Synthesis, spectral, thermal and electrochemical studies of oxomolybdenum(V) and dioxomolybdenum(VI) complexes of an azo dye derived from 4-amino-2,3-dimethyl-1-phenyl pyrazol-5-one

M L Harikumaran Naira,* & A Sheela b

a,* Department of Chemistry, University College, Thiruvananthapuram 695 034, India
Email: dmlhnair@gmail.com
b Department of Chemistry, M.S.M. College, Kayamkulam 690 502, India

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Some novel complexes of oxomolybdenum(V) and dioxomolybdenum(VI) with an azodye derived from 4-amino-antipyrine and 3-methoxyphenol have been synthesised and characterized by elemental analyses, molar conductance values, magnetic susceptibility measurements, IR, electronic, ESR, and 1H NMR spectra and cyclic voltammetric studies. The physico-chemical studies and spectral data indicate that the ligand acts as neutral bidentate. All the complexes are found to be monomeric and neutral with distorted octahedral geometry. The X-ray diffraction studies of [MoO(MOPAAP)Cl₃] and [MoO₂(MOPAAP)Cl₂] indicate that the complexes are orthorhombic with the unit cell dimensions a = 7.3277 Å, b = 9.6663 Å and c = 15.8897 Å; and a = 8.5534 Å, b = 9.598 Å, c = 15.4056 Å respectively. The CV profile of the complex [MoO(MOPAAP)Cl₃] shows a quasireversible peak, which indicates that the metal-ligand linkage is more covalent in nature. The thermal stabilities of the complexes have been compared and show that [MoO(MOPAAP)Cl₃] is more stable than [MoO₂(MOPAAP)Cl₂].

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The potential for biological and physiological activity and the industrial use of molybdenum complexes have stimulated the discovery of a variety of molybdenum complexes in various oxidation states. The higher oxidation states of molybdenum are dominated by complexes that contain the oxo and dioxomolybdenum groups. A variety of chemical reactions have been reported to be catalysed by coordination compounds of molybdenum. The complexes of molybdenum have also been studied as models for molybdenum containing enzymes.

A number of complexes of azodyes derived from 4-aminoantipyrine with some d-block and f-block metal ions have been reported.

In view of the importance of oxomolybdenum(V) and dioxomolybdenum(VI) complexes, we have isolated and characterized some new complexes of a potential multidentate ligand, 2,3-dimethyl-1-phenyl-4-(2-hydroxy-4-methoxyphenylazo) pyrazol-5-one (methoxyphenolazo antipyrine-MOPAAP).

**Materials and Methods**

MoCl₅ (Aldrich Chemicals, USA), 4-aminoantipyrine (Fluka, Switzerland), 3-methoxy phenol (Alfa Aesar, Lancaster) and MoO₃ (Loba Chemie, Mumbai) were used as such. All other chemicals used were of A R grade.

**Synthesis of methoxyphenolazo antipyrine (MOPAAP)**

MOPAAP (C₁₈H₁₆N₄O₃) (I) was synthesised from 4-amino antipyrine and 3-methoxyphenol by diazotization and coupling as given in literature. 4-Aminoantipyrine (10 g, 50 mmol) was converted to the hydrochloride using 1:1 hydrochloric acid (28 ml) and the solution was cooled below 0°C in an ice-salt bath. A solution of sodium nitrite (3.8 g, 55 mmol) in

![Chemical Structure of MOPAAP](image)
water (20 ml) was chilled using the ice-salt bath. The pre-cooled nitrite solution was then added in small volumes to the cold amine hydrochloride solution with good stirring. The temperature was always kept below 10°C and small amounts of crushed ice were used when required. The last part of the nitrite solution was added slowly and dropwise till a slight excess of nitrous acid was present which was indicated by an immediate blue colour, imparted to a starch potassium iodide paper. After keeping the diazonium chloride solution in ice bath for a few minutes, the temperature was allowed to rise to about 5°C.

3-Methoxyphenol (7 ml, 50 mmol) was dissolved in 45 ml of 10% sodium hydroxide solution. The solution was then cooled below 5°C in an ice bath followed by the direct addition of about 25 g of crushed ice. The cold diazonium chloride solution was added very slowly to the solution of 3-methoxyphenol with vigorous stirring. The colour of the solution became brown red and a solid product separated slowly. After the addition of the entire amount of the diazo compound, the mixture was allowed to stand in the bath for about 30 min. with occasional stirring. The solid product obtained was then filtered under gentle suction, washed well with cold water and recrystallised from alcohol. The purity was tested by TLC, elemental analysis, m.pt. determination and also characterized by IR and NMR spectral data.

Synthesis of oxomolybdenum(V) complexes

A methanolic solution of MoCl₃ (2 mmol) was dissolved in 2 mmol solution of the ligand (2 mmol) with vigorous stirring. The dark brown solution which formed was heated over a water bath at ca. 65°C for 10 min. The precipitated complex was suction filtered and washed several times with aqueous methanol (1:1) and finally with dry ether. It was then dried over P₂O₅ in vacuo.

The following general method was adopted for the preparation of the thiocyanate, nitrate and perchlorate complexes. A solution of MoCl₃ (2 mmol) was dissolved in minimum quantity of hot conc. HCl. This solution was added to a hot methanolic solution of the ligand (2 mmol) with vigorous shaking. The reddish brown solution obtained was concentrated, suction filtered, washed several times with aqueous methanol and finally with dry ether. It was then dried over P₂O₅ in vacuo.

The following general method was adopted for the preparation of thiocyanate, nitrate and perchlorate complexes. A solution of MoO₃ (2 mmol) dissolved in minimum quantity of conc. HCl, containing ∼0.5 g NH₄NCS/∼ 0.5 g LiNO₃/ 3-4 drops of HClO₄ as the case may be, was added to a hot methanolic solution of the ligand (2 mmol) with vigorous stirring. The resulting solution was refluxed for 1-2 h and cooled. The solid complexes which separated out were suction filtered, washed with aqueous methanol and dried over P₂O₅ in vacuo.

Metal, chloride and perchlorate were estimated by standard methods.¹ Elemental analyses were carried out at Sophisticated Test and Instrumentation Centre (STIC), Kochi. The IR spectra of the ligand and the complexes were recorded in the region 4000-400 cm⁻¹ on a Perkin–Elmer 397 spectrophotometer. Electronic spectra of the complexes were recorded in methanol on a Jasco-V-550-UV-vis spectrophotometer. Molar conductances of the complexes in nitrobenzene, acetonitrile and methanol were measured at room temperature using an Elico direct reading conductivity meter at a concentration of ~10⁻³ M. Magnetic susceptibility measurements were carried out at room temperature by Gouy method. ¹H NMR spectra of the ligand and the complexes were recorded on a 300 MHz FT NMR instrument using TMS as reference. Cyclic voltammetric profile of the complex [MoO(MOPAAP)Cl₃] was run on a BAS CV-50 W voltammetric analyzer using glassy carbon as the working electrode. The ESR spectrum of [MoO(MOPAAP)Cl₃] was taken in polycrystalline form at room temperature with DPPH as reference material. X-ray powder diffraction patterns of [MoO(MOPAAP)Cl₃] and [MoO₂(MOPAAP)Cl₃] were recorded using Philips X-ray PW 1710 diffractometer. Thermal analyses of [MoO(MOPAAP)Cl₃] and [MoO₂(MOPAAP)Cl₃] were carried out on a Mettler TG-50 thermobalance.
Results and Discussion

All the complexes were brownish red, non-hygroscopic and stable crystalline solids. They are partially soluble in common organic solvents and soluble in DMF and DMSO. The molar conductivity values indicate that all the complexes are non-electrolytes (Table 1). The magnetic moments (Table 1) of oxomolybdenum(V) complexes are in the range 1.73-1.84 BM which correspond to the spin-only value (1.73 BM) expected for oxomolybdenum(V) complexes indicating the absence of any Mo-Mo interaction. All the dioxomolybdenum(VI) complexes are diamagnetic as expected.

In the IR spectra of the free ligand and its complexes, the stretching frequency of the hydrogen bonded hydroxyl group is observed at ~3100 cm\(^{-1}\) as a broad band of medium intensity, indicating the presence of –OH group and its non-involvement in complexation. The \(v_{\text{C=O}}\) and \(v_{\text{N=N}}\) observed at ~1640 cm\(^{-1}\) and ~1490 cm\(^{-1}\), respectively in the spectrum of the ligand show a downward shift to ~1600 cm\(^{-1}\) and ~1450 cm\(^{-1}\) in the spectra of the complexes, showing the participation of the carbonyl oxygen and one of the nitrogens of the diazo group in coordination. Thus, the ligand MOPAAP acts as a neutral bidentate chelating agent in all these complexes.

A very strong band at ~960 cm\(^{-1}\) in the spectra of all the oxomolybdenum(V) complexes is assigned to Mo=O stretching frequency. Also, two strong bands exhibited by dioxomolybdenum(VI) complexes in the region 930-960 and 900-910 cm\(^{-1}\) are attributed to \(\nu_{\text{sym}}(\text{O}=\text{Mo}=\text{O})\) and \(\nu_{\text{asym}}(\text{O}=\text{Mo}=\text{O})\), respectively of cis-MoO\(_2\) moiety. The MoO\(_2\) prefers to form a cis configuration due to maximum utilization of the d\(_t\) orbitals of the metal for bonding with the oxo groups. The Mo-N stretching frequency lies between ~510-520 cm\(^{-1}\) and 510-515 cm\(^{-1}\) in the case of oxomolybdenum(V) and dioxomolybdenum(VI) complexes respectively. Medium to weak intensity bands occurring at ~430 cm\(^{-1}\) and 420-440 cm\(^{-1}\) is attributed to the \(\nu_{\text{Mo-O}}\) in oxomolybdenum(V) and dioxomolybdenum(VI) complexes respectively.

The N-coordinated nature of the thiocyanate group is indicated by the \(\nu_{\text{C=S}}\) (~840 cm\(^{-1}\)) and \(\delta\text{NCS}~(~490~cm^{-1})\) bands. The strong to medium intensity bands occurring at ~1500 cm\(^{-1}\) (\(\nu_1\)), ~1380 cm\(^{-1}\) (\(\nu_2\)) and ~1050 cm\(^{-1}\) (\(\nu_3\)) in the IR spectra of the nitrate complexes are suggestive of the monodentately coordinated nitrate group. For the perchlorate complexes, two bands (split bands) observed at ~1114 and 1030 cm\(^{-1}\) assigned to \(\nu_1\) and \(\nu_2\) ~626 cm\(^{-1}\) are characteristic of unidentate coordination of perchlorate groups.

The \(^1\)H NMR spectrum of the ligand displays three singlets, which correspond to the methyl protons. The \(>\text{C-CH}_3\) group of pyrazolone ring appears as a sharp singlet in the region \(\delta ~2.62-2.69\) while the \(>\text{N-CH}_3\) signal is observed as another singlet in the region \(\delta ~3.28-3.34\) and -OCH\(_3\) signal is observed at \(\delta ~3.78-4.00\). The signal due to the five aromatic protons of the antipyrine phenyl ring appear as multiplet between \(\delta ~7.26-7.73\) and these due to the

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>(\text{M} )</th>
<th>(\text{C} )</th>
<th>(\text{H} )</th>
<th>(\text{N} )</th>
<th>(\text{Cl} )</th>
<th>Molar cond. (\times 10^3) (ohm(^{-1}) cm(^{2}) mol(^{-1}))</th>
<th>(\mu_{\text{eff}}) (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MoO(MOPAAP)Cl(_2)]</td>
<td>Brown</td>
<td>17.65</td>
<td>38.22</td>
<td>3.48</td>
<td>9.99</td>
<td>19.55</td>
<td>1.3</td>
<td>1.73</td>
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<tr>
<td>[MoO(MOPAAP)(NCS)Cl(_2)]</td>
<td>Brownreddish</td>
<td>15.03</td>
<td>40.43</td>
<td>2.64</td>
<td>14.00</td>
<td>5.73</td>
<td>3.2</td>
<td>1.79</td>
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<tr>
<td>[MoO(MOPAAP)(NO(_3))Cl(_2)]</td>
<td>Brownreddish</td>
<td>16.98</td>
<td>37.63</td>
<td>3.51</td>
<td>12.52</td>
<td>12.86</td>
<td>5.8</td>
<td>1.77</td>
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<tr>
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<td>Brownreddish</td>
<td>15.01</td>
<td>35.24</td>
<td>2.98</td>
<td>9.58</td>
<td>11.95</td>
<td>56.5</td>
<td>1.84</td>
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<tr>
<td>[Mo(_2)(MOPAAP)(NCS)Cl(_2)]</td>
<td>Brownreddish</td>
<td>17.55</td>
<td>41.03</td>
<td>3.65</td>
<td>12.96</td>
<td>6.28</td>
<td>3.5</td>
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<tr>
<td>[Mo(_2)(MOPAAP)(NO(_3))Cl(_2)]</td>
<td>Brown</td>
<td>17.53</td>
<td>38.07</td>
<td>3.01</td>
<td>12.98</td>
<td>5.83</td>
<td>5.4</td>
<td>&quot;</td>
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<tr>
<td>[Mo(_2)(MOPAAP)(ClO(_4))Cl(_2)]</td>
<td>Brown</td>
<td>15.97</td>
<td>36.31</td>
<td>2.47</td>
<td>9.66</td>
<td>6.08</td>
<td>24.6</td>
<td>&quot;</td>
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</table>
protons of phenyl rings are observed as multiplet between δ (6.39-6.54). The signal due to phenolic –OH proton appears at δ 12.50. On analyzing the spectrum of the complex [MoO2(MOPAAP)Cl2], no appreciable change of signal is observed. The presence of singlet due to phenolic proton in the spectrum of the complex indicates the non-participation of the –OH group during coordination, which is further confirmed by the IR spectra.

All the oxomolybdenum(V) complexes show a broad band in the region 400-375 nm, which may be assigned to charge transfer transitions. A medium intensity band at ~500 nm and a comparatively weak broad band in the region 710-650 nm, in the spectra of the complexes can be attributed to the (dxy → d2z2−y2) and (dxz → dxy, dyz) transitions respectively. The third band due to (dxy → d2z2) is not observed in the spectra of the complexes, probably masked by the intense charge transfer bands. The electronic spectra thus indicate octahedral environment for all the complexes. No bands are observed above 1000 nm and hence the possibility of tetrahedral structure can be ruled out. The complexes can be at best considered as octahedral with strong tetragonal distortion resulting from the Mo=O multiple bond.

The X-band ESR spectrum of [MoO(MOPAAP)Cl3] has been recorded in the polycrystalline form at room temperature using DPPH free radical as the g marker. The spectrum is characterized by only a single line with unresolved parallel and perpendicular components. The absorption at ~3300 G is characteristic of Mo5+ species and the absence of any half field signal at ~1500 G rules out any metal-metal interaction in the complex. The ESR parameters were found to be $g_\| =1.9347$, $g_\perp =1.9097$ and $g_{av} =1.9180$. The calculated $g_{av}$ value indicates that the complex is monomeric with molybdenum in the pentavalent state.

The electrochemical behaviour of the complex [MoO(MOPAAP)Cl3] was examined by cyclic voltammetry in the potential range of −2000 mV to +2000 mV at a scan rate of 100 mVs⁻¹ after deaereating 10⁻³ M solution of the complex in acetonitrile. The complex shows a quasi-reversible peak at −0.890 V (Fig. 1) which can be attributed to the Mo(V)/Mo(IV) redox system. The electrochemical process is diffusion controlled and adsorption of molybdenum on the electrode is not involved.

The molecular structure of oxomolybdenum(V) and dioxomolybdenum(VI) complexes were studied by X-ray diffraction, (Fig. 2 (a & b)). The complexes [MoO(MOPAAP)Cl3] and [MoO2(MOPAAP)Cl2]
were found to be orthorhombic. The lattice constants for [MoO(MOPAAP)Cl₃] were found to be as follows: A = 0.01105, B = 0.00635 and C = 0.00235 and unit cell dimensions \(a = 7.3277 \text{ Å}, b = 9.6663 \text{ Å}, \text{ and } c = 15.8897 \text{ Å.}\) For [MoO₂(MOPAAP)Cl₂], \(A = 0.00811, B = 0.00644 \text{ and } C = 0.0025 \text{ and unit cell dimensions } a = 8.5534 \text{ Å}, b = 9.5986 \text{ Å}, \text{ and } c = 15.4056 \text{ Å.}\)

Thermal decomposition behaviour of the complexes [MoO(MOPAAP)Cl₃] and [MoO₂(MOPAAP)Cl₂] were studied using TG and DTG techniques by heating in air at a rate of 10°C per min. The TG and DTG curves of the complexes exhibit a plateau up to 200°C indicating the absence of coordinated water or other solvent molecules and also that the complexes are stable up to this temperature. The complexes then decomposed in three stages as denoted by the DTG peaks at 243, 350 and 540°C, (Fig. 3a) for [MoO(MOPAAP)Cl₃], and at 223, 301 and 375°C, (Fig. 3b) for [MoO₂(MOPAAP)Cl₂]. The absence of a

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**Fig. 3—TG and DTG curves of (a) [MoO(MOPAAP)Cl₃], and, (b) [MoO₂(MOPAAP)Cl₂].**

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Table 2—Kinetic parameters for the three stages of thermal decomposition of [MoO(MOPAAP)Cl₃]

<table>
<thead>
<tr>
<th>Stage</th>
<th>Peak temp. (°C)</th>
<th>Activation energy (E) (kJ mol(^{-1}))</th>
<th>(A) (s(^{-1}))</th>
<th>(\Delta S) (JK(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>243</td>
<td>176.57</td>
<td>4.9592 × 10(^{12})</td>
<td>-6.4309</td>
</tr>
<tr>
<td>II</td>
<td>350</td>
<td>155.72</td>
<td>6.2714 × 10(^{7})</td>
<td>-101.78</td>
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<tr>
<td>III</td>
<td>540</td>
<td>285.26</td>
<td>1.0411 × 10(^{13})</td>
<td>-4.04</td>
</tr>
</tbody>
</table>

Table 3—Kinetic parameters for the three stages of thermal decomposition of [MoO₂(MOPAAP)Cl₂]

<table>
<thead>
<tr>
<th>Stage</th>
<th>Peak temp. (°C)</th>
<th>Activation energy, (E) (kJ mol(^{-1}))</th>
<th>(A) (s(^{-1}))</th>
<th>(\Delta S) (JK(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>223</td>
<td>193.79</td>
<td>1.8264 × 10(^{15})</td>
<td>43.03</td>
</tr>
<tr>
<td>II</td>
<td>301</td>
<td>126.25</td>
<td>1.4817 × 10(^{7})</td>
<td>-132.25</td>
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<tr>
<td>III</td>
<td>375</td>
<td>116.40</td>
<td>1.3705 × 10(^{13})</td>
<td>-172.20</td>
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</table>
plateau in between these stages show that it is difficult to isolate and identify the intermediate products. Finally the ligand and anionic parts are completely removed and MoO$_3$ is obtained as the residue at the end.

The kinetic parameters were calculated using Coats-Redfern equation. The values of log $\frac{g(\alpha)}{T^2}$ versus $1/T \times 10^3$ plots were linear. The fitness was tested by evaluating the correlation coefficient. The entropy of activation ($\Delta S$) was also calculated (Tables 2 & 3). The initial decomposition temperature is frequently used to define the thermal stability of the metal chelates. Based on experimental results, [MoO(MOPAAP)Cl$_3$] is found to be thermally more stable than [MoO$_2$(MOPAAP)Cl$_2$].

On the basis of the above physico-chemical studies, a hexa-coordinate and tetragonally distorted octahedral geometry is tentatively suggested for oxymolybdenum complexes of MOPAAP (II) and dioxomolybdenum complexes of MOPAAP (III).

The computer model of the proposed configuration of [MoO(MOPAAP)Cl$_3$] was constructed by using the software Hyperchem 7.5. The geometrical optimization of the structure obtained is presented in Fig. 4.

References