no d-d transitions are observed for these complexes. The molar conductance (Λ<sub>M</sub>) values for all dioxomolybdenum(VI) complexes in DMF at ca. 10<sup>-3</sup> M suggest 1:1 type electrolytes. The molar conductivity values of these complexes lie between 95 - 115 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Finally, the above details support the tentative structures of dioxomolybdenum(VI) complexes of the type (I) and macrocyclic complexes of the type (II) as shown in the scheme.

**3.5 Antibacterial activity.** The results of the antimicrobial activities of synthesized dioxomolybdenum(VI) complexes are given in table 3. The synthesized dioxomolybdenum(VI) complexes were tested against *Staphylococcus aureus*, *Enterobacter aerogenes*, *Salmonella typhi* and *Bacillus subtilis* using cup and well diffusion method. The reference material is doxycycline. All tested complexes showed low to moderate activity against *S. aureus*, while the  $[\text{MoO}_2(\text{mac}^1)](\text{acac})_2$  complex showed moderate activity against *E. aerogenes* and *B. subtilis*. The slight increment in the antibacterial activity of dioxomolybdenum(VI) complexes can be explained on the basis of chelation theory [40,41].

**Table 3:** Antibacterial activities of macrocyclic complexes of dioxomolybdenum(VI)

Complex	<i>Staphylococcus aureus</i>	<i>Enterobacter aerogenes</i>	<i>Salmonella typhi</i>	<i>Bacillus subtilis</i>	Doxycycline
$[\text{MoO}_2(\text{L})](\text{acac})_2$	14	20	18	19	25
$[\text{MoO}_2(\text{mac}^1)](\text{acac})_2$	18	22	16	22	24
$[\text{MoO}_2(\text{mac}^2)](\text{acac})_2$	15	17	18	20	23
$[\text{MoO}_2(\text{mac}^3)](\text{acac})_2$	16	20	18	20	26
$[\text{MoO}_2(\text{mac}^4)](\text{acac})_2$	18	18	--	--	24

## 4. CONCLUSIONS

This work demonstrate simple synthetic paths to obtain new dioxomolybdenum(VI) with Schiff base. The applied spectroscopic techniques have confirmed the Schiff base condensation of the nil which is a versatile chelating agent having two reactive carbonyl groups with diamines and their cyclizations with  $\beta$ -diketones undergoing formation of macrocyclic products to ensure controlled geometry around  $\text{MoO}_2(\text{VI})$  centre. The geometry of sphere around Mo is distorted octahedral. The kinetic template effect of dioxomolybdenum(VI) cation plays an important role in the preparation of Schiff base using thenil and diamines in ethanol medium. Prepared Schiff bases behave as tetradentate ligands by coordinating to the metal ion through the azomethine nitrogen atoms. The presence of one metal ion per ligand molecule is supported by analytical data. The mononuclear six coordination of all these *cis*- dioxomolybdenum(VI) complexes, and the six coordinate distorted octahedral structure have been proposed for these complexes. X - ray crystallographic data, which might confirm the tentative structures, could not be possible because suitable crystals were not isolated. All *cis*- dioxomolybdenum(VI) complexes were capable of inhibiting bacterial growth to a certain extent.

## 5. ACKNOWLEDGMENT

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