Synthesis and characterization of dinuclear molybdenum(VI) peroxo complexes with aroyl hydrazones

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The reactions of ammonium molybdate with hydrogen peroxide and ethanolic solutions of aroylhydrazones, viz. benzoic acid [1-(Furan-2-yl) methylene] hydrazide (BFMH), benzoic acid [(thiophen-2-yl)methylene] hydrazide (BTMH), benzoic acid [1-(thiophen-2-yl) ethylidene] hydrazide (BTEH), benzoic acid (phenyl methylene) hydrazide (BPMH) and benzoic acid [1-(anisol-3-yl) methylene] hydrazide (BAMH), result in the precipitation of the dinuclear complexes, Mo$_2$O$_4$(O$_2$)$_2$L-L(H$_2$O)$_4$ (where L-L = BFMH, BTMH, BTEH, BPMH and BAMH). The complexes have been characterized by elemental analysis, and studies on conductivity and magnetic susceptibility, IR and electronic spectra, $^1$H NMR spectra, and TGA/DTA. The dinuclear complexes have been found to preserve the individuality of the molybdenum oxo peroxo core. The complexes exhibit significant in vitro antifungal effects against the Keratolytic fungus as compared to ligands.

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Peroxo complexes of transition metals have received special importance due to their role in a variety of industrial, pharmaceutical and biological processes. They are widely used for catalytic oxidation in organic and biochemical reactions, e.g. in the oxidation of thioanisole, methyl benzene, tertiary amines, alkenes, alcohols, bromide and also in olefin epoxidation. They also act as isomerization catalysts for some allylic alcohols and have been applied in the bleaching processes.

Peroxo complexes of molybdenum (VI) have been known for a long time. A variety of peroxo molybdates coordinated with nitrogen and oxygen donors have been characterized structurally and studied in solution and solid state. Polynuclear molybdenum(VI) peroxo complexes containing amino acids have been synthesized and spectroscopically characterized. These complexes have the composition, Mo$_2$O$_4$(O$_2$)$_2$L$_2$(H$_2$O)$_4$ (L = methionine, serine) and Mo$_3$O$_7$(O$_2$)$_2$L(H$_2$O)$_6$ (L = lysine, histidine) with organic ligand bonded to molybdenum oxo peroxo core in a bidentate manner. Metal complexes of aroylhydrazones have broad application in biological processes such as in the treatment of tumors, tuberculosis, leprosy and mental disorders. These are also known to act as herbicides, insecticides and acaricides. The biological activity has been attributed to the complex forming abilities of the ligands with metal ions present in the cells and involvement of molybdenum in molybdenum oxo-transferase enzymes. In view of the importance of aroylhydrazone complexes and in continuation to our work on peroxo complexes of molybdenum and tungsten, we report herein the dinuclear molybdenum(VI) oxoperoxo complexes of aroylhydrazones, viz. benzoic acid [1-(Furan-2-yl) methylene] hydrazide (BFMH), benzoic acid [(thiophen-2-yl)methylene] hydrazide (BTMH), benzoic acid [1-(thiophen-2-yl) ethylidene] hydrazide (BTEH), benzoic acid (phenyl methylene) hydrazide (BPMH) and benzoic acid [1-(anisol-3-yl) methylene] hydrazide (BAMH). These dinuclear complexes have the general composition, Mo$_2$O$_4$(O$_2$)$_2$L-L(H$_2$O)$_4$ (where L-L = BFMH, BTMH, BTEH, BPMH, BAMH). The structures of ligands are:

BFMH (X = O & R = H), BTMH (X = S & R = H), BTEH (X = S & R = CH$_3$)

BPMH (R$^1$ = H), BAMH (R$^1$ = OCH$_3$)
Experimental
Reagent grade furfuraldehyde (Himedia), thiophen-2-carboxaldehyde (Himedia), 2-acetylthiophene (Himedia), benzaldehyde (Ranbaxy), anisaldehyde (Himedia) and benzhydrazide (Fluka) were used as received. The solvent used for the synthesis of ligands and their molybdenum(VI) peroxo complexes were distilled before use. Ammonium molybdate and other chemicals used were of reagent grade used without further purification. The ligands were prepared by the reported method\textsuperscript{31}. C, H, N and S were analysed microanalytically using CHNS analyzer Leco make model-932. Molybdenum analysis was done by gravimetric method\textsuperscript{32}. Molar conductivity in DMF (10\textsuperscript{3} M) at room temperatures was measured using an Elico conductivity Bridge, type CM82T and a conductivity cell with cell constant of 0.74. Magnetic susceptibility of the complexes was recorded at room temperature using Gouy’s balance and using Hg[Co (NCS)\textsubscript{4}] as a standard. IR spectra of complexes over the region 4000-400 cm\(^{-1}\) were recorded on a Perkin Elmer FTIR spectrophotometer using KBr disc. The electronic spectra of the complexes were recorded using a double beam UV spectrophotometer type SL-164. Thermogravimetric analysis (DTA-DTG-TG) of complexes was recorded on Perkin-Elmer (Pyris model-932). Molybdenum analysis was done by gravimetric method. Molar conductivity in DMF (10\textsuperscript{3} M) at room temperatures was measured using an Elico conductivity Bridge, type CM82T and a conductivity cell with cell constant of 0.74. Magnetic susceptibility of the complexes was recorded at room temperature using Gouy’s balance and using Hg[Co (NCS)\textsubscript{4}] as a standard. IR spectra of complexes over the region 4000-400 cm\(^{-1}\) were recorded on a Perkin Elmer FTIR spectrophotometer using KBr disc. The electronic spectra of the complexes were recorded using a double beam UV spectrophotometer type SL-164. Thermogravimetric analysis (DTA-DTG-TG) of complexes was recorded on Perkin-Elmer (Pyris model-932). Molybdenum analysis was done by gravimetric method. Molar conductivity in DMF (10\textsuperscript{3} M) at room temperatures was measured using an Elico conductivity Bridge, type CM82T and a conductivity cell with cell constant of 0.74. Magnetic susceptibility of the complexes was recorded at room temperature using Gouy’s balance and using Hg[Co (NCS)\textsubscript{4}] as a standard.

### Table 1 — Analytical data and some physical properties of the synthesized complexes of the type [Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}L(H\textsubscript{2}O)\textsubscript{4}]

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complex</th>
<th>Colour</th>
<th>Decomp. temp. (°C)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>Mo</th>
<th>(\lambda_\text{m}) (ohm(^{-1})cm(^{2})mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}BFMH(H\textsubscript{2}O)\textsubscript{4}</td>
<td>Light brown</td>
<td>158</td>
<td>23.79</td>
<td>2.96</td>
<td>4.65</td>
<td>-</td>
<td>31.70</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}BTMH(H\textsubscript{2}O)\textsubscript{4}</td>
<td>Yellow</td>
<td>165</td>
<td>23.20</td>
<td>2.90</td>
<td>4.50</td>
<td>5.17</td>
<td>30.80</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}BTEH(H\textsubscript{2}O)\textsubscript{4}</td>
<td>Yellow</td>
<td>175</td>
<td>24.52</td>
<td>3.21</td>
<td>4.39</td>
<td>5.20</td>
<td>30.19</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}B TPMH (H\textsubscript{2}O)\textsubscript{4}</td>
<td>Off white</td>
<td>168</td>
<td>27.33</td>
<td>3.28</td>
<td>4.52</td>
<td>-</td>
<td>31.19</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}BAMH(H\textsubscript{2}O)\textsubscript{4}</td>
<td>Light yellow</td>
<td>160</td>
<td>27.85</td>
<td>3.44</td>
<td>4.36</td>
<td>-</td>
<td>29.73</td>
<td>27</td>
</tr>
</tbody>
</table>

### Table 2 — IR spectra of complexes of the type [Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}L(H\textsubscript{2}O)\textsubscript{4}]

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complex</th>
<th>(\nu) (Mo-O)</th>
<th>(\nu) (C=N)</th>
<th>(\nu) (C=O)</th>
<th>(\nu) (N-H)</th>
<th>(\nu) (O-O)</th>
<th>(\nu) ([\text{Mo-O(O2)}])</th>
<th>(\nu) ([\text{Mo-O(O2)}])</th>
<th>(\nu) (OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}BFMH(H\textsubscript{2}O)\textsubscript{4}</td>
<td>950</td>
<td>1620</td>
<td>1644</td>
<td>3227</td>
<td>895</td>
<td>638</td>
<td>592</td>
<td>3480</td>
</tr>
<tr>
<td>2</td>
<td>Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}BTMH(H\textsubscript{2}O)\textsubscript{4}</td>
<td>958</td>
<td>1604</td>
<td>1648</td>
<td>3235</td>
<td>890</td>
<td>645</td>
<td>574</td>
<td>3470</td>
</tr>
<tr>
<td>3</td>
<td>Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}BTEH(H\textsubscript{2}O)\textsubscript{4}</td>
<td>952</td>
<td>1610</td>
<td>1640</td>
<td>3240</td>
<td>890</td>
<td>649</td>
<td>580</td>
<td>3465</td>
</tr>
<tr>
<td>4</td>
<td>Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}B TPMH (H\textsubscript{2}O)\textsubscript{4}</td>
<td>960</td>
<td>1615</td>
<td>1642</td>
<td>3236</td>
<td>893</td>
<td>644</td>
<td>590</td>
<td>3475</td>
</tr>
<tr>
<td>5</td>
<td>Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}BAMH(H\textsubscript{2}O)\textsubscript{4}</td>
<td>953</td>
<td>1609</td>
<td>1638</td>
<td>3260</td>
<td>892</td>
<td>650</td>
<td>585</td>
<td>3468</td>
</tr>
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</table>

The analytical and spectroscopic results (Tables 1 and 2) show that all complexes are dinuclear with general formula, Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}L-L(H\textsubscript{2}O)\textsubscript{4} (where L-L = BFMH, BTMH, BTEH, BPMH, BAMH). All the complexes are coloured, stable in air and soluble in DMSO and DMF. The complexes do not have sharp 10°C/min in an atmosphere of nitrogen. All the experiments were carried out at room temperature.

Ammonium molybdate (1 mmol, 0.196 g) was dissolved in 30% (w/v) hydrogen peroxide (60 cm\(^3\)). The resulting solution was stirred and heated for 4 h at 40°C. An equimolar solution of ligand (L-L) in ethanol [L-L = BFMH, BTMH, BTEH, BPMH, BAMH] was added to this solution while stirring and the stirring continued for about 5 h at 40°C. The reaction mixture was allowed to stand overnight at room temperature. The precipitates so formed were filtered and repeatedly washed with aqueous-ethanol to remove unreacted reactants and dried in a dessicator. Yield: 60-70%. The reaction was repeated by taking ammonium molybdate and corresponding ligands in 1:2 and 1:3 ratios. The products isolated were identical with those obtained when reactants were taken in equimolar ratio.

Results and discussion
The analytical and spectroscopic results (Tables 1 and 2) show that all complexes are dinuclear with general formula, Mo\textsubscript{2}O\textsubscript{4}(O\textsubscript{2})\textsubscript{2}L-L(H\textsubscript{2}O)\textsubscript{4} (where L-L = BFMH, BTMH, BTEH, BPMH, BAMH). All the complexes are coloured, stable in air and soluble in DMSO and DMF. The complexes do not have sharp
melting points and decompose above 150°C. Moreover, magnetic susceptibility measurements at 30°C indicate the diamagnetic nature of complexes.

**Conductance measurement**

The molar conductivity measured in 10$^{-3}$ M DMF solution of these complexes is in the range of 25-34 mho cm$^2$ mol$^{-1}$ which is much less than the value of 70-160 mho cm$^2$ mol$^{-1}$ obtained for 1:1 electrolyte in this solvent. Thus, it can be concluded that these complexes are undissociated which indicates the non-electrolytic nature of these complexes.

**Infrared spectra**

The IR data of all the complexes are summarized in Table 2. In the 1000-300 cm$^{-1}$ region both the Mo-O (O$_2$), O-O and Mo-O-Mo vibrations are expected$^{13-35}$. The bands are broad and poorly resolved, indicating the polymeric nature of the species. The bands between 950-960 cm$^{-1}$ are assigned to ν(Mo=O) and those between 890-895 cm$^{-1}$ as ν(O-O) of the peroxo ligand$^{36}$. Generally, monoperoxo species exhibits ν(O-O) above 900 cm$^{-1}$ whereas diperoxo species exhibits ν(O-O)$^{37}$ below 900 cm$^{-1}$. Our results are consistent with these findings. The bands at 638-650 cm$^{-1}$ and 574-592 cm$^{-1}$ arise due to ν$_{as}$ and ν$_{s}$ Mo-O(O$_2$) asymmetric and symmetric stretches, respectively$^{38}$. All the complexes exhibit peak at ca. 3450 cm$^{-1}$ assigned to the OH stretching mode of the coordinated water molecule.

The IR spectra for free ligands is consistent with existence of aroyl hydrazones. A strong and sharp band at ca. 3250 cm$^{-1}$ in all ligands due to ν(N-H) stretching mode. Two strong bands at 1660-1650 cm$^{-1}$ and 1640-1625 cm$^{-1}$ are attributed to amide ν(C=O) and ν(C=N) modes respectively, indicating that ligands exist in keto form$^{39}$. All complexes exhibit a strong absorption band at 3227-3260 cm$^{-1}$ due to ν(N-H) stretching mode, suggesting that all the ligands remain protonated in chelation. The amide bands ν(C=O) and ν(C=N) shift to lower frequencies in the spectra of complexes (Table 2) suggesting the involvement of carbonyl oxygen and azomethine nitrogen in coordination with metal$^{40}$. Thus, the ligands behave as neutral bidentate chelating type coordinating metal through carbonyl oxygen and azomethine nitrogen.

**Electronic spectra**

The electronic spectra of complexes (Table 3) suggesting the involvement of carbonyl oxygen and azomethine nitrogen.

**TGA/DTA studies**

The TG curve for the complex Mo$_2$O$_4$(O$_2$)$_2$BTMH(H$_2$O)$_4$ shows initially gradual weight loss of 11.13% starting from 100°C up to 199°C corresponding to a loss of four water molecules (calculated wt. loss=11.57%). This is also indicated by a sharp endothermic peak of 27.0 μV at 178°C in the DTA curve. Further heating results in gradual and continuous total weight loss of 10.20% up to about 301°C which corresponds to loss of two peroxo groups as molecular oxygen (calculated wt. loss=10.28%). This is also indicated by a sharp endothermic peak of 33.5 μV in the DTA curve at 300°C and a DTG peak of 1.3mg/min at 302°C. Further heating up to 800°C results in weight loss of about 37.75% corresponding to possibly oxidation/decomposition of ligand (calculated wt. loss =37.01%) leading to the formation of 2MoO$_2$ as end product. (weight loss found =59.08%, calc. wt. loss = 58.86%).

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complexes</th>
<th>πO$_2^2$→d Mo</th>
<th>O$_2^2$→d Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mo$_2$O$_4$(O$_2$)$_2$BFMH(H$_2$O)$_4$</td>
<td>350</td>
<td>274</td>
</tr>
<tr>
<td>2</td>
<td>Mo$_2$O$_4$(O$_2$)$_2$BTMH(H$_2$O)$_4$</td>
<td>338</td>
<td>276</td>
</tr>
<tr>
<td>3</td>
<td>Mo$_2$O$_4$(O$_2$)$_2$BTEH(H$_2$O)$_4$</td>
<td>341</td>
<td>285</td>
</tr>
<tr>
<td>4</td>
<td>Mo$_2$O$_4$(O$_2$)$_2$BPMH(H$_2$O)$_4$</td>
<td>344</td>
<td>281</td>
</tr>
<tr>
<td>5</td>
<td>Mo$_2$O$_4$(O$_2$)$_2$BAMH(H$_2$O)$_4$</td>
<td>342</td>
<td>284</td>
</tr>
</tbody>
</table>
Table 4 — Antifungal activity of the ligands and their complexes

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>Zone of inhibition (mm)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>DMSO</td>
<td>16.5</td>
</tr>
<tr>
<td>2</td>
<td>BTEH</td>
<td>8.0</td>
</tr>
<tr>
<td>3</td>
<td>BTMH</td>
<td>12.0</td>
</tr>
<tr>
<td>4</td>
<td>MoO$_2$(O$_2$)$_2$BTEH(H$_2$O)$_4$</td>
<td>16.0</td>
</tr>
<tr>
<td>5</td>
<td>MoO$_2$(O$_2$)$_2$BTMH(H$_2$O)$_4$</td>
<td>24.0</td>
</tr>
</tbody>
</table>

Antifungal activity

The in vitro biological screening effects of the investigated compounds were tested against the Keretolytic fungus by the well diffusion method using potato dextrose agar as the medium. The screening effects of the corresponding ligands against the same fungus were also tested and results were compared with those obtained with complexes. The test solutions were prepared by dissolving the ligands and complexes in DMSO. In a typical procedure, a well was made on the agar medium inoculated with microorganisms. The well was filled with the test solution using micropipette and the plate was incubated at 30°C for 48 h. During this period, the test solution was diffused and the growth of the inoculated microorganisms was affected. The inhibition zone developed on the plate was measured. Here DMSO was used as the control. The zone of inhibition values of the compounds against the growth of microorganisms are given in Table 4. A comparative study of the ligands and complexes indicate that the complexes exhibit higher activity than the free ligand.

The above study shows that all the complexes are dimeric with composition, MoO$_2$(O$_2$)$_2$L(L-L)(H$_2$O)$_4$ (where L-L=BFMH, BTMH, BTEH,BPMH and BAMH) and +6 oxidation state for Mo. The proposed structure for the complexes is:

![Proposed Structure](image)

### References