

New Insights into the Chemistry of *cis*-Dioxomolybdenum(VI) Schiff Base Complexes with Macrocyclic Ligands

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Abstract: Preparation of one parent dioxomolybdenum(VI) complex of formula $[\text{MoO}_2(\text{L})](\text{acac})_2$ with a Schiff base, obtained from condensation of thenil with 2,3-diamino-5-chloropyridine and four new complexes having formula $[\text{MoO}_2(\text{ML})](\text{acac})_2$, derived from cyclization of $[\text{MoO}_2(\text{L})](\text{acac})_2$ with β -diketones are reported in this research paper. The prepared five dioxomolybdenum(VI) complexes have been described by elemental analyses, molar conductance, UV-Vis, IR, NMR and thermal studies. The feasibility of coordination number of molybdenum metal is six. All five complexes of dioxomolybdenum(VI) have octahedral geometry. The octahedral coordination circle of molybdenum in synthesized dioxomolybdenum complexes is completed by two oxo oxygen atoms and four nitrogen atoms from derived ligand. The shape of synthesized dioxomolybdenum(VI) complexes have distorted octahedral. All the synthesized complexes showed moderate activity against *S. aureus* and *S. typhi*, the improvement in the antibacterial activity being explained on the basis of chelation hypothesis.

Keywords: Dioxomolybdenum(VI), Thenil, β -Diketones, Macrocyclic complexes, Schiff base

Introduction

A macrocyclic complex is characterized as a cyclic complex with at least nine individuals (counting all hetero atoms) and with at least three donor atoms. The field of coordination chemistry of macrocyclic complexes has experienced dynamite development amid the previous quarter century¹⁻⁴. Schiff bases assume a significant job in chemistry as they effectively structure stable edifices with most transition metal ion. Schiff base complexes edifices may serious as models for biologically significant species. Severe research efforts have been governed to study the transition metal complexes of high denticity ligands with a

view to obtain the metal complexes of unusual configuration and coordination number⁵. Molybdenum is adaptable in nature due to its various oxidation states ranging from -2 to +6 just as coordination numbers which fluctuate from four to eight⁶. The capacity to arrangement of molybdenum buildings with nitrogen, oxygen and sulfur containing ligands prompted improvement of molybdenum Schiff base edifices which are productive impetuses in homogeneous and furthermore in heterogeneous reactions⁷⁻¹². The dioxomolybdenum(VI) complexes with denticity ligands have extraordinary significance in theoretical and practical area especially for biological processes. Mo(VI) is available as a simple molybdate $[\text{MoO}_4]^{2-}$ ion in aqueous medium be dependent on the concentration and pH of the solution. The $[\text{MoO}_4]^{2-}$ ion can perform as oxygen atom transfer agents¹³. Their oxygen atom transfer properties play a vital role within functioning mechanism of molybdenum oxotransferase^{14,15}. It is significant in the totally oxidized states of a number of redox enzymes, in which their active sites consists of a *cis*-dioxomolybdenum moiety¹⁶⁻¹⁸.

In the second series of transition metals, solely molybdenum is into account as biometal which is important for human, animal and plants pathogenic microorganisms^{19,20}. The coordination chemistry of Mo(VI) is an effectively interest of present research because of their catalytic properties and biological activities²¹⁻²⁴. Physiological functions of oxomolybdoenzymes are established by molybdenum²⁵⁻²⁷. Thenil could be a versatile chelating agent. Thenil has two reactive carbonyl groups which are capable of undergoing Schiff base condensation with several di- and polyamines. Therefore, thenil has played a vital role within the synthesis of macrocyclic ligands.

With on top of context, some dioxomolybdenum(VI) complexes with high denticity ligands can synthesize from condensation of thenil with diamine. The synthesized complex has capability of undergoing cyclization with β -diketones via the metal template effect will be prepare, characterize and their provisional structures are supported by molar conductivity, elemental analysis, electronic, infra red and nuclear magnetic resonance spectroscopy. A large number of metallic complexes of obviously occurring porphyrins, corrins and phthalocyanines were investigated, due to their relation to important naturally occurring macrocycles together with heam. Cytochromes or chlorophyll, because of their ability as dyestuffs pigments. The extent of interest in such complexes may be imagined.

Keeping in view of the significance of dioxomolybdenum(VI) cations in oxygen transfer reactions, a new sequence of dioxomolybdenum(VI) macrocyclic complexes have been synthesized. These dioxomolybdenum(VI) macrocyclic complexes with new chelate ligands got from condensation of thenil with 2,3-diamino-5-chloropyridine capable to undergoing cyclization with β -diketones through the metallic template effect have been synthesized. Herein, the synthesis and their ascertain structures, based on molar conductivity, elemental analyses, electronic IR, NMR and TGA/DTA are reported.

Experimental

All chemicals used for the synthesis of Schiff base (ligands) and complexes had been of reagent grade and employed as purchased from commercial assets. Molybdenyl acetylacetonate, 2,3-diamino-5-chloropyridine, thenil and β -diketones (acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane) had been purchased from Aldrich and employed without similarly purification.

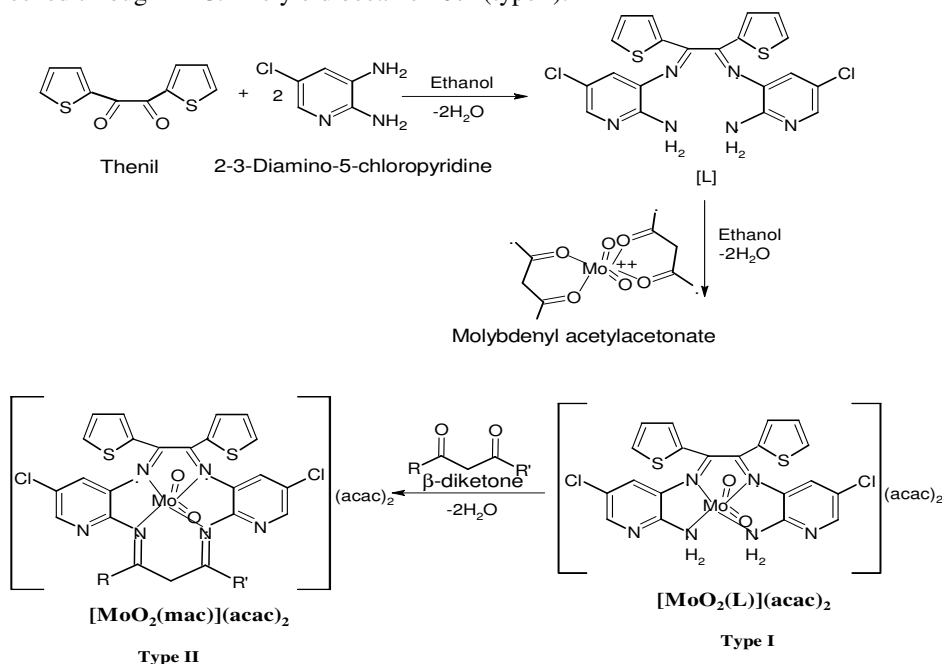
Analytical methods and physical measurements

Elemental analyses of carbon, hydrogen and nitrogen for the complexes had been done at valuable Central Research Facility, NERIST, Nirjuli, Itanagar, Arunachal Pradesh, India by

using CHN analyser. Kjeldahl's method becomes used to estimate nitrogen for the prepared complexes. After decomposition of the complex, molybdenum was estimated gravimetrically via standard method²⁸. Estimation of sulfur became achieved as barium sulfate²⁹. General method changed into used for determining uncorrected melting factors with the help of sulfuric acid bath. The electronic absorption spectral measurements (the UV-Visible spectra) of the complexes had been recorded on Labinda-UV 3000⁺ UV/VIS spectrophotometer within the ranges 1100-220 nm by using ethanol as solvent at UPTTI Kanpur, U.P., India. The IR of the synthesized dioxomolybdenum complexes (4000-400 cm⁻¹) were recorded in KBr on Perkin-Elmer spectrum model 10.03.06 spectrophotometers at IIT Kanpur. NMR spectra have been acquired on JMM ECS-400 (JEOL) spectrometer with 400 MHz for proton (¹H NMR). Thermograph of the prepared parent complex [MoO₂(L)](acac)₂ was done under nitrogen atmosphere in the temperature range 50-600 °C at the heating rate 10 °C min⁻¹ using TG/DTA-Perkin Elmer, USA thermal analyzers.

In-situ synthesis of dioxomolybdenum(VI) complexes with ligands derived by condensation of thenil with 2,3-diamino-5-chloropyridine with β-diketones

Given Scheme 1 shows the procedure manner of [MoO₂(ML)](acac)₂. An ethanolic solution of molybdenyl acetylacetonate (2.5 mmol, 0.81537 g) was added drop wise to a refluxing solution of thenil (2.5 mmol, 0.5570 g) and 2,3-diamino-5-chloropyridine (5 mmol, 0.71785 g) in ethanol (50 mL) in RB flask. The resulting reaction mixture turned into mild refluxed for 2 h. The coloration of the mixture turned into brown. The obtained solid product was filtered off, washed with ethanol and isolated under *in vacuo* over silica gel. Purity of the complex checked through TLC. The yield became 46% (type I).



Where, L = Thenil +2,3-diamino-5-chloropyridine; mac = macrocyclic ligands carried out from condensation of L with β-diketones in presence of dioxmolybdenum(VI) cation

Scheme 1. Synthesis of [MoO₂(L)](acac)₂ and of [MoO₂(mac)](acac)₂

The solution of type I suspended in ethyl alcohol uniformly reacted for 2 h with β -diketones viz., acetylacetone, benzoylacetone, thenoyltrifluoroacetone or dibenzoylmethane (1:1) to obtain macrocyclic solid products (type II). The purity of the macrocyclic complexes becomes checked by means of TLC. Elemental analyses (Table 1 & 2) of the complexes exhibited 1:1 metal to ligand stoichiometry.

Table 1. Physical and analytical data of the ligand and complexes

Complex	Empirical Formula	F.W.	Yield, %	m.p., °C	C% Calcd. (found)	H% Calcd. (found)	N% Calcd. (found)	Mo% Calcd. (found)	S% Calcd. (found)
L	C ₂₀ H ₁₄ N ₆ S ₂ Cl ₂	273.40	60	110	50.74 (49.01)	2.98 (2.90)	17.75 (17.90)	--	13.54 (13.85)
[MoO ₂ (L)] (acac) ₂	C ₃₀ H ₂₈ N ₆ MoS ₂ O ₆ Cl ₂	799.56	46	145	45.06 (45.00)	3.52 (3.50)	10.51 (10.41)	11.99 (11.60)	8.02 (8.00)
[MoO ₂ (ML ¹)](acac) ₂	C ₃₅ H ₃₂ N ₆ MoS ₂ O ₆ Cl ₂	863.65	60	115	48.67 (48.50)	3.73 (3.66)	9.73 (9.55)	11.10 (11.00)	7.42 (7.40)
[MoO ₂ (ML ²)](acac) ₂	C ₄₀ H ₃₄ N ₆ MoS ₂ O ₆ Cl ₂	925.72	55	128	51.89 (51.66)	3.70 (3.63)	9.07 (9.00)	10.36 (10.00)	6.92 (6.50)
[MoO ₂ (ML ³)](acac) ₂	C ₃₈ H ₂₉ N ₆ MoO ₆ S ₃ Cl ₂ F ₃	985.72	63	125	46.30 (46.66)	2.96 (2.50)	8.52 (8.40)	9.73 (9.55)	9.75 (9.53)
[MoO ₂ (ML ⁴)](acac) ₂	C ₄₅ H ₃₆ N ₆ MoS ₂ O ₆ Cl ₂	987.79	52	110	54.71 (54.65)	3.67 (3.60)	8.50 (8.40)	9.71 (9.66)	6.49 (6.48)

Table 2. Structural details

For macrocyclic	R	R'	β -diketone	Structure
ML ¹	CH ₃	CH ₃	acetylacetone	
ML ²	C ₆ H ₅	CH ₃	benzoylacetone	
ML ³	C ₄ H ₃ S	CF ₃	thenoyltrifluoroacetone	
ML ⁴	C ₆ H ₅	C ₆ H ₅	dibenzoylmethane	

Where, L= ligand obtained by condensation of thenil with 2,3-diamino-5-chloropyridine (1:2);

ML¹ = macrocyclic ligand obtained by condensation of ligand (L) with β -diketone-acetylacetone;

ML² = macrocyclic ligand obtained by condensation of ligand (L) with β -diketone-benzoylacetone;

ML³ = macrocyclic ligand obtained by condensation of ligand (L) with β -diketone-thenoyltrifluoroacetone;

ML⁴ = macrocyclic ligand obtained by condensation of ligand (L) with β -diketone-dibenzoylmethane.

Antibacterial activity assay

The antibacterial interest of the synthesized dioxomolybdenum(VI) complexes have been evaluated *in vitro* against four bacterial strains i.e. *Staphylococcus aureus*, *Bacillus subtilis*, *Enterobacter aerogene* and *Salmonella typhi* using cup and agar-well diffusion method²⁰⁻²². Doxycycline was used as the same standard antibacterial agent. Wells having size of 6 mm in diameter had been dug in the agar media with the help of metallic borer. The density of every bacterial suspension in each well changed into adjusted to 3×10^5 colony-forming units (CFU) mL⁻¹. The standardized suspensions had been spread on the surface of the agar. The synthesized complexes were dissolved in 1% DMSO and concentration of the check sample was 300 μ g mL⁻¹. The test samples were introduced inside the corresponding wells. Other wells

had been packed with DMSO and antibacterial agent doxycycline (0.05%). Growth inhibition was examined after 28 h incubation at 35 °C.

Results and Discussion

Infrared spectra

The complexes of dioxomolybdenum(VI) with Schiff base were prepared by the use of an *in-situ* method by refluxing the reaction mixture of thenil, 2,3-diamino-5-chloropyridine and molybdenyl acetylacetonate in 1:2:1 molar ratio in aqueous ethanol which result in macrocyclic complexes according to scheme. Significant IR spectral bands of the ligand and the dioxomolybdenum(VI) and their tentative assignments are given in Table 3. The coordination of nitrogen atoms of azomethine groups to the molybdenum in all macrocyclic complexes have been evidenced by using the shift of $\nu_{C=N}$ to decrease frequencies³⁰⁻³³. The spectral bands region 1651-1655 cm^{-1} is associated with $>C=N$ absorption, which normally appears at 1675 cm^{-1} in isolated ligands³⁰⁻³². New absorption band at around 456-475 cm^{-1} can be assigned to $\nu_{\text{Mo-N}}$ vibration³⁴, that is absent in free ligands. The coordination of two keto groups of thenil via carbonyl oxygen with diamines was supported³⁵⁻³⁶ via the appearance of $>C=N$ band and the absence of the $>C=O$ band around 1710 cm^{-1} . Infra red spectra of the ligand and its complexes of dioxomolybdenum(VI) are complicated due to the presence of various ring vibrations and C-H vibrations. A broad band targeted at 3350 cm^{-1} for $\nu_{\text{asym}}(\text{N-H})$ and 3190 cm^{-1} for $\nu_{\text{sym}}(\text{N-H})$. In the complex $[\text{MoO}_2(\text{L})](\text{acac})_2$ bands stay unchanged however absent in complex $[\text{MoO}_2(\text{ML})](\text{acac})_2$ due to the this implies non-participation of the NH group in the bonding³⁷. The dioxomolybdenum(VI) complexes to create preferentially a *cis*-dioxo group due to the most utilization of the d-orbital for bonding. The dioxomolybdenum(VI) complexes showed two Mo=O stretching bands at 903-910 cm^{-1} and 930-946 cm^{-1} because of two stretching vibrations: asymmetric and symmetric stretching of the *cis*- $[\text{MoO}_2]^{2+}$ moiety in C_{2v} symmetry³⁸. Those two infrared spectral bands are assigned to $\nu_{\text{asym}}(\text{O=Mo=O})$ and $\nu_{\text{sym}}(\text{O=Mo=O})$ vibrations respectively³⁸⁻⁴⁴. $\nu_{\text{asym}}(\text{O=Mo=O})$ vibrations are lesser than those of $\nu_{\text{sym}}(\text{O=Mo=O})$ ^{45,46}. The presence of acetylacetonate group present in outer coordination sphere is affirmed by the bands appearing around 1540 – 1565 cm^{-1} and 1465-1485 cm^{-1} are appointed to $\nu_{C=O}$ and $\nu_{C=C}$ vibrations⁴⁷. Infrared spectral bands of the macrocyclic complexes display the same pattern of spectral bands. The asymmetrical and symmetrical N-H stretching modes of terminal amino groups disappear as a result of coordination of those amino groups with carbonyl group of β -diketones in cyclization processes^{47,48}.

Table 3 Infrared spectral bands (v/cm^{-1}) of molybdenum complexes. All spectra had been recorded using KBr within the range 4000-400 cm^{-1}

Complex	$\nu_{C=N}$	$\nu_{\text{Mo-N}}$	$\nu_{C=O}$ of acetylacetonate	$\nu_{C=C}$ of acetylacetonate	ν_{asym} (O=Mo=O)	ν_{sym} (O=Mo=O)	ν_{asym} (N-H)	ν_{sym} (N-H)
L	1675s	-	-	-	-	-	3350br	3190br
$[\text{MoO}_2(\text{L})](\text{acac})_2$	1651s	473m	1540s	1485m	910s	936s	3338br	3167br
$[\text{MoO}_2(\text{ML}^1)](\text{acac})_2$	1655s	469s	1565m	1472m	905s	930s		
$[\text{MoO}_2(\text{ML}^2)](\text{acac})_2$	1650s	465m	1559s	1465m	900s	940s		
$[\text{MoO}_2(\text{ML}^3)](\text{acac})_2$	1646s	475m	1545s	1470m	905m	938m		
$[\text{MoO}_2(\text{ML}^4)](\text{acac})_2$	1648m	456m	1560m	1480m	903m	946s		

¹H NMR spectra

¹H NMR spectra of ligand and all synthesized molybdenum complexes had been recorded in DMSO- D_6 (Table 4). ¹H NMR spectrum of synthesized free ligand suggests signal because of NH_2 at δ (10.22) which is also present in $[\text{MoO}_2(\text{L})](\text{acac})_2$ at δ (10.09) but absent in different

four macrocyclic complexes $[\text{MoO}_2(\text{ML})](\text{acac})_2$ which suggest the cyclization by β -diketones. The ten protons present as multiplets within the range δ (6.60-7.26) for the ligand and molybdenum complexes. The protons of aromatic ring showed by peaks around δ (7.26). ^1H NMR spectrum around δ (3.5-4.6) assigned to the CH_2N fragment. The appearance of these chemical shifts may be because of the formation of two types of azomethine that is involved in the formation of the macrocyclic complex. The sharp singlet signal located at δ (2.36) may be due to the water present in $\text{DMSO}-\text{D}_6$ sample used.

Table 4. ^1H NMR spectral data of prepared ligand and dioxomolybdenum complexes (in δ)

Complex	HC-Ar	N-H	C-H ₃	C-H
L	7.12 10H	10.22 4H	-	-
$[\text{MoO}_2(\text{L})](\text{acac})_2$	6.58 10H	10.09 4H	2.56 12H	5.65 2H
$[\text{MoO}_2(\text{ML}^1)](\text{acac})_2$	7.26 10H	-	2.62 12H	5.57 2H
$[\text{MoO}_2(\text{ML}^2)](\text{acac})_2$	7.15 10H	-	2.55 12H	5.68 2H
$[\text{MoO}_2(\text{ML}^3)](\text{acac})_2$	6.60 10H	-	2.62 12H	5.58 2H
$[\text{MoO}_2(\text{ML}^4)](\text{acac})_2$	6.87 10H	-	2.54 12H	5.70 2H

UV-Visible spectra

The Ultraviolet-Vis spectra of tetradentate tetraaza ligand and the dioxomolybdenum(VI) complexes were recorded in ethanol and these spectral bands are measured according to reported energy level scheme^{49,50}. The spectra of the dioxomolybdenum(VI) complexes with tetradentate ligand are similar as one another thereby suggesting a standard structure for all. Since Mo(VI) ion has no d -electron, the absorption bands of pure d - d origins do not seem to be expected to appear. The bands for all complexes may perhaps to be appointed as charge transfer transition from nitrogen orbital to a molybdenum metal d -orbital $[\text{N}(\pi) \rightarrow d(\text{Mo})]$. The ultraviolet-vis spectra are similar to other complexes of dioxomolybdenum(VI) having nitrogen donor atoms. The ultraviolet-vis spectra of these complexes are characterized by strong absorption bands within the UV region at ≈ 290 nm and at ≈ 333 nm seem to be due to intraligand transition and $n \rightarrow \pi^*$ / $\pi \rightarrow \pi^*$ transitions. A moderately intense band appeared within the region ≈ 385 nm-390 nm is attributed to $\text{N}(\pi) \rightarrow d(\text{Mo})$. The band because of the transition $^2B_2 \rightarrow ^2A_1$ ($d_{xy} \rightarrow d_{x^2-y^2}$) is maybe covert by the above bands and should be appointed for $\text{L} \rightarrow \text{M}$ charge - transfer transition between the lowest unoccupied molybdenum d -orbital and highest occupied ligand molecular orbital^{51,52}. Ballhausen - Gray energy level scheme have provided energy level scheme for these complexes. The electronic spectra designate a distorted octahedral geometry for all the complexes⁵³.

Magnetic and molar conductance measurements

The dioxomolybdenum(VI) complexes are diamagnetic, as needless to say for d^0 configuration. Since there is no electron present in d -orbital, no d - d transitions are determined for these complexes. The molar conductivity (ΛM) values for all dioxomolybdenum(VI) complexes in DMF at ca. 10^{-3} M recommend 1:1 sort electrolytes. The molar conductance values of those complexes lie between $95 - 110 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. In last, the on top molar conductance values support the tentative structures of dioxomolybdenum(VI) complexes of the type I and macrocyclic complexes of the type II as shown within the schemes.

Thermogravimetric analyses

The thermogravimetric examination of $[\text{MoO}_2(\text{L})](\text{acac})_2$ complex was directed in the temperature range 50 - 600 $^\circ\text{C}$ with a 10 $^\circ\text{C min}^{-1}$ temperature interim. No transparent decomposition observed beneath 145 $^\circ\text{C}$ (Figure 1). The thermograph of the $[\text{MoO}_2(\text{L})](\text{acac})_2$

complex is appeared in Figure 1. The $[\text{MoO}_2(\text{L})](\text{acac})_2$ complex undergoes decomposition in two stages: (a) first stage of decomposition (145-250 °C) is due to the loss of ligand (mass loss obs. 45%, calcd. 48%) (b) in the second stage, the second progressive weight reduction of at raised temperature (300-450 °C) giving a mass loss about 42% against calculated mass loss of 48%. At last, a residue obtained generally compares to MoO_3 (obs. Residual mass = 14.50%, calcd. = 15.75%) have been left after 450 °C. Two vertexes were gotten in DTA curve. First vertex is endothermic decay because of melting of the complex (145 °C). The second vertex is due to the exothermic effect. Close to this exothermic vertex in DTA curve an exothermic hump was also observed at 435 °C which may because of exothermic decay of the leftover mass in the second step.

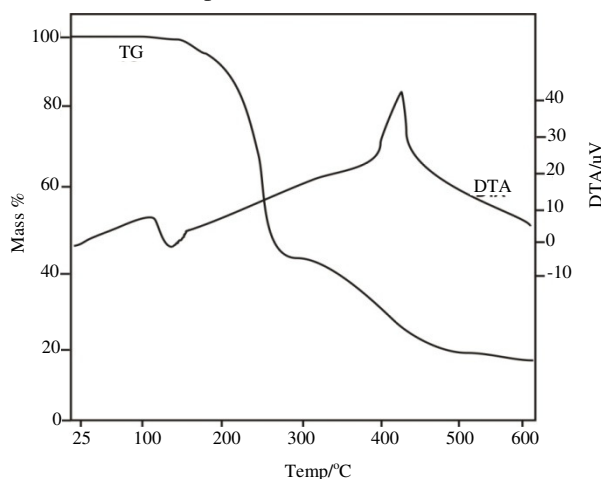


Figure 1. TG and DTA thermographs of $[\text{MoO}_2(\text{L})](\text{acac})_2$

Antibacterial activity

The results of the antimicrobial exercises of the synthesized dioxomolybdenum(VI) complexes are given in Table 5. The prepared dioxomolybdenum(VI) complexes were tried against *Staphylococcus aureus*, *Bacillus subtilis*, *Enterobacter aerogenes* and- *Salmonella typhi*. The upgrade in the antibacterial activity of dioxomolybdenum(VI) complexes can be clarified on the basis of chelation hypothesis^{47,48}. The reference material is doxycycline medicine. Practically all the complexes indicated low to moderate activity against *S. aureus* and *S. typhi*.

Table 5. 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
$[\text{MoO}_2(\text{L})](\text{acac})_2$	15	15	18	21	25
$[\text{MoO}_2(\text{ML}^1)](\text{acac})_2$	17	20	16	-	23
$[\text{MoO}_2(\text{ML}^2)](\text{acac})_2$	16	19	-	17	25
$[\text{MoO}_2(\text{ML}^3)](\text{acac})_2$	14	20	19	22	23
$[\text{MoO}_2(\text{ML}^4)](\text{acac})_2$	14	17	17	20	26

Conclusion

The present investigation exhibit basic synthetic paths to get new dioxomolybdenum(VI) with Schiff base. The utilized spectroscopic procedures have affirmed the Schiff base condensation

of thenil which is a versatile chelating agent having two responsive carbonyl groups with diamines and their cyclizations with β -diketones undergoing formation of macrocyclic products to guarantee controlled geometry around MoO₂(VI) centre. The shape around Mo is distorted octahedral. The kinetic template effect of dioxomolybdenum(VI) cation assumes a significant role in the preparation of Schiff base using thenil and diamines in ethanol medium. Prepared Schiff bases act as tetradentate ligands by coordinating to the metal ion through the azomethine nitrogen atoms. The existence of one metal ion per ligand molecule is affirmed by analytical data. The mononuclear six coordination of all the synthesized cis-dioxomolybdenum(VI) complexes, and the six coordinate distorted octahedral structure have been proposed for these complexes. X-ray crystallographic data, which may affirm the tentative structures, couldn't be possible, as appropriate crystals were not isolated.

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