Synthesis and spectral analysis of oxomolybdenum(V) and dioxomolybdenum(VI) complexes of 1,2-dihydro-1,5-dimethyl-2-phenyl-4-(2-hydroxy-naphthyl azo)-3H-pyrazol-3-one

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A few oxomolybdenum(V) complexes of the formulae \([\text{MoO}(\text{LH})\text{Cl}_3]\), \([\text{MoO}(\text{LH})\text{Cl}_2\text{Br}]\), \([\text{MoO}(\text{LH})\text{Br}_3]\), \([\text{MoO}(\text{LH})\text{Cl}(\text{ClO}_4)_2]\), \([\text{MoO}(\text{LH})\text{NCS}\text{Cl}_2]\), \([\text{MoO}(\text{LH})\text{NO}_3\text{Cl}_2]\), \([\text{MoO}(\text{LH})\text{I}_2]\) and dioxomolybdenum(VI) complexes of the formulae \([\text{MoO}_2(\text{LH})\text{Cl}_2]\), \([\text{MoO}_2(\text{LH})\text{Br}_2]\), \([\text{MoO}_2(\text{LH})\text{NCS}\text{Cl}]\), \([\text{MoO}_2(\text{LH})\text{NO}_3\text{Cl}]\) and \([\text{MoO}_2(\text{L})\text{Cl}(\text{ClO}_4)_2]\) (\(\text{LH} = \text{NAAPH}\)) have been synthesised and characterised by elemental analysis, IR, electronic, ESR, magnetic and conductance measurements. The X-ray powder diffraction patterns of the two complexes have also been examined.

Molybdenum is one of the most biologically active transition elements and is an essential micro-nutrient for micro organisms, plants and animals. It possesses a large number of stable accessible oxidation states and higher oxidation states contain mono oxo or cis-dioxo Mo species. Nature has incorporated Mo into a number of redox enzymes.

In view of the importance of the oxomolybdenum(V) and dioxomolybdenum(VI) complexes, we have isolated and characterised some new complexes of a potential multidentate ligand, 1,2 dihydro-1,5-dimethyl-2-phenyl-4-(2-hydroxynaphthylazo)-3H-pyrazol-3-one (naphtholazo antipyrine, NAAPH), derived from biologically active molecule, 4-aminoantipyrine. NAAPH is a potential tridentate monobasic ligand, which can exist in keto (I) and enol (II) forms.

Materials and Methods

\(\text{MoCl}_3\) (Aldrich chemicals), 4-aminoantipyrine (Fluka) and \(\text{MoO}_3\) (Lobo) were used as such. All the other chemicals used were of AR grade. The ligand NAAPH was synthesised from 4-aminoantipyrine and 2-naphthol by diazotiazation and coupling as described in the literature.

Preparation of \(\text{Mo(V)}\) complexes \([\text{MoO(NAAPH)}\text{Cl}_3]\)

A methanolic solution of \(\text{MoCl}_3\) (2mmol) was mixed with the ligand (2 mmol) in chloroform and heated for 10-15 min on a water bath till the reaction was complete. The solid separated was suction filtered, washed with aq. methanol and dried over \(\text{P}_2\text{O}_5\) in vacuo.

\([\text{MoO(NAAPH)}\text{Br}_3]\)

\(\text{MoCl}_3\) (2 mmol) dissolved in hydrobromic acid (~ 1ml) was added to the ligand solution (2mmol, 20ml) in chloroform and heated for 10-15 min at 70-80°C on a water bath. The precipitated complex was suction filtered, washed with aq. methanol and dried over \(\text{P}_2\text{O}_5\) in vacuo.

\([\text{MoO(NAAPH)}\text{BrCl}_2\text{I}_2]\), \([\text{MoO(NAAPH)}\text{Cl}_2\text{I}_2]\) and \([\text{MoO(NAAPH)}\text{Cl}(\text{ClO}_4)_2]\) were mixed with a hot ligand solution in chloroform (2mmol) and heated for ~ 10 min at 70-80°C. The precip-
iated complexes were filtered, washed with aq. methanol and dried over $P_2O_{10}$ in vacuo.

$[\text{MoO(OAAAPH)}(\text{NCS})\text{Cl}_2]$ and $[\text{MoO(OAAAPH)}(\text{NO}_3)\text{Cl}_2]$

MoCl₅ (2mmol) dissolved in methanol containing 0.5g NH₄CNS or LiNO₃ was mixed with a chloroform solution of the ligand (2mmol). The thiocyanate complex precipitated instantaneously while the nitrate complex separated on refluxing the solution for $\sim 2$h. The complexes were filtered, washed free of excess metal halide, thiocyanate or LiNO₃ with aq. methanol. It was then dried over $P_2O_{10}$ in vacuo.

Preparation of Mo(VI) complexes $[\text{MoO}_2(\text{NAAP})\text{Cl}_2]$, $[\text{MoO}_2(\text{NAAP})\text{Br}_2]$ and $[\text{MoO}_2(\text{NAAP})(\text{ClO}_4)]$

The following general method was adopted for the preparation of these complexes. To a solution of $[\text{MoO}_2(\text{acac})_2]$ (2mmol) in THF-methanol mixture, 3-4 drops of HCl/HBr/HClO₄ as the case may be were added and mixed well with the ligand solution (2mmol) in the same solvent. The complexes separated on refluxing the solution for 1-2h were suction filtered, washed with aq. methanol and dried over $P_2O_{10}$ in vacuo.

$[\text{MoO}_2(\text{NAAP})\text{NO}_3\text{Cl}]$ and $[\text{MoO}_2(\text{NAAP})(\text{NCS})\text{Cl}]$

MoO₃ (1mmol) was dissolved in conc. HCl and to this, $\sim 0.5g$ NH₄CNS or LiNO₃ was added and the resulting solution stirred well with the ligand (1mmol) solution in THF-CH₃OH mixture. The solid complexes separated were suction filtered, washed with THF-CH₃OH mixture and dried over $P_2O_{10}$ in vacuo. (For the nitrate complex, the mixture was refluxed for $\sim 2$h).

Metal, halide, perchlorate and sulphur in the complexes were estimated by standard methods. The IR spectra of the ligand and complexes were recorded in the region 4000-400 cm⁻¹ on a Perkin-Elmer 397 spectrophotometer. The electronic spectra of the complexes in solid state and in solution (CH₂OH or CH₃CN) were recorded on a Hitachi 220 A spectrophotometer. The conductances of the complexes in CH₃NO₂, CH₃OH and CH₃CN (ca. 10⁻³M) were measured at 300 ± 2K using an Elico conductivity bridge type CM82T with a diptype cell (ec-03) fitted with platinum electrodes (cell constant = 1.68 cm⁻¹). The magnetic susceptibilities at room temperature (300 ± 2K) were measured on a Gouy balance using Hg[Co(NCS)₄] as the calibrant. Diamagnetic corrections for various atoms and structural units were computed using Pascal's constants. $\chi_{\text{Dia}} = -14 \times 10^{-6}$ C.G.S units for Mo⁵⁺ and temperature independent paramagnetism for Mo⁵⁺ = $60 \times 10^{-6}$ C.G.S units were also incorporated. The X-ray powder diffraction patterns of the complexes $[\text{MoO(OAAAPH)(NCS)Cl}_2]$ and $[\text{MoO}_2(\text{NAAP})\text{Cl}_2]$ were obtained on Philips XRD (PW 1712) model (34 KW-10MA) employing CuKα radiation, with a scan speed 0.05°/s and $\lambda = 1.5418$ Å ESR spectrum of one of the complexes $[\text{MoO(OAAAPH)(NCS)Cl}_2]$ was run on a Varian E-112 X-Q band spectrophotometer with DPPH as the reference material. $^1$H NMR spectrum of the ligand OAAAPH was recorded in CDCl₃ using a 60 MHz NMR spectrometer with TMS as reference.

Results and Discussion

All the complexes are dark coloured, non-hygroscopic solids, soluble in hot C₆H₅NO₂, CH₃NO₂ and CH₃CN and sparingly soluble in other common organic solvents.

The analytical data (Table 1) corresponds to the composition MoOLX₃ (L = neutral ligand and X = Cl, Br, I, NO₃, ClO₄ or NCS) for Mo(V) complexes and MoO₃LX₂ for Mo(VI) complexes.

In some complexes, mixed anions are present. The molar conductances (Table 1) show that except the iodide and perchlorate complexes, all the other complexes of Mo(V) behave as non-electrolytes. The magnetic moments (Table 1) of Mo(V) complexes are in the range 1.73-1.84 B.M and indicate the absence of any Mo-Mo interaction. All the dioxomolybdenum(VI) complexes are diamagnetic as expected.

The $^1$H NMR spectrum showed that the ligand exists exclusively in the enol form (II). The signal of =C–CH₃ group of pyrazolone ring appears as a sharp singlet (3H) at δ 2.7. The =N–CH₃ signal is observed as another singlet at δ 3.25. The aromatic protons of the compound appear as multiplet at δ 7.5 (comprising eleven protons). The OH proton signal appears as a doublet at δ 8.68.

In the infrared spectra, the free ligand exhibits a broad medium intensity band $\sim 2900$ cm⁻¹, assignable to the hydrogen bonded OH group. This band disappears on complexation in all the cases. A new band $\sim 3450$ cm⁻¹ appears in all except the perchlorate complex of Mo(VI), suggesting the non-participation of OH group in coordination. In the Mo(VI) perchlorate complex, the hydroxyl group is deprotonated. The vC=O
### Table 1—Analytical and physical data of molybdenum complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Found (% Calcd)</th>
<th>Molar conductances (ohm cm² mol⁻¹)</th>
<th>η_{off} (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>M   C   N   H   Cl   Br   I   CIO₄⁻</td>
<td>C₆H₅NO₂</td>
<td>CH₂CN</td>
</tr>
<tr>
<td>[MoO(NAAPh)Cl]₂</td>
<td>Brownish Black</td>
<td>16.7 44.4 9.8 3.2 18.5</td>
<td>0.9</td>
<td>5.7</td>
</tr>
<tr>
<td>[MoO(NAAPh)BrCl]₂</td>
<td>Reddish Brown</td>
<td>15.5 40.5 9.1 2.9 11.4 12.8</td>
<td>1.2</td>
<td>4.2</td>
</tr>
<tr>
<td>[MoO(NAAPh)Br]₂</td>
<td>Reddish Brown</td>
<td>13.5 (40.6) (9.0) (2.9) (11.4) (12.9)</td>
<td>3.6</td>
<td>8.3</td>
</tr>
<tr>
<td>[MoO(NAAPh)Cl]₃</td>
<td>Brownish Red</td>
<td>13.5 (33.7)</td>
<td>9.8 (3.4) (18.4)</td>
<td>5.7</td>
</tr>
<tr>
<td>[MoO(NAAPh)BrCI]₂</td>
<td>Brownish Red</td>
<td>9.1 (47.6) (10.6) (3.3) (3.4) (18.6)</td>
<td>55.7</td>
<td>360.8</td>
</tr>
<tr>
<td>[MoO(NAAPh)NO₃]₂</td>
<td>Reddish Brown</td>
<td>16.0 (40.5) (9.1) (2.9) (11.4) (12.9)</td>
<td>1.3</td>
<td>4.9</td>
</tr>
<tr>
<td>[MoO(NAAPh)Cl]₄</td>
<td>Reddish Brown</td>
<td>13.5 (33.7)</td>
<td>9.8 (3.4) (18.4)</td>
<td>5.7</td>
</tr>
<tr>
<td>[MoO(NAAPh)NCS Cl]₂</td>
<td>Black</td>
<td>7.9 (41.1) (9.2) (2.9) (31.5)</td>
<td>42.6</td>
<td>131.2</td>
</tr>
<tr>
<td>[MoO₂(NAAPh)Cl]₂</td>
<td>Reddish Brown</td>
<td>17.3 (41.1) (9.2) (2.9) (31.5)</td>
<td>1.0</td>
<td>4.1</td>
</tr>
<tr>
<td>[MoO₂(NAAPh)BrCl]₂</td>
<td>Reddish Brown</td>
<td>14.7 (38.9) (8.7) (2.9) (31.5)</td>
<td>10.6</td>
<td>14.9</td>
</tr>
<tr>
<td>[MoO₂(NAAPh)NCS Cl]₂</td>
<td>Reddish Brown</td>
<td>16.7 (39.0) (8.6) (2.9) (31.5)</td>
<td>1.1</td>
<td>7.0</td>
</tr>
<tr>
<td>[MoO₂(NAAPh)NO₃Cl]₂</td>
<td>Reddish Brown</td>
<td>16.3 (43.1) (9.6) (2.9) (31.5)</td>
<td>18.0</td>
<td>152.0</td>
</tr>
<tr>
<td>[MoO₂(NAAPh)NO₃Cl]₂</td>
<td>Dark Red</td>
<td>16.4 (43.1) (9.6) (2.9) (31.5)</td>
<td>5.4</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Observed ~ 1650 cm⁻¹ in the ligand spectrum is shifted to 1560 cm⁻¹ in the spectra of the complexes, indicating its participation in complexation. The vibrational band assigned to the N=N group at ~ 1455 cm⁻¹ in the ligand spectrum shows slight downward shift by about 15-25 cm⁻¹ in all the complexes, suggesting the participation of this group in coordination. Thus the ligand is neutral bidentate in all the complexes, except the perchlorate complex of Mo(VI), where it is an anionic tridentate chelating agent.

For the perchlorate complexes, ν₁ and ν₂ appear as strong and medium intensity bands ~ 1090 and ~ 625 cm⁻¹ respectively, indicating the ionic nature of perchlorate group. The N-coordinated nature of the thiocyanate group is indicated by the νC−N (~ 2080), νC−S (~ 780) and δ NCS (~ 470 cm⁻¹). The IR spectra of the nitrate complexes are suggestive of monodentately coordinated nitrate groups (~ 1540, ν₁ ~ 1420 and ν₂ ~ 1010 cm⁻¹).

A very strong band found ~ 960 cm⁻¹ in the spectra of Mo(V) complexes corresponds to νMo=O (refs. 1,20,21). Also, strong bands exhibited by the dioxomolybdenum (VI) complexes in the region 940-950 and 895-915 cm⁻¹ are attributed to ν_{sym} O=Mo=O and ν_{asym} O = Mo−= O respectively of cis-MoO₂ moiety. The MoO₂ prefers to form a cis-MoO₂ configuration due to maximum utilization of the available dτ orbitals for bonding with the oxo groups. The Mo−N stretching frequency (νMo−N) lies at 500-520 cm⁻¹ in the complexes. Medium to weak intensity bands occurring at 435-445 cm⁻¹ are attributed to νMo−O in the complexes.

The electronic spectral bands of Mo(V) complexes in solution together with the tentative assignments, are discussed. The Mo(V) complexes usually exhibit three distinct absorption bands in the ligand field region at ~ 13500-14500 J, ~ 19000-22000 and ~ 22500-26000 cm⁻¹, assignable to the transitions 2B₂−→2E (d_{xy}−d_{x^2})−→2B₁ (d_{xy}−d_{x^2}), 2B₂−→2A₁ (d_{xy}−d_{x^2})−→2B₁ (d_{xy}−d_{x^2}). Usually, the third band may be obscured by the more intense charge-transfer transition O(n)−→d(Mo) involving the excitation of an electron from the highest filled π bonding MO (associated mainly with oxygen) to the d orbitals of Mo. All the Mo(V) complexes show bands in the region 13986-15503, 19230-20833 and 25000-26315 cm⁻¹. The electronic spectra indicate octahedral environment for all the complexes and are in confor-
nity with the Ballhausen-Gray scheme for an octahedral geometry\textsuperscript{25}. No bands are observed below 10000 cm\(^{-1}\) and hence the possibility of a tetrahedral structure can be ruled out. The complexes can be best considered as octahedral with strong tetragonal distortion (\(C_4v\) symmetry), resulting from the Mo = O multiple bond.

The complexes [MoO(NAAPH)(NCS)Cl\(_2\)] and [MoO\(_2\)(NAAPH)Cl\(_2\)] were found to be orthorhombic by X-ray powder diffraction method and were indexed using Hesse and Lipson’s procedure\textsuperscript{26,27}. The unit cell dimensions a, b and c for the complexes were found to be 10.395 Å, 14.31 Å and 19.9 Å respectively for [MoO(NAAPH)(NCS)Cl\(_2\)] and 10.49 Å, 13.84 Å and 17.7 Å respectively for [MoO\(_2\)(NAAPH)Cl\(_2\)]. The number of molecules per unit cell in each case were found to be four.

The ESR spectrum of one of the complexes [MoO(NAAPH)(NCS)Cl\(_2\)] was recorded in polycrystalline form at room temperature, which exhibited a single line only. The ESR parameters were found to be \(g|| = 1.9928\), \(g_{\perp} = 1.959\) and \(g_{av} = 1.9759\). The \(g_{av}\) value indicates that the pentavalent Mo in the complex is monomeric\textsuperscript{28}.

On the basis of the above evidences, a distorted octahedral geometry is suggested for the complexes (III).

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References