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Synthesis and characterization of trichloromolybdenum(V) aryloxides

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The complexes of composition \([\text{MoCl}_3(\text{OAr})_2]\) (where \(\text{OAr}=\text{OC}_6\text{H}_4\text{Bu}'-4\), \(\text{OC}_6\text{H}_4\text{OMe}-4\) and \(\text{OC}_6\text{H}_2\text{Bu}~2-6\)-Me-4) have been synthesized by the reaction of molybdenum(V) chloride with the respective phenols in 1:2 molar ratios in carbon tetrachloride. These complexes have been characterized by elemental analyses, molar conductance, molecular weight determinations, magnetic susceptibility, infrared, electronic spectral data and thermal studies. The reactions of complexes with equimolar amounts of aliphatic amines yield products of the type \([\text{MoCl}_3(\text{OAr})_2\text{amine}]\).

In recent years, the synthesis of transition metal complexes containing the bulky aryloxide ligands has been a subject of considerable interest. A special feature of such complexes is that their structural assignments involve a subtle interplay of both steric and electronic factors. The interesting observations of Chamberlain et al. with chloroaryloxides of tantalum(V) and of Quignard and coworkers with aryloxide complexes of tungsten(VI) have shown that the number of chlorine atoms that may be substituted in TaCl, or WCl, respectively is strongly dependent on the nature, the number and the position of the substituents on the aromatic ring of the phenol. However, compared to the chloroaryloxides of tungsten(VI) and tantalum(V), the preparation of closely related aryloxides of molybdenum(V) from metal halides is scarcely investigated. Therefore, we thought it worthwhile to undertake the synthesis, characterization and thermal behaviour of trichloromolybdenum aryloxides. The reactions of these complexes with different aliphatic amines have also been investigated.

Experimental

\(\text{MoCl}_3\) (fluka grade) (correct Cl analysis) was used as such without further purification. 4-t-Butylphenol, 4-methoxyphenol and 2, 6-di-t-butyl-4-methylphenol purchased from Fluka with sharp melting points (99°C, 56°C and 71°C respectively) were used for the synthesis of complexes. The amines were purified by literature methods.

Preparation of \([\text{MoCl}_3(\text{OC}_6\text{H}_4\text{Bu}'-4)_2], \text{MoCl}_3(\text{OC}_6\text{H}_4\text{OMe}-4)_2\) and \([\text{MoCl}_3(\text{OC}_6\text{H}_2\text{Bu}~2-6\text{-Me-4})_2]\)

These complexes were prepared by the addition of bimolar amounts of different phenols taken in CCl, to the solution of \(\text{MoCl}_3\) in dry CCl, The reaction mixture was stirred under reflux for 5-6 h till the evolution of hydrogen chloride gas ceased. The resulting solution was then filtered and the filtrate concentrated by distilling off the solvent. The addition of pet. ether to the concentrated solution or allowing it to stand overnight gave the products as coloured solids (70-75% yield). These were recrystallised from dichloromethane and dried in vacuo.

Preparation of \([\text{MoCl}_3(\text{OAr})_2\text{amine}]\)

Complexes of composition \(\text{MoCl}_3(\text{OAr})_2\) were mixed with equimolar amount of amines in carbon tetrachloride and the reaction mixture stirred thoroughly for 12 h followed by refluxing for 1 h. The progress of the reaction was indicated by a colour change of the mixture solution. The resulting products were obtained either as solids or were extracted by concentrating the mixture solution followed by the addition of pet. ether. These were recrystallised from dichloromethane and dried under vacuum.

The molybdenum content in the complexes was determined as bis(8-hydroxyquinolino)dioxomolybdenum(VI); chlorine by Volhard's method and amines by steam distillation with alkali and titration of the distillate with sulphuric acid using Bromphenol Blue. The oxidation number of molybdenum in complexes was determined by direct ceric sulphate titration in cold. The elemental analysis was performed on Colemann C-H-N analyzer. The conductivities of 10^{-3}M solutions of the complexes in nitrobenzene at 25 ± 0.1°C were measured on an Elco conductivity Bridge CM Type 82T. The molecular weights were determined cryoscopically in nitrobenzene using a Beckmann thermometer.

The IR spectra were recorded as KBr discs, as well as nujol mulls on Perkin Elmer 337 and 621 spectrophotometers. The room temperature magnetic
moments of the complexes were measured by Guoy method using Hg[Co(NCS)₄] as calibrant. The electronic spectra was recorded on UV-visible Beckman Du-6 spectrophotometer. Thermal studies were carried out in air with the heating rate of 20°C min⁻¹ on a DTG-40 (simultaneous DTA-TG module SHIMADZU Coorporation) using Pt crucible and Pt/Pt:Ph thermocouple.

Results and discussion

Treatment of MoCl₅ with two equivalents of various phenols in carbon tetrachloride solvent leads to desired degree of substitution of OAr for Cl to yield coloured crystalline complexes MoCl₅(OAr)₂ according to the reaction,

\[ \text{MoCl}_5 + 2\text{HOAr} \rightarrow \text{MoCl}_5(\text{OAr})_2 + 2\text{HCl} \]

I,OC₆H₄Bu'-4; II,OC₆H₄OMe-4; III,OC₆H₂Bu'-2, 6-Me-4

Elemental analyses of the isolated complexes established their 1:2 (metal : ligand) stoichiometries (Table I).

All these complexes are dark grey to black solids, soluble in most of the common organic solvents. The molar conductance values of 10⁻³ M solutions of these complexes in nitrobenzene show their non-electrolytic behaviour. Molecular weight determinations in nitrobenzene by cryoscopic method are indicative of the dimeric nature of these complexes.

The infrared spectrum of the complexes show a complete absence of broad bands observed in the regions 3500-3400 cm⁻¹ and 1365-1330 cm⁻¹ due to intermolecular hydrogen bonded phenolic –OH group and v(ring) + δ(OH) respectively present in free phenols. The v(C — O) stretching vibrations in the region 1260-1225 cm⁻¹ in free phenols are significantly lowered by 50-60 cm⁻¹ in the complexes indicating coordination through oxygen. The coordination from oxygen of the substituted phenols is further confirmed by the appearance of new and sharp bands (not present in free ligand) at 510, 517 and 520 cm⁻¹ in MoCl₅(OC₆H₄Bu'-4), MoCl₅(OC₆H₄OMe-4), and MoCl₅(OC₆H₂Bu'-2, 6-Me-4) respectively assigned to the terminal v(Mo — O) stretching frequencies.

The presence of bands ~ 740 and 560 cm⁻¹ in the complexes have been attributed to v(As)(MoObMo) and v(kv)(MoObMo) vibrations respectively indicating that all the complexes are binuclear. Sharp bands observed ~ 340 cm⁻¹ have been assigned to v(Mo-Cl) stretching frequency.

The calculated room temperature magnetic moments (1.43, 1.39 and 1.51 BM) for the complexes MoCl₅(OC₆H₄Bu'-4), MoCl₅(OC₆H₄OMe-4) and MoCl₅(OC₆H₂Bu'-2, 6-Me-4) are lower than the magnetically dilute compounds of molybdenum(V) (~efr value for one unpaired electron 1.73-1.70 B.M.). This reflects antiferromagnetic coupling between molybdenum(V) metal atoms bridged through aryloxy groups. Furthermore, observed variation in the magnetic moment values

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour, physical state</th>
<th>Found (Calcd), %</th>
<th>( \lambda_{\text{cm}} )</th>
<th>Mol. wt. Found (Calcd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MoCl₅(OC₆H₄Bu'-4)]₂(II)</td>
<td>Dark grey Solid</td>
<td>19.11 21.29 47.98 5.15 1.72</td>
<td>992(1001)</td>
<td></td>
</tr>
<tr>
<td>[MoCl₅(OC₆H₄OMe-4)]₂(II)</td>
<td>Black Solid</td>
<td>21.39 23.68 37.49 3.05 2.50</td>
<td>875(892)</td>
<td></td>
</tr>
<tr>
<td>[MoCl₅(OC₆H₂Bu'-2, 6-Me-4)]₂(II)</td>
<td>Black Solid</td>
<td>14.90 16.55 56.20 7.15 2.8</td>
<td>1260(1282)</td>
<td></td>
</tr>
<tr>
<td>[MoCl₅(OC₆H₄Bu'-4), Pr&quot;NH₃]</td>
<td>Brown Solid</td>
<td>17.08 18.95 49.15 6.28 2.59</td>
<td>540(559)</td>
<td></td>
</tr>
<tr>
<td>[MoCl₅(OC₆H₄OMe-4), Et₂NH]</td>
<td>Reddish Brown Solid</td>
<td>16.78 18.51 50.08 6.38 2.51</td>
<td>590(573)</td>
<td></td>
</tr>
<tr>
<td>[MoCl₅(OC₆H₄OMe-4), Bu&quot;NH₃]</td>
<td>Brown Solid</td>
<td>18.28 20.35 41.39 4.63 2.77</td>
<td>482(507)</td>
<td></td>
</tr>
<tr>
<td>[MoCl₅(OC₆H₄OMe-4), PrNH₂]</td>
<td>Light brown Solid</td>
<td>18.88 20.88 40.17 4.38 2.77</td>
<td>492(521)</td>
<td></td>
</tr>
<tr>
<td>[MoCl₅(OC₆H₄OMe-4), Bu'NH₂]</td>
<td>Light brown Solid</td>
<td>18.17 20.31 41.30 4.61 2.56</td>
<td>492(521)</td>
<td></td>
</tr>
<tr>
<td>[MoCl₅(OC₆H₄Bu'-2, 6-Me-4), Pr&quot;NH₂]</td>
<td>Brown Solid</td>
<td>13.59 15.09 30.63 4.48 1.78</td>
<td>700(741)</td>
<td></td>
</tr>
</tbody>
</table>
seem to be markedly dependent upon the nature of the substituent on the ring of the aryloxide ligand i.e. its electron releasing tendency and size. With an increase in the electron releasing tendency of the substituents, the increased electron density in the π orbitals of the bridging ligand permits an increased interaction between the unpaired electron in the d-orbital of molybdenum ions and the oxygen πr electrons. The lowest value of magnetic moment in MoCl₃(O₆H₄Bu'-OMe-4)₂ and the next higher value in MoCl₃(O₆H₄Bu'-4)₂ indicates greater electron density in the πr orbitals of oxygen in the former case and less electron density in the latter case. However, in spite of the high electron releasing effect of tert-butyl groups in 2, 6-di-t-butyl-4-methylphenol, the bulky nature of the groups and thereby the role of steric interactions result into weak antiferromagnetic coupling and hence largest magnetic moment values.

The electronic absorption spectra of the complexes MoCl₃(O₆H₄Bu'-4)₂, MoCl₃(O₆H₄OMe-4)₂ and MoCl₃(O₆H₄Bu'-2, 6-Me-4)₂ in acetonitrile exhibits only one broad unsymmetrical band observed at 20950, 22275 and 20400 cm⁻¹ respectively. The band positions move in a manner than can be related to the aryloxide ligand field strength to cause d-orbital splittings. Thus, from the magnetic moment values and electronic absorption spectral data, the ligand OC₆H₄Bu'-4 is the strongest ligand followed by OC₆H₄Bu'-4 and OC₆H₄Bu'-2, 6-Me-4.

Based on the above studies, these complexes may tentatively be proposed to have a dimeric structure bridged through aryloxy groups involving distorted octahedral coordination around molybdenum metal atom.

The DTA/TGA curves of the complexes MoCl₃(O₆H₄Bu'-4)₂, MoCl₃(O₆H₄OMe-4)₂ and MoCl₂(O₆H₂Bu'-2, 6-Me-4)₂ in air, have indicated them to be stable up to 95°C, 92°C and 70°C respectively and begin to lose weight ~100°C, 95°C and 78°C. The decomposition seems to proceed in two stages. An initial weight loss of 56.12%, 51.28% and 65.79% for I, II and III respectively and begin to lose weight in the regions 1090-1020 cm⁻¹, 1190-1170 cm⁻¹ and 1145-1130 cm⁻¹ in secondary amines and 1230-1030 cm⁻¹ in tertiary amines shift to higher spectral regions in the complexes which is in agreement with the previous reports. Thus it is proposed that the complexes of MoCl₃(O₆H₄Bu'-4)₂, MoCl₃(O₆H₄OMe-4)₂ and MoCl₃(O₆H₂Bu'-2, 6-Me-4)₂ with amines have an octahedral arrangement around molybdenum. However, no evidence for aminolysis has been obtained.

From these studies, it may be concluded that molybdenum-chlorine bond is comparatively stable than the molybdenum-oxygen bond in the complexes.

Reactions with amines

The reactions of MoCl₃(O₆H₄Bu'-4)₂, MoCl₃(O₆H₄OMe-4)₂ and MoCl₂(O₆H₂Bu'-2, 6-Me-4)₂ complexes with various aliphatic amines such as diethylamine, n-propylamine, isopropylamines, n-butylamine, t-butylamine and triethylamine in equimolar ratio lead to the formation of complexes of composition [MoCl₃(OAr)₂] amine. The elemental analyses of the complexes are in accordance with the proposed stoichiometry (Table I). They are hygroscopic and change their colour on exposure to moisture. The molar conductance values indicate them to be non-electrolytes while the cryoscopic molecular weight determinations indicate their monomeric nature. A significant feature of the IR spectra of the complexes is the disappearance of bands due to the bridging Mo—Mo modes observed in the parent compounds which suggests a possible breakdown of the dimeric structure of the compounds I, II and III on reacting with amines. The appearance of new bands ~320 cm⁻¹ assigned to ν(Mo—N) stretching frequencies have confirmed that coordination of the amine to molybdenum has occurred.

The infrared spectra of the complexes also exhibit bands in the region 3450-3200 cm⁻¹ due to ν(NH) stretching vibrations. The occurrence of νNH in the lower region compared to those of free amines suggest that bonding of N-H to molybdenum has occurred. The bands observed in the regions 1650-1580 cm⁻¹ and 1580-1490 cm⁻¹ in primary and secondary amines respectively are slightly shifted towards lower regions. The C—N stretching absorptions occurring in the regions 1090-1020 cm⁻¹, 1190-1170 cm⁻¹ and 1145-1130 cm⁻¹ in secondary amines and 1230-1030 cm⁻¹ in tertiary amines shift to higher spectral regions in the complexes which is in agreement with the previous reports. Thus it is proposed that the complexes of MoCl₃(O₆H₄Bu'-4)₂, MoCl₃(O₆H₄OMe-4)₂ and MoCl₃(O₆H₂Bu'-2, 6-Me-4)₂ with amines have an octahedral arrangement around molybdenum. However, no evidence for aminolysis has been obtained.

References

17 Stewart J E, J chem Phys, 30 (1959) 1259.