Synthesis and characterization of indole-3-acetates and indole-3-butyrate s of Mo(VI) and W(VI)

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Reaction of indole-3-acetic acid (In-3-AcH) and indole-3-butyr ica id (In-3-BuH) with MoO3 and WO3 in aqueous ammonia afforded complexes of the type MO3(In-3-Ac)2 and MO3(In-3-Bu)2 (M=Mo or W) containing cis O=M=O bonds. The complexes have been characterized by elemental analysis, molar conductance, IR, UV-vis, TGA/DTA and cyclic voltammetric techniques. Indole-3-carboxylates are coordinated to the metal ion in a symmetrical bidentate fashion through two oxygen atoms of carboxylate group. Thermal studies indicate continuous weight loss till a stable oxide is formed.

Molybdenum, one of the biologically active elements, occurs in the redox active sites of over a dozen molybdoenzymes involved in nitrogen, sulfur and carbon metabolism1-3, for example oxidation of aldehydes, xanthine and other purines4 and reduction of nitrate and molecular nitrogen5-7. The biochemical importance of molybdenum is due to its ability to provide facile electron transfer pathways, a consequence of easy interconvertibility of different oxidation states and to form bonds with nitrogen, oxygen and sulfur donors which are sufficiently strong to permit the existence of stable complexes but also sufficiently labile to permit facile ligand exchange reactions or change of molybdenum coordination number. Moreover, indole-3-acetic acid and indole-3-butyric acid are well known plant growth hormones and their biproduction, propagation and distribution in different organs of plants have been studied8-10. Clinical significance of indole-3-acetic acid in gastric cancer patients is also well established11. A few indole carboxylates of some transition and inner transition elements have also been reported12-14. In the present study we report the synthesis and characterization of four complexes, MO3(In-3-Ac)2 and MO3(In-3-Bu)2, where M=Mo or W.

Experimental

MoO3 was prepared by heating ammonium molybdate and WO3 was prepared by heating tungstic acid. Indole-3-acetic acid and indole-3-but yric acid were used as such. The analysis of metals (Mo or W) was carried out by reported methods15. Carbon, hydrogen and nitrogen analysis were performed by microanalytical methods. Molar conductivity in DMF (10-3 M) at room temperature was measured using Elico Conductivity Bridge, type CM82T and conductivity cell with a cell constant of 0.74. IR spectra of complexes over the region 4000-400 cm^-1 were recorded on SP1200 and SP 2000 IR spectrophotometer using KBr disc. Thermogravimetric analysis (TGA/DTA) of complexes were recorded on DTG 60 ther ma l analys er at the heating rate of 20°C/ min. Cyclic voltammometric measurements were made in DMSO at 295K using a BAS CV-50 W electrochemical analyzer using a three electrode system, with Pt disc as working electrode, Pt wire as counter electrode and Ag/AgCl as reference electrode. Tetraethylammonium perchlorate was used as supporting electrode. Experiments were carried out at room temperature.

Preparation of complexes

Bis (indole-3-acetates) and bis (indole-3-butyrate s) of Mo and W were obtained by reaction of MoO3 and WO3 with indole-3-acetic acid and indole-3-butyr ica id in 1:2 molar ratio in aqueous ammonia under vigorous stirring. Complex formation was indicated by the appearance of deep colour in solution after 10 min. The complexes were precipitated by adjusting the pH of the solution at 3-4 by dropwise addition of 50% nitric acid. Precipitates were filtered, washed with aqueous ammonia and dried in air.
Results and discussion

The analytical and spectroscopic results (Tables 1 and 2) showed that all the complexes are mononuclear with general formulae MO$_2$(X)$_2$, where M=Mo or W and X=indole-3-acetate or indole-3-butyrate. All the complexes are coloured, stable in air and are soluble in common organic solvents methanol, ethanol, chloroform DMF and DMSO. They are thermally stable and have characteristic melting points. The behaviour of the complexes as non-electrolytes is indicated by their conductivity measurements.

Characteristic IR frequencies of the complexes are listed in Table 2. All the complexes show bands characteristic of indoles, more or less of same intensity and at the same position as that found in free acids$^{16}$. The OH band at 3391 cm$^{-1}$ for uncoordinated acids disappears on complex formation, suggesting coordination of deprotonated hydroxyl oxygen. An intense band at 3390-3395 cm$^{-1}$ assigned to v(N-H) stretching and also the v(C=O) stretching frequency around 1680-1685 cm$^{-1}$ in free acids have a positive shift of 10-25 cm$^{-1}$ indicating coordination of carbonyl oxygen. Tanner reported three acyl indoles to exist as strongly hydrogen bonded polymers in solid state on the basis of shift shown by N-H and C=O bands to higher frequencies upon dilution in tetrahydrofuran$^{17,18}$. The observed shifts in v(N-H) and v(C=O) indicate decrease in hydrogen bonding on complexation. Moreover, the bands present at 600-700 cm$^{-1}$ may be assigned to v(M-O). The presence of two strong bands at 900-955 cm$^{-1}$ in Mo complex and at 700-835 cm$^{-1}$ in W complex are characteristic of MoO$/^+$ and WO$^2-$ groups, an observation analogous to that of Chakravarty$^{19}$.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Complex (Empirical Formulae)</th>
<th>Colour</th>
<th>M.P. (°C)</th>
<th>Found (Calcd.)</th>
<th>Molar conductivity nho cm$^{-2}$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>MoO$_2$(In-3-Ac)$_2$ {MoO$<em>2$C$</em>{10}$H$_8$NO$_2$)$_2$}</td>
<td>Shining purple</td>
<td>185</td>
<td>50.72 (50.39) 3.56 (3.38) 6.02 (5.88)</td>
<td>20.23 (20.14) 21</td>
</tr>
<tr>
<td>2.</td>
<td>MoO$_2$(In-3-Bu)$<em>2$ {MoO$<em>2$C$</em>{12}$H$</em>{11}$NO$_2$)$_2$}</td>
<td>Yellowish brown</td>
<td>173</td>
<td>54.32 (54.90) 4.72 (4.54) 5.38 (5.26)</td>
<td>18.34 (18.02) 13</td>
</tr>
<tr>
<td>3.</td>
<td>WO$_2$(In-3-Ac)$_2$ {WO$<em>2$C$</em>{10}$H$_8$NO$_2$)$_2$}</td>
<td>Orange</td>
<td>220</td>
<td>43.14 (42.57) 3.12 (2.86) 5.13 (4.96)</td>
<td>32.67 (32.58) 12</td>
</tr>
<tr>
<td>4.</td>
<td>WO$_2$(In-3-Bu)$<em>2$ {WO$<em>2$C$</em>{12}$H$</em>{11}$NO$_2$)$_2$}</td>
<td>Dark brown</td>
<td>280</td>
<td>46.94 (46.43) 4.21 (3.90) 4.88 (4.51)</td>
<td>30.11 (29.64) 14</td>
</tr>
</tbody>
</table>

| Table 2– Important IR spectral bands (cm$^{-1}$) and their assignment |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| v(N-H)          | v(C-N)          | v(C=O)          | v$_1$(O-C-O)    | v$_2$(O-C-O)    | v(O=Mo=O)       | v(M-O)          |
| ln-3-AcH        | 3390            | 1296            | 1680            | ------          | ------          | ------          |
| ln-3-BuH        | 3395            | 1293            | 1655            | ------          | ------          | ------          |
| MoO$_2$(ln-3-Ac)$_2$ | 3415          | 1255            | ------          | 1430            | 1570            | 900,950         | 700            |
| MoO$_2$(ln-3-Bu)$_2$ | 3420          | 1270            | ------          | 1430            | 1555            | 905,955         | 690            |
| WO$_2$(ln-3-Ac)$_2$ | 3400          | 1265            | ------          | 1435            | 1565            | 780,825         | 610            |
| WO$_2$(ln-3-Bu)$_2$ | 3405          | 1270            | ------          | 1435            | 1550            | 890,835         | 600            |
The TG curves obtained for all the complexes are almost similar and weight loss continues till a stable oxide $\text{MO}_2$ (M=Mo or W) is formed. The DTA curves of all the complexes show two endothermic peaks. The first peak is small and corresponds to the initial weight loss of CO$_2$ in the temperature range of 160-300°C. Thereafter a continuous mass loss is observed up to the temperature range of 500-680°C, which gives second endothermic peak and loss of organic part of the complex, possibly indole-3-methylene carbocation and indole-3-methylene carbanion may be attributed in this temperature range. On further increasing the temperature no weight loss is observed which may be attributed to the formation of stable metal oxide, $\text{MO}_2$.

Coats-Redfern methods have been used for finding the kinetic parameters of the complexes. The fractional weight loss and the corresponding $(1-\alpha)^n$ values have been calculated from the TG curves at different temperatures, where $n$ depends upon the reaction model and $\alpha = (W_0 - W) / (W_0 - W_f)$. The weighted least square method (LSM) was used for obtaining the best-fit linear plots and kinetic parameters were calculated. The decomposition of all the complexes have been observed to follow first order kinetics, as is evident from the linear plot of $-\log [-\log (1-\alpha)/T^\prime]$ vs. $1/T$. The value of intercept, slope and activation energy ($E$) were obtained from the plots. The value of frequency factor ($Z$) and entropy of activation ($\Delta S^*$) was calculated from the equations $\text{Intercept} = \log ZR/\beta E$ and $(\Delta S^*) = 2.303 R \log Z \beta k T$ Where $k$ is Boltzmann constant, $\hbar$ the Planks constant, $T$ the peak temperature and $\beta$ the heating rate. The thermoanalytical data of all the complexes is given in Table 3.

The electrochemical data on the basis of CV plots is listed in Table 4. The cyclic voltammogram of the complexes displays an irreversible reduction peak at $-920$ to $-1140$ mV assigned to reduction of $\text{M}^{\text{VI}} \rightarrow \text{M}^{\text{V}}$ (M=Mo or W). The chemical stability of metal complexes may be responsible for their irreversible reduction. The cathodic peak potential ($E_c$) of butyrate complexes is higher than the corresponding acetate complexes, indicating lower electron donating ability of butyrate.

All the complexes show two high energy absorption bands in DMSO in the region 350-430 nm for molybdenum complexes and 380-450 nm for tungsten complexes, assigned to $n-n^*$ and $n-\pi^*$ LMCT transitions. It seems reasonable to assume that characteristic molybdenyl and tungstenyl bands do not occur in this region.

This study has revealed the presence of $\text{Mo}^{\text{VI}}$ dioxo complexes containing coordination units resembling the Mo cofactor of the oxo transfer molybdoenzymes. The synthesis of the complexes is a good indication that these complexes are resistant to dimer formation.
References