Synthesis, characterization and antibacterial evaluation of five dioxomolybdenum(VI) complexes coordinated by Schiff derivatives

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ABSTRACT

The synthesis of new five dioxomolybdenum(VI) complexes with tetradentate Schiff base ligand, derived from condensation of thenil with 2,3-diaminophenazine and their cyclization with β-diketones described in this paper. The compounds were characterized by elemental analyses, molar conductivity, UV-Vis and IR spectral studies. The octahedral coordination of molybdenum in synthesized complexes is completed by two oxo oxygens, four nitrogens from derived ligand. Synthesized dioxomolybdenum(VI) complexes have distorted octahedral geometry.

Keywords: cis-dioxomolybdenum(VI), thenil, Schiff base, tetradentate ligand.

1. INTRODUCTION

Molybdenum complexes have been widely used with large number of stable oxidation states, among which +4, +5 and +6 have received considerable attention and coordination numbers varying from four to eight [1]. Molybdenum complexes with Schiff base have great importance due to their potential for biological and physiological activity [2,3]. A large variety of dioxomolybdenum(VI) complexes with Schiff bases have been reported for synthesis, characterization and reactivity studies [4,5]. Molybdenum is essential for the nitrogenase enzyme and many chemical reactions have been catalyzed by molybdenum complexes [6-8]. Dioxomolybdenum(VI) complexes have been stated as oxidation catalysts for epoxidation of olefins [9-12]. Some of the molybdenum complexes possess oxygen atom transfer properties like oxidizing thiols, polyketones and tertiary phosphines [13,14]. Thenil have versatile nature due to their two reactive carbonyl groups which undergo Schiff base condensation with di- and polyamines. Thus, thenil has played important role in the synthesis of macrocyclic ligands and such ligands form macrocyclic complexes with molybdenum [15]. In recent years, their antimicrobial potency has gained special attention against both human and plant pathogenic microorganisms [16,17]. The aim of the present study was to synthesize a new series of dioxomolybdenum(VI) macrocyclic complexes with macrocyclic ligands derived from condensation of thenil with 2,3-diaminophenazine capable of undergoing cyclization with β-diketones via the metal template effect have been prepared.

The author reports herein the synthesis and tentative structures of these complexes based on molar conductance, elemental analyses, TGA/DTA, electronic and- IR spectra.
mL) in RB flask (figure 1). The color of the reaction mixture turned into dirty yellow after mild refluxed for 2h. Precipitate was filtered off, washed with cold ethanol and isolated under in vacuum desicator over silica gel. Purity of the prepared complex was checked by TLC (yield: 60 %, type I). Ethanolic mixture of type I complex further reacted for 2h with β-diketones such as acetylacetone or benzoylacetone or thenoyltrifluoroacetone or dibenzoylmethane (1:1) to get macrocyclic complex (type II). The purity of the synthesized macrocyclic product was checked by TLC (yield 45 %).

Elemental analyses (table 1) of the complexes proved 1:1 molar ratio of metal to ligand stoichiometry.

![Scheme: Preparation of [MoO₃(mac)](acac)₂ and of [MoO₂(L)](acac)₂](image)

Where, L = thenil + 2,3-diaminophenazine; mac = macrocyclic ligands carried out from condensation of L with β-diketones in presence of dioxomolybdenum(VI) cation; R = CH₃, C₆H₅, C₆H₅S, C₆H₅OCH₂CH₃, CF₃, C₆H₅; respective β-diketone = (i) acetylacetone, (ii) benzoylacetone, (iii) thenoyltrifluoroacetone, (iv) dibenzoylmethane.

**Figure 1.** Scheme for in-situ preparation of macrocyclic complexes of cis-dioxomolybdenum(VI).

### Table 1. Elemental analysis of the dioxomolybdenum(VI) complexes.

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="acac">MoO₃(L)</a>₂</td>
<td>C₄₄H₃₇N₃MoO₆S₂</td>
<td>932.89</td>
<td>50</td>
<td>135</td>
<td>56.65</td>
<td>3.88</td>
<td>12.01</td>
<td>10.28</td>
<td>6.87</td>
</tr>
<tr>
<td><a href="acac">MoO₃(mac¹)</a>₂</td>
<td>C₄₀H₄₀N₃MoO₆S₂</td>
<td>996.97</td>
<td>65</td>
<td>140</td>
<td>59.03</td>
<td>4.04</td>
<td>11.23</td>
<td>9.62</td>
<td>6.43</td>
</tr>
<tr>
<td><a href="acac">MoO₃(mac²)</a>₂</td>
<td>C₃₃H₃₉N₃MoO₆S₂</td>
<td>1059.05</td>
<td>65</td>
<td>130</td>
<td>61.24</td>
<td>3.99</td>
<td>10.58</td>
<td>9.05</td>
<td>6.05</td>
</tr>
<tr>
<td><a href="acac">MoO₃(mac³)</a>₂</td>
<td>C₃₂H₂₇N₃MoO₆S₂F₃</td>
<td>1119.05</td>
<td>50</td>
<td>132</td>
<td>61.00</td>
<td>3.75</td>
<td>9.15</td>
<td>8.65</td>
<td>5.90</td>
</tr>
<tr>
<td><a href="acac">MoO₃(mac⁴)</a>₂</td>
<td>C₃₂H₂₄N₃MoO₆S₂</td>
<td>1061.07</td>
<td>55</td>
<td>125</td>
<td>61.12</td>
<td>4.17</td>
<td>10.56</td>
<td>9.04</td>
<td>6.04</td>
</tr>
</tbody>
</table>

### 2.4. Antibacterial activity assay

The complexes were evaluated in vitro for their antibacterial activities against four bacterial strains i.e. *Staphylococcus aureus, Enterobacter aerogenes, Salmonella typhi* and *Bacillus subtilis* using cup and agar-well diffusion method [20,22]. Here, doxycycline was taken as the standard antibacterial agent. In this method, nutrient agar was used for bacteria. Wells having size of 6 mm in diameter were dug in the agar media. The density of microbial inoculum in each well was adjusted to $3 \times 10^4$ colony-forming units (CFU) mL⁻¹ were spread over the surface of the
The synthesized dioxomolybdenum(VI) complexes dissolved in 1 % DMSO were added to the test sample. The concentration of test sample was 300 µg mL⁻¹ in DMSO. Prepared test samples were distributed in separate wells. Left wells were filled with DMSO and the antibacterial agent doxycycline. Finally, growth inhibition was evaluated as millimeters (mm) diameter after 24 h incubation at 35 °C.

3. RESULTS SECTION

The five 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 resulted in macrocyclic dioxomolybdenum(VI) complexes according to Figure 1.

3.1. Infrared spectra

The IR spectra of all the complexes and their tentative assignments are summarized in table 2. The bonding of nitrogen atoms of azomethine groups to the molybdenum in all macrocyclic complexes were proved by the shift of νC=N to lower frequencies [22-26]. The IR bands around 1655 - 1644 cm⁻¹ is associated with νsym(O=Mo=O) vibrations respectively [31-34]. Generally, the vibrational frequencies of νsym(O=Mo=O) vibrations are higher than those of νasym(N-H) vibrations [35,36]. The existence of acetylacetonate group present at outer coordination sphere is proved by the bands appearing around 1525 - 1550 cm⁻¹ and 1450 - 1465 cm⁻¹ are assigned to νc=O and νc=c vibrations [37]. IR bands of the macrocyclic complexes of type II show the same pattern of spectral bands. The νsym(N-H) and νasym(N-H) N-H stretching modes of terminal amino groups disappear due to bonding of these amino groups with carbonyl group of β-diketones in cyclization processes [37-38].

<table>
<thead>
<tr>
<th>Complex</th>
<th>νC=N</th>
<th>νMo=O</th>
<th>νC=O of acetylacetonate</th>
<th>νsym</th>
<th>νasym</th>
<th>ΛΩ(M)</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="acac">MoO₂(L)</a>₂</td>
<td>1655s</td>
<td>475s</td>
<td>1525s</td>
<td>1458s</td>
<td>905s</td>
<td>935m</td>
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<tr>
<td><a href="acac">MoO₂(mac¹)</a>₂</td>
<td>1644m</td>
<td>478s</td>
<td>1548s</td>
<td>1465m</td>
<td>904s</td>
<td>945s</td>
</tr>
<tr>
<td><a href="acac">MoO₂(mac²)</a>₂</td>
<td>1650s</td>
<td>480m</td>
<td>1545m</td>
<td>1450s</td>
<td>900s</td>
<td>952s</td>
</tr>
<tr>
<td><a href="acac">MoO₂(mac³)</a>₂</td>
<td>1652s</td>
<td>482s</td>
<td>1550s</td>
<td>1465m</td>
<td>903m</td>
<td>946m</td>
</tr>
<tr>
<td><a href="acac">MoO₂(mac⁴)</a>₂</td>
<td>1655m</td>
<td>482m</td>
<td>1545m</td>
<td>1462m</td>
<td>905m</td>
<td>955s</td>
</tr>
</tbody>
</table>

3.2. UV - Visible spectra

The electronic spectra of the dioxomolybdenum(VI) complexes were observed in 10⁻³ mol L⁻¹ DMF solution and these bands are interpreted according to reported energy level scheme [37,38]. The electronic spectra are similar to other cis-dioxomolybdenum(VI) complexes having nitrogen as donor atoms. The electronic spectra of these dioxomolybdenum(VI) complexes are characterized by strong absorption bands in the UV region at ≈ 285 nm and at ≈ 390 nm seem to be due to ligand-to-metal charge – transfer (LMCT) and intraligand n → π* / π → π* transitions. The bathochromic shift about 20 nm confirmed that linkage of the azomethine nitrogen to the molybdenum. Since Mo(VI) has a lone d-electron, in some complexes, a medium intense bands shown in the region at 365 nm and at ≈ 405 nm may be assigned for LMCT transition between the lowest unoccupied d-orbital of molybdenum and highest occupied molecular orbital ligands [41,42]. Ballhausen-Gray scheme energy level scheme applied for these complexes and the electronic spectra show a distorted octahedral structure for all the complexes [43].

3.3. Magnetic and molar conductance measurements

Experimentally, the Mo(VI) complexes are diamagnetic, as expected for d⁰ configuration and no d-d transitions are observed. The molar conductivity (ΛΩ) for all synthesized complexes in DMF at ca. 10⁻³ M suggests 1:1 type electrolytes. The molar conductance values of dioxomolybdenum(VI) complexes lie between 95 - 110 Ω⁻¹ cm² mol⁻¹. The above data support the tentative structures of the complexes of the type (I) and macrocyclic complexes of the type (II) as shown in the Figure 1.

3.4. Thermogravimetric analyses

The thermogram of [MoO₂(L)](acac)₂ complex was captured in the temperature range 50 - 600 °C at the heating rate of 10 °C min⁻¹. This complex was stable up to 135 °C. For [MoO₂(L)](acac)₂ complex two quite fast decomposition steps were observed (a) first step of decomposition is due to partial...
isolation of ligand (135 - 230 °C; mass loss obs. 55 %, calcd. 65 %), (b) the second step is the left residue of first step decomposed gradually at elevated temperature (290 - 460 °C) giving a mass loss about 25 % (calcd. 20 %). A residue nearly corresponds to MoO3 (obs. residual mass = 10 %, calcd. = 16.8 %) have been left after 435 °C. Two peaks were appeared in DTA curve. First peak is endothermic which is due to decomposition of the complex (120 °C) and second peak is exothermic. Neighbour to exothermic peak an exothermic hump was observed at 430 °C which may due to exothermic decomposition of the residual mass in the second step.

3.5. Antibacterial activity

The data of the antibacterial activities of synthesized complexes are given in table 3. Almost all the synthesized dioxomolybdenum(VI) complexes showed low to moderate activity against the tested strains. The enhancement in the antibacterial activity of dioxomolybdenum(VI) complexes, as compared with their ligand against S. aureus (complexes [MoO2(mac2)](acac)2 and [MoO2(mac4)](acac)2) and E. aerogenes (all complexes) can be explained on the basis of chelation theory [44-45].

<table>
<thead>
<tr>
<th>Complex</th>
<th>Staphylococcus aureus</th>
<th>Enterobacter aerogenes</th>
<th>Salmonella typhi</th>
<th>Bacillus subtilis</th>
<th>Doxycycline</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="acac">MoO2(L)</a>2</td>
<td>18</td>
<td>22</td>
<td>16</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td><a href="acac">MoO2(mac2)</a>2</td>
<td>18</td>
<td>20</td>
<td>16</td>
<td>--</td>
<td>24</td>
</tr>
<tr>
<td><a href="acac">MoO2(mac2)</a>2</td>
<td>17</td>
<td>22</td>
<td>16</td>
<td>19</td>
<td>24</td>
</tr>
<tr>
<td><a href="acac">MoO2(mac2)</a>2</td>
<td>18</td>
<td>18</td>
<td>15</td>
<td>21</td>
<td>24</td>
</tr>
</tbody>
</table>

*In vitro*, cup and well diffusion method, conc. 300 μg/mL in DMSO; Zone of inhibition (mm): dash indicate inactivity; 15-18 = moderate activity; 19-22 = good activity; 23-26 = strong activity; Doxycycline as reference antibiotic drug.

4. CONCLUSIONS

Five new dioxomolybdenum(VI) complexes with Schiff base have been prepared and structurally characterized - using elemental analysis, electronic spectra, IR spectra and molar conductance. Used spectroscopic techniques have confirmed the formation of macrocyclic products to ensure controlled geometry around MoO2(VI) centre. The geometry around Mo is distorted octahedral in synthesized dioxomolybdenum(VI) complexes. Prepared Schiff bases behave as tetradentate ligands by bonding to the metal ion through the nitrogen atoms of azomethine. Analytical data proved the presence of one metal ion in ratio to one ligand molecule. X - ray crystallographic data of the synthesized dioxomolybdenum(VI) complexes, which might confirm the tentative structures, could not be possible because suitable crystals were not isolated. Low to moderate antibacterial activity exhibited by all complexes, but improved as compared with the Schiff base ligand.

5. REFERENCES

Synthesis, characterization and antibacterial evaluation of five dioxomolybdenum(VI) complexes coordinated by Schiff derivatives

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6. ACKNOWLEDGEMENTS

This work was supported by the UGC, New Delhi, India [project F. No. 39 - 740/2010 (SR)]. The author greatly acknowledges the Secretary, Board of Management, D.A-V. P.G. College, Kanpur, U.P., India for providing laboratory facilities. Author is also grateful to SAIF, IIT, Bombay, India and STIC, Kochi, India for providing analytical facilities.