



# SYNTHESIS AND STUDIES OF SOME *cis*-MoO<sub>2</sub>(VI) COMPLEXES WITH NITROGEN DONOR MACROCYCLIC LIGANDS

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A complex of formula [MoO<sub>2</sub>(L)](acac)<sub>2</sub> is obtained on treating molybdenyl acetylacetonate with di-2-thienylethanedione with 2,3-diaminotoluene. This complex was reacted with four 1,3-diketones to yield four new complexes, [MoO<sub>2</sub>(ML)](acac)<sub>2</sub>. The complexes were characterized by elemental analysis, spectral studies and molar conductance. In these compounds, molybdenum exhibited a coordination number of six. Distorted octahedral environment surrounds molybdenum in these complexes. The ligand geometry was completed by two oxo O-atoms and four N-atoms. The synthesized complexes show moderate activity versus *S. aureus* and *S. typhi*.

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## INTRODUCTION

A macrocyclic complex is marked as a cyclic complex with at least 9 individuals (counting all hetero atoms) and with at least 3 donor atoms. The field of coordination chemistry of macrocyclic complexes has experienced tremendous improvement during the last quarter of a century.<sup>1-4</sup> A number of reports about synthetic work, physicochemical studies<sup>5</sup> and biochemical applications of metal complexes<sup>6-10</sup> has appeared. Some Schiff bases had been utilized as fungicidal, which has been correlated with their chemical structure.<sup>11-13</sup> One of the examples is the transamination reactions, catalyzed by metals ions template through the formation of intermediate Schiff bases containing vitamin B<sub>6</sub>.<sup>14</sup> Schiff base complexes were used as medicines and show e antiviral,<sup>15,16</sup> anti-inflammatory<sup>17</sup> and antitumor activities.<sup>18</sup>

In bioinorganic chemistry, Schiff base complexes are used as artificial models for the metal containing sites in metallo-proteins and enzymes.<sup>19</sup> Various Schiff base ligands show anticancer activity and this activity of their metal complexes is greater in comparison to that of the free ligands.<sup>20,21</sup> Additionally they exhibit catalytic activity in different chemical reactions,<sup>22</sup> surfactant activities<sup>23</sup> and as memory storage devices in electronics.<sup>24-26</sup>

Schiff bases have been used as stable complexes with transition metal in many applications in chemical studies. Intense efforts has been directed to study the transition metal complexes of excessive denticity ligands with a view to obtain the metal complexes of unusual geometry and coordination number.<sup>27</sup> Molybdenum is adaptable in nature because of its diverse oxidation states ranging from -2 to +6 just as coordination numbers which fluctuate from four to eight.<sup>28</sup> The capability of molybdenum to form complexes

with nitrogen, oxygen and sulfur containing ligands resulted in development of molybdenum Schiff base edifices that are efficient in homogeneous and heterogeneous reactions.<sup>29-34</sup> The dioxomolybdenum(VI) complexes with high denticity ligands have importance in theoretical and practical chemistry mainly for biological processes. Mo(VI) complex is extracted as molybdate [MoO<sub>4</sub>]<sup>2-</sup> ion in aqueous medium be based on the concentration and pH of the solution. The [MoO<sub>4</sub>]<sup>2-</sup> ion can act as oxygen atom transfer agents.<sup>35</sup> Their O-atom transfer properties play a critical role in functioning of molybdenum oxotransferase.<sup>36,37</sup> It is present in the oxidized states of a number of redox enzymes, in which their active sites consist of a *cis*-dioxomolybdenum moiety.<sup>38-40</sup>

In the second series of transition metals, only molybdenum is crucial for human, animal and vegetation pathogenic microorganisms.<sup>41,42</sup> The Mo(VI) coordination chemistry is interesting because of their catalytic activities and biological properties.<sup>43-46</sup> Physiological functions of oxomolybdoenzymes are set up via molybdenum.<sup>47-49</sup> Di-2-thienylethanedione is a versatile chelating agent. This ligand has two reactive carbonyl groups also which are capable of undergoing Schiff base condensation with several di- and polyamines. Therefore, di-2-thienylethanedione is a useful synthon for the synthesis of macrocyclic ligands.

Some dioxomolybdenum(VI) complexes with high denticity ligands can be synthesized by condensation of di-2-thienylethanedione with a diamine. The synthesized complex has functionality of undergoing cyclization with 1,3-diketones via the metal template impact. It can be prepared, characterized and their provisional structures are supported by way of molar conductivity, elemental analysis, electronic, infrared and nuclear magnetic resonance spectroscopy.

In view of the importance 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 multidentated ligands derived from

condensation of di-2-thienylethanedione with 3-methylbenzene-1,2-diamine and 1,3-diketones have been synthesized.

## EXPERIMENTAL

All chemicals, used in the preparation of Schiff base (ligands) and complexes, were of reagent grade and were used as obtained from business resources. Starting chemicals like [MoO<sub>2</sub>(acac)<sub>2</sub>], the diamine, di-2-furanylethanedione and 1,3-diketones (2,4-pentanedione, 1-phenyl-1,3-butanedione, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, and 1,3-diphenyl-1,3-propanedione were obtained from Aldrich. They were utilized without further purifications.

The elemental examinations of carbon, hydrogen and nitrogen is done for the ligand and MoO<sub>2</sub>(VI) complexes by using CHN analyser at CRF, NERIST, Nirjuli, Itanagar, Arunachal Pradesh, India. To estimate nitrogen Kjeldahl's method is used. After decomposition of the complex, molybdenum was assessed gravimetrically by standard technique.<sup>50</sup> Sulfur was estimated as barium sulfate.<sup>51</sup> Uncorrected melting points were determined with the assistance of sulfuric acid bath. The UV-Visible spectra of the complexes have been recorded on Labinda-UV 3000<sup>+</sup> UV/VIS spectrophotometer in the 1100 - 220 nm range in ethyl alcohol as solvent at UPTTI Kanpur, U.P., India. IR spectra of the ligand and complexes of MoO<sub>2</sub>(VI) were recorded at IIT Kanpur on Perkin-Elmer spectrophotometer (10.03.06) in the range of 4000-400 cm<sup>-1</sup> with KBr pellet. <sup>1</sup>HNMR spectra were obtained on JMM ECS-400 (JEOL) spectrometer at 400 MHz with DMSO-*d*<sub>6</sub> and were expressed in δ (ppm) relative to TMS. TGA/DTA of the parent complex [MoO<sub>2</sub>(L)](acac)<sub>2</sub> were performed on Perkin Elmer (USA) thermal analyzers, under N<sub>2</sub> atmosphere in the temperature range of 50-600 °C at the heating rate of 10 °C min<sup>-1</sup>.

### Synthesis of MoO<sub>2</sub>(VI) complexes

A solution of di-2-thienylethanedione (0.5570 g, 2.5 mmol) and 2,3-diaminotoluene (0.61164 g, 5 mmol) in 50 mL ethanol was refluxed. This solution was then added to an ethanolic solution of molybdenyl acetylacetonate (0.81537 g, 2.5 mmol) drop by drop. The reaction mixture was refluxed for 3 h. The solution turned brown. The solid complex formed was filtered and washed with ethanol. The yield was 46 %. This product was placed in ethyl alcohol and treated for 3 h with one of the 1,3-diketones viz. 2,4-pentanedione, 1-phenyl-1,3-butanedione, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione or 1,3-diphenyl-1,3-propanedione, in molar ratio 1:1, to obtain the macrocyclic dirty yellow solid product. TLC was used to ascertain the purity of the products. The 1:1 stoichiometry of Mo and the ligand was confirmed by elemental analyses (Table 1).

### Antibacterial activity for the testing of 4-bacterial strains

The antibacterial action of the synthesized complexes of MoO<sub>2</sub>(VI) was examined by in vitro test. This test was performed against four bacterial strains viz., *Staphylococcus aureus*, *Salmonella typhi*, *Enterobacter aerogene* and

*Bacillus subtilis*. Cup and agar-well diffusion technique was used for the antibacterial test of synthesized MoO<sub>2</sub>(VI) complexes.<sup>42-44</sup> Doxycycline was taken as the standard material. For this purpose we made trench having dimensions of 6 mm in diameter inside the agar media with the help of a metallic borer. The concentration of bacterial solution in every channel was 3 × 10<sup>5</sup> colony forming units (CFU) mL<sup>-1</sup>. The MoO<sub>2</sub>(VI) complexes were dissolved in D to make an 1 % solution. The concentration of the test complex was 300 µg mL<sup>-1</sup>. The test samples have been added within the corresponding wells. The rest of the wells were packed with DMSO and antibacterial standard doxycycline (0.05 %). Growth inhibitions were tested after 30 h incubation at 35 °C.

## RESULTS AND DISCUSSION

The reaction of a mixture of di-2-thienylethanedione, 2,3-diaminotoluene and molybdenyl acetylacetonate in 1:2:1 molar ratio in aqueous ethyl alcohol yielded the macrocyclic complexes of MoO<sub>2</sub>(VI) with Schiff base. IR frequencies of the ligand and the MoO<sub>2</sub>(VI) complexes and their assignments are recorded in Table 2.

Lowering of ν<sub>C=N</sub> frequencies is the major evidence for the proof of the coordination of nitrogen atoms of azomethine groups to the molybdenum in all macrocyclic complexes.<sup>52-55</sup> The spectral bands placed at 1604-1645 cm<sup>-1</sup> is related to >C=N absorption, which is usually seen at 1665 cm<sup>-1</sup> in isolated ligands.<sup>52-54</sup> New absorption band at 508-591 cm<sup>-1</sup> may be allocated to ν<sub>Mo-N</sub> vibration,<sup>56</sup> that is absent in free ligands. The linkage of both keto groups of di-2-thienylethanedione via >C=O oxygen with diamines is proved by the presence of >C=N band and the absence of >C=O band around 1710 cm<sup>-1</sup>.<sup>57,58</sup>

IR spectra of the ligand and its complexes of MoO<sub>2</sub>(VI) are complex as a result of the nearness of various ring vibrations and C-H vibrations. A wide band located at 3433 cm<sup>-1</sup> is due to ν<sub>asym(N-H)</sub> and that at 3065 cm<sup>-1</sup> is due to ν<sub>sym(N-H)</sub>. Within the complex [MoO<sub>2</sub>(L)](acac)<sub>2</sub> these bands remain unchanged but are absent in complex [MoO<sub>2</sub>(ML)](acac)<sub>2</sub>, this implies non-participation of the NH group in the bonding.<sup>59</sup> The dioxomolybdenum(VI) complexes form preferentially a cis-dioxo group because of the preferential usage of the d-orbital for bonding. The dioxomolybdenum(VI) complexes revealed two Mo=O stretching bands at 893-910 cm<sup>-1</sup> and 964-981 cm<sup>-1</sup> due to asymmetric and symmetric stretching vibrations of the cis-[MoO<sub>2</sub>]<sup>2+</sup> moiety with C<sub>2v</sub> symmetry.<sup>60</sup> Those two IR spectral bands are allocated to ν<sub>asym(O=Mo=O)</sub> and ν<sub>sym(O=Mo=O)</sub> vibrations, respectively.<sup>60-66</sup> ν<sub>asym(O=Mo=O)</sub> vibrations are lower than ones of ν<sub>sym(O=Mo=O)</sub>.<sup>67,68</sup>

The presence of acetylacetonate group in the MoO<sub>2</sub>(VI) complexes is inferred from the bands round 1552 - 1569 cm<sup>-1</sup> and 1467-1480 cm<sup>-1</sup>, attributable to ν<sub>C=O</sub> and ν<sub>C-C</sub> vibrations.<sup>69</sup> Infrared bands of the MoO<sub>2</sub>(VI) macrocyclic complexes exhibit similar spectral bands. Vibrations of terminal amino groups (the asymmetrical and symmetrical N-H stretching) disappear because of the reaction of the amino groups with carbonyl group of 1,3-diketones in the cyclization process.<sup>69,70</sup>

**Table 1.** Elemental and physical data of the ligand and MoO<sub>2</sub>(VI) complexes.

Complex	Empirical formula	F.W.	Yield, %	M.p., °C	Elementary analysis: calculated (found)				
					C%	H%	N%	Mo%	S%
L	C <sub>24</sub> H <sub>22</sub> N <sub>4</sub> S <sub>2</sub>	430.59	45	115	66.94 (66.93)	5.14 (5.15)	13.01 (13.00)	--	14.89 (14.87)
[MoO <sub>2</sub> (L)] (acac) <sub>2</sub>	C <sub>34</sub> H <sub>36</sub> N <sub>4</sub> MoS <sub>2</sub> O <sub>6</sub>	756.75	50	125	53.96 (53.98)	4.79 (4.78)	7.40 (7.41)	12.67 (12.64)	8.47 (8.46)
[MoO <sub>2</sub> (ML <sup>1</sup> )] (acac) <sub>2</sub>	C <sub>39</sub> H <sub>40</sub> N <sub>4</sub> MoS <sub>2</sub> O <sub>6</sub>	820.84	52	110	57.06 (57.05)	4.91 (4.91)	6.82 (6.81)	11.68 (11.69)	7.81 (7.80)
[MoO <sub>2</sub> (ML <sup>2</sup> )] (acac) <sub>2</sub>	C <sub>44</sub> H <sub>42</sub> N <sub>4</sub> MoS <sub>2</sub> O <sub>6</sub>	882.91	53	120	59.85 (59.86)	4.79 (4.78)	6.34 (6.34)	10.86 (10.85)	7.26 (7.24)
[MoO <sub>2</sub> (ML <sup>3</sup> )] (acac) <sub>2</sub>	C <sub>42</sub> H <sub>37</sub> N <sub>4</sub> MoO <sub>6</sub> S <sub>3</sub> F <sub>3</sub>	942.91	58	118	53.50 (53.48)	3.95 (3.96)	5.94 (5.95)	10.17 (10.16)	10.20 (10.22)
[MoO <sub>2</sub> (ML <sup>4</sup> )] (acac) <sub>2</sub>	C <sub>49</sub> H <sub>44</sub> N <sub>4</sub> MoS <sub>2</sub> O <sub>6</sub>	944.98	55	122	62.28 (62.29)	4.69 (4.67)	5.92 (5.90)	10.15 (10.14)	6.78 (6.75)

L = ligand derived via condensation of di-2-thienylethanedione with 2,3-diaminotoluene (1:2)

ML<sup>1</sup> = macrocyclic ligand derived via condensation of ligand (L) with 1,3-diketone: 2,4-pentanedione;

ML<sup>2</sup> = macrocyclic ligand derived via condensation of ligand (L) with 1,3-diketone: 1-phenyl-1,3-butanedione

ML<sup>3</sup> = macrocyclic ligand derived via condensation of ligand (L) with 1,3-diketone: 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione

ML<sup>4</sup> = macrocyclic ligand obtained by the reaction of ligand (L) with dibenzoylmethane

**Table 2.** IR spectral bands ( $\nu$  cm<sup>-1</sup>) of the ligand and dioxomolybdenum complexes.

Complex	$\nu_{C=N}$	$\nu_{Mo-N}$	$\nu_{C=O}$ of acac	$\nu_{C=C}$ of acac	$\nu_{asym}$ (O=Mo=O)	$\nu_{sym}$ (O=Mo=O)	$\nu_{asym}$ (N-H)	$\nu_{sym}$ (N-H)
L	1665s	---	---	---	---	---	3323br	3130br
[MoO <sub>2</sub> (L)](acac) <sub>2</sub>	1604s	508m	1569s	1467m	893s	981s	3433br	3065br
[MoO <sub>2</sub> (ML <sup>1</sup> )](acac) <sub>2</sub>	1645m	580m	1555m	1470m	902s	975s		
[MoO <sub>2</sub> (ML <sup>2</sup> )](acac) <sub>2</sub>	1640s	591s	1564s	1480s	905m	964s		
[MoO <sub>2</sub> (ML <sup>3</sup> )](acac) <sub>2</sub>	1644m	585s	1552m	1475m	910s	965m		
[MoO <sub>2</sub> (ML <sup>4</sup> )](acac) <sub>2</sub>	1640s	524m	1560s	1472m	902m	968s		

<sup>1</sup>H NMR spectrum of the free ligand exhibits signal of NH<sub>2</sub> protons at 5.80 which is present in [MoO<sub>2</sub>(L)](acac)<sub>2</sub> at 5.10 but missing in the four macrocyclic complexes [MoO<sub>2</sub>(ML)](acac)<sub>2</sub> which indicates a cyclization by 1,3-diketones. The ten protons present as multiplets inside the range of 7.06-7.84 for the ligand and molybdenum complexes.

The protons of aromatic ring appeared by peaks at about 7.26. <sup>1</sup>H NMR signal about 3.29-3.82 are due to the CH<sub>2</sub>N fragment. These chemical shifts might be a direct result of arrangement of two types of azomethine that is engaged in the formation of the macrocyclic complex. The sharp singlet signal at 2.47 might be because of the water present in DMSO-*d*<sub>6</sub> sample used. The <sup>1</sup>H NMR data of the ligand and complexes are summarized in Table 3.

The UV-Vis spectra of the tetradentate tetraaza ligand and the dioxomolybdenum(VI) complexes had been recorded in ethanol and these spectral bands are consistent with suggested strength energy level scheme.<sup>71,72</sup> The spectra of the dioxomolybdenum(VI) complexes with tetradentate ligand are comparable to each other thereby suggesting a common structure for all. In view of the fact that Mo(VI) ion has no d-electron, the absorption bands of pure d-d origins are not expected to appear. The bands for all complexes may perhaps to be attributed to charge transfer transition from nitrogen orbital to a molybdenum metal d-

orbital [N( $\pi$ ) $\rightarrow$ d(Mo)]. The UV-VIS spectra are similar to those of other complexes of dioxomolybdenum(VI) having nitrogen donor atoms. The UV-VIS spectra of these complexes are distinguished by strong absorption bands within the UV region at  $\approx$  292 nm and at  $\approx$  311 nm, which appear to be due to intraligand transition and  $n\rightarrow\pi^*/\pi\rightarrow\pi^*$  transitions. A fairly intense band appearing in the vicinity of  $\approx$ 380-395 nm is attributed to N( $\pi$ ) $\rightarrow$ d(Mo).

**Table 3.** <sup>1</sup>HNMR spectral data of the ligand and dioxomolybdenum complexes (in  $\delta$  ppm).

Complex	HC-Ar	N-H	C-H <sub>3</sub>	C-H
L	7.12 10H	5.80 4H	--	--
[MoO <sub>2</sub> (L)](acac) <sub>2</sub>	7.74 10H	5.10 4H	2.46 12H	5.71 2H
[MoO <sub>2</sub> (ML <sup>1</sup> )](acac) <sub>2</sub>	7.42 10H	--	2.69 12H	5.58 2H
[MoO <sub>2</sub> (ML <sup>2</sup> )](acac) <sub>2</sub>	7.06 10H	--	2.45 12H	5.70 2H
[MoO <sub>2</sub> (ML <sup>3</sup> )](acac) <sub>2</sub>	7.84 10H	--	2.70 12H	5.52 2H
[MoO <sub>2</sub> (ML <sup>4</sup> )](acac) <sub>2</sub>	7.15 10H	--	2.49 12H	5.58 2H

**Table 4.** Antibacterial activities of the MoO<sub>2</sub>(VI) complexes.

Complex	<i>Staphylococcus aureus</i>	<i>Enterobacter aerogenes</i>	<i>Salmonella typhi</i>	<i>Bacillus subtilis</i>	Doxycycline
[MoO <sub>2</sub> (L)](acac) <sub>2</sub>	17	17	19	20	26
[MoO <sub>2</sub> (ML <sup>1</sup> )](acac) <sub>2</sub>	14	20	17	22	23
[MoO <sub>2</sub> (ML <sup>2</sup> )](acac) <sub>2</sub>	14	17	16	20	24
[MoO <sub>2</sub> (ML <sup>3</sup> )](acac) <sub>2</sub>	15	19	19	--	25
[MoO <sub>2</sub> (ML <sup>4</sup> )](acac) <sub>2</sub>	17	19	--	22	25

The band due to the transition  ${}^2B_2 \rightarrow {}^2A_1$  ( $d_{xy} \rightarrow d_{x^2-y^2}$ ) is perhaps covered by the above bands and ought to be attributed to L→M charge - transfer transition among the lowest unoccupied molybdenum d-orbital and highest occupied ligand molecular orbital.<sup>73,74</sup> Ballhausen-Gray energy level diagram is applicable to the energy level scheme for these complexes. The electronic spectra represent a distorted octahedral configuration for all the complexes.<sup>75</sup>

#### Molar conductance and magnetic and measurements

These complexes are diamagnetic, as obvious for d<sup>0</sup> configuration. Since no electron is present in d-orbital, no d-d transitions are observed for these complexes. The molar conductivity ( $\Lambda_M$ ) values for all MoO<sub>2</sub>(VI) complexes in DMF at ca. 10<sup>-3</sup> molar solution indicate to be 1:1 electrolytes. The conductance ( $\Lambda_M$ ) estimations of prepared MoO<sub>2</sub>(VI) complexes ranges between the 100 - 115 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. The molar conductance supports the tentative structures of dioxomolybdenum(VI) complexes of the type (I) and macrocyclic complexes of the type (II) as shown in the schemes.

#### Thermogravimetric analyses

The thermogravimetric investigation of [MoO<sub>2</sub>(L)](acac)<sub>2</sub> complex has been studied in the temperature range of 50-600 °C at the rate of 10 °C min<sup>-1</sup>. No apparent decomposition occurred beneath 170 °C. The [MoO<sub>2</sub>(L)](acac)<sub>2</sub> complex undergoes decay in one step. After that it ignites and decomposes giving a sharp weight loss.

#### Antibacterial activity

The MoO<sub>2</sub>(VI) complexes had been tested for antibacterial test towards *Staphylococcus aureus*, *Bacillus subtilis*, *Enterobacter aerogenes* and *Salmonella typhi* (Table 5). The higher in the antibacterial activity of the dioxomolybdenum(VI) complexes can be explained on the basis of chelation hypothesis.<sup>47,48</sup> The reference material was doxycycline. Nearly all the complexes showed low to moderate activity towards *S. aureus* and *S. typhi*.

#### CONCLUSIONS

In absence of crystal structure study, which is due to of the amorphous nature of the synthesized molecules, we cannot suggest exact structures of these compounds. However, in view of the elemental and spectral studies, we

suggest that all the synthesized complexes may be represented as [MoO<sub>2</sub>(L)](acac)<sub>2</sub> and [MoO<sub>2</sub>(ML<sup>1</sup>)](acac)<sub>2</sub>. The study of antibacterial activity indicated that the complexes are biologically active.

The present study established new synthetic paths to get novel dioxomolybdenum(VI) complexes with Schiff base. The applied spectroscopic methods confirmed the condensation of di-2-thienylethanedione, which is a flexible chelating agent having two responsive carbonyl groups, with diamines and their cyclizations with 1,3-diketones leading to the formation of macrocyclic products of assured geometry around MoO<sub>2</sub>(VI) centre. The arrangement around Mo is distorted octahedral geometry. The kinetic template impact of dioxomolybdenum(VI) cation assumes a considerable function in the condensation of Schiff base using diamines and di-2-thienylethanedione in ethanol. Bonding of the metal ion with the azomethine N-atoms proved that Schiff bases act as tetradentate ligands. The analytical data confirmed the existence of one metal ion per ligand molecule. The distorted octahedral shape have been suggested for all the prepared cis- MoO<sub>2</sub>(VI) complexes.

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