Synthesis, characterisation and adduct formation of (3,4-dimethylphenoxo) tantalum(V) chlorides

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New 3,4-dimethylphenoxotantalum(V) chlorides of the type Ta(OC₆H₃Me₂-3,4)x Cl₅₋ₓ (1a-c), (where x = 1,2,3) have been synthesised by the interaction of tantalum(V) chloride and 3,4-dimethylphenol in benzene (or dichloromethane), under refluxing conditions. Treatment of 1a-c with donor ligands such as pyridine (Py) or tetrahydrofuran(THF) yields molecular adducts of the types, Ta(OC₆H₃Me₂-3,4)x Cl₅₋ₓ(Py) (2a-c) and Ta(OC₆H₃Me₂-3,4)x Cl₅₋ₓ(THF) (3a-c) (x = 1,2,3). Interaction of sodium 3,4-dimethylphenol with TaCl₅ in THF and benzene in different stoichiometric ratios yields adducts of the type Ta(OC₆H₃Me₂-3,4)xCl₅₋ₓ(THF) (3e-c) (x = 3,4,5). These derivatives have been characterised by elemental analyses, IR and PMR spectral data as well as molecular weight determinations.

During recent years, an increasing number of publications has appeared on tantalum(V) phenoxides, particularly with sterically demanding phenoxide ligands1−7.

Alkoxides, aryloxides and dialkyamide chemistry of early transition metals in higher oxidation state is characterised by the interaction of lone pair electrons in p-orbitals of σ-bonded oxygen or nitrogen atom of the ligand with the vacant d-orbitals of the metal7−11. This tends to attenuate the Lewis acidity of such derivatives.

Despite such extensive studies on sterically hindered aryloxides of tantalum(V), very few compounds in which tantalum is bonded to relatively less demanding aryloxide ligands have been reported in recent years. Further substitution on the phenyl ring is expected to enhance electron density around tantalum due to σ−d interaction, reducing the electrophilic character of the metal centre.

In view of the above, synthesis and spectroscopic and coordination chemistry of chloro(3,4-dimethylphenoxo) tantalum(V) is of considerable interest, which forms the subject matter of this paper.

Material and Methods
The glass apparatus used were preheated at 150° for 2 hr and cooled in a desiccator.

Tantalum pentachloride (BDH/Fluka; 99.9%), was used as such; 3,4-dimethylphenol (Fluka) was crystallised from n-hexane followed by distillation at 60°/0.3 mm Hg. It was obtained as a white crystalline solid, m.p.64°.

Tetrahydrofuran(b.p.65°) (BDH/E Merck,AR), n-hexane(b.p.61°) and benzene(b.p.80.1°) (BDH/E Merck,AR) were dried over sodium/benzophenone ketyl12.

IR spectra were recorded in nujol using CsI cells in the range 4000-200cm⁻¹ on a Perkin-Elmer 577 instrument and the PMR spectra at 85.69 MHz on a JEOL-FX 90Q NMR instrument. Molecular weights were determined ebullioscopically.

(a) Preparation of Ta(OC₆H₃Me₂-3,4)Cl₅ (1a)
To a suspension of TaCl₅(1.11g, 3.11 mmole) in dichloromethane (40 ml), was added 3,4-dimethylphenol (0.38g, 3.11 mmole) and the reaction stirred for 4hr followed by refluxing for 4hr. After removal of the excess solvent under reduced pressure, 1a (1.38g, 100%) was obtained as a red brown solid.

(b) Preparation of Ta(OC₆H₃Me₂-3,4)Cl₄(THF) (1b)
Addition of 3,4-dimethylphenol (1.13g, 9.25 mmole) to a suspension of TaCl₅(1.65g, 4.61 mmole) in benzene (40 ml) resulted in an exothermic reaction with evolution of HCl gas. The colour of the reaction mixture changed from yellow-lemon to orange. The reaction mixture was refluxed for 18hr. Removal of the excess solvent under reduced pressure furnished 1b (2.38g, 98.8%) as yellow-orange powdery solid.

Complex Ta(OC₆H₃Me₂-3,4)Cl₂ (1c) was prepared in a similar manner.

(c) Preparation of Ta(OC₆H₃Me₂-3,4)₄Cl(THF) (3d)
A clear solution of sodium 3,4-dimethylphenolate, prepared from sodium (0.37g, 16.05 mmole) and 3,4-dimethylphenol (1.96g, 16.05 mmole) in THF (40 ml), was slowly added to a suspension of TaCl₅ (1.43g, 4.0 mmole) in benzene (20 ml). After refluxing for 6hr, the reaction mixture was filtered to remove the precipitated white sodium chloride (0.93g, 15.95 mmole),
and the filtrate concentrated under reduced pressure (0.3 mm Hg) to afford 3d (3.12g, 100%) as a light-yellow viscous mass.

In a similar manner were prepared Ta(OC₆H₃Me₂-3,4)Cl₂(THF) (3c) and Ta(OC₆H₃Me₂-3,4)₂(THF) (3e).

(d) Preparation of Ta(OC₆H₃Me₂-3,4)Cl₄ (Py) (2a)
Pyridine (0.12g, 1.32 mmole) in benzene (10 ml) was added to a benzene (30 ml) solution of l (0.58g, 1.30 mmole). The reaction mixture was stirred for 18hr. Removal of excess benzene under reduced pressure (0.3 mm Hg) afforded the adduct 2a (0.70g, 100%) as a yellow-orange powdery solid.

Similar procedure was employed to prepare Ta(OC₆H₃Me₂-3,4)Cl₃(Py) (2b), Ta(OC₆H₃Me₂-3,4)Cl₂(Py) (2c), Ta(OC₆H₃Me₂-3,4)Cl(Py) (2d), Ta(OC₆H₃Me₂-3,4)Cl₄ (THF) (3a), Ta(OC₆H₃Me₂-3,4)Cl₃ (THF) (3b) and Ta(OC₆H₃Me₂-3,4)Cl₂(THF) (3c).

Results and Discussion
Treatment of tantalum(V) pentachloride with 3,4-dimethylphenol in 1:1 molar ratio in benzene under refluxing condition leads to the formation of a mixture of mono- and bis-products instead of the expected Ta(OC₆H₃Me₂-3,4)Cl₄. However, the same reaction when carried out in dichloromethane at room temperature followed by refluxing for 4hr, leads to a brown-red solid product having the composition Ta(OC₆H₃Me₂-3,4)Cl₄ (1a).

When the above reaction is carried out in 1:2 and 1:3 molar ratios under refluxing conditions over a period of 18hr and 36hr respectively, the products obtained have been characterised as Ta(OC₆H₃Me₂-3,4)₂Cl₂ (1b) and Ta(OC₆H₃Me₂-3,4)₃Cl₂ (1c).

The tetrakis and pentakis-derivatives of the type Ta(OC₆H₃Me₂-3,4)Cl₄, Ta(OC₆H₃Me₂-3,4)Cl₃ and Ta(OC₆H₃Me₂-3,4)Cl₂ could not be isolated in analytically pure form by the direct reaction of tantalum(V) chloride with 3,4-dimethylphenol in molar ratios of 1:4 and 1:5 respectively. However, the reaction of sodium 3,4-dimethylphenolate (in tetrahydrofuran) with benzene suspension of tantalum(V) pentachloride in 4:1 and 5:1 ratios under refluxing conditions lead to the formation of addition complexes, Ta(OC₆H₃Me₂-3,4)Cl₄(THF) (3d) and Ta(OC₆H₃Me₂-3,4)Cl₃(THF) (3e) respectively (see Eq. 1).

\[ \text{TaCl}_5 + x(\text{NaOC}_6\text{H}_3\text{Me}_2-3,4) + \text{THF} \xrightarrow{\text{PhH}} \text{Ta(OC}_6\text{H}_3\text{Me}_2-3,4)_x\text{Cl}_5 \cdot x(\text{THF}) + x \text{NaCl} \]

\[ x = 4; \ 3d; \ x = 5; \ 3e \]

In a similar manner adduct of the type Ta(OC₆H₃Me₂-3,4)Cl₂(THF) (3c) has also been isolated.

The interaction of 1a-c with pyridine or tetrahydrofuran in 1:1 stoichiometric ratio in benzene leads to the formation of addition complexes 2a-c and 3a-c, respectively.

All these derivatives are coloured solids or viscous mass (Table 1), soluble in common organic solvents (such as benzene, toluene, dichloromethane, chloroform and carbon tetrachloride). The colour of these derivatives may be due to the charge transfer from the aryloxy ligand to the vacant d orbitals of tantalum (V).

The molecular weight determinations of (1a-c) appear to indicate their dimeric nature in boiling benzene.

Infrared studies
Characteristic v(C-O) & v(Ta-O) (bridging and terminal) in the IR spectra of the compounds prepared presently have been assigned by a comparison of these spectra with that of Ta₂(OEt)₁₀.¹⁴ The v(C-O) modes in these new aryloxy derivatives appear at lower wavenumbers in the region 1188-1200 cm⁻¹ as compared to that of the parent phenol¹⁵ (Δv = 35 ± 5 cm⁻¹). The v(Ta-O) modes in 1a-c, which appear in the region of 575 ± 10 and 540 ± 10 cm⁻¹ are consistent with the terminal and bridging modes respectively. The v(Ta-Cl) in 1a-c appear in the region of 380 ± 10, 370 ± 5 and 345 ± 5 cm⁻¹. This is in conformity with the terminal v(Ta-Cl) modes in octahedral species¹⁶,¹⁷. In the molecular adducts with tetrahydrofuran 3a-3e or pyridine 2a-d, the v(Ta-O) and v(Ta-Cl) modes appear in the region of 595 ± 10, 560 ± 20; and 380 ± 5, 355 ± 5, 340 ± 10 cm⁻¹ respectively. In addition, in the IR spectra of 3a-e the v(C-O-C) modes appear, in the range of 970-1020 cm⁻¹. The v(C = N) in the complexes 2a-d are observed in the range of 1610-1625 cm⁻¹.

In these new adducts of pyridine and THF v(C = N) and v(C-O-C) modes are observed at higher and lower wavenumbers as compared to those of free pyridine and THF respectively. This is characteristic of coordination through nitrogen¹⁸ (in pyridine complexes) and oxygen¹⁹ (in THF complexes).

As expected the characteristic IR features of the new complexes prepared herein are indicative of a decrease in Lewis acidity of these chloro aryloxy derivatives with increase in the number of aryloxy ligand.

Proton magnetic resonance
In the PMR spectrum of 3,4-dimethylphenol the protons attached to C-2 and C-6 (both ortho to OH) appear at δ 6.65(d, J = 2.5Hz) (C₂-H) and 6.57(dd)
Table 1—Characterisation data of (3,4-dimethylphenoxo) tantalum(V) chlorides and their molecular adducts

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Reactants (g, mmole)</th>
<th>Product yield (g)</th>
<th>Physical characteristics</th>
<th>Analysis (Ta, Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TaCl₅ + HOC₆H₃Me₂-3,4, (1.11, 3.10) (0.38, 3.11)</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₄ (1a)</td>
<td>Brown-red solid, soluble in benzene, CH₂Cl₂</td>
<td>Ta (40.17), Cl (31.22)</td>
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<tr>
<td>2</td>
<td>TaCl₅ + HOC₆H₃Me₂-3,4, (1.65, 4.61) (1.13, 9.25)</td>
<td>Ta(OC₆H₃Me₂-3,4)₂Cl₂ (1b)</td>
<td>Yellow-orange powder, soluble in benzene</td>
<td>Ta (34.54), Cl (19.85)</td>
</tr>
<tr>
<td>3</td>
<td>TaCl₅ + HOC₆H₃Me₂-3,4, (1.35, 3.75) (1.36, 11.15)</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₃ (1c)</td>
<td>Yellow-lemon crystalline solid, soluble in benzene</td>
<td>Ta (29.74), Cl (11.82)</td>
</tr>
<tr>
<td>4</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₄ + Py, (0.58, 1.30) (0.12, 1.32)</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₄(Py) (2a)</td>
<td>Yellow-orange powder, partially soluble in benzene</td>
<td>Ta (35.09), Cl (26.82)</td>
</tr>
<tr>
<td>5</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₄ + Py, (0.71, 1.35) (0.13, 1.66)</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₄(Py) (2b)</td>
<td>Yellow-green viscous mass, slightly soluble in benzene</td>
<td>Ta (29.36), Cl (17.56)</td>
</tr>
<tr>
<td>6</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₄ + Py, (0.53, 0.86) (0.07, 0.92)</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₄(Py) (2c)</td>
<td>Yellow viscous mass, partially soluble in benzene</td>
<td>Ta (25.55), Cl (9.98)</td>
</tr>
<tr>
<td>7</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₄ + THF, (0.41, 0.91) 20ml</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₄(THF) (3a)</td>
<td>Green viscous mass, soluble in benzene, THF</td>
<td>Ta (34.88), Cl (27.22)</td>
</tr>
<tr>
<td>8</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₄ + THF, (0.37, 0.70) 20ml</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₄(THF) (3b)</td>
<td>Yellow-green viscous mass, soluble in benzene, THF</td>
<td>Ta (26.43), Cl (17.25)</td>
</tr>
<tr>
<td>9</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₄ + THF, (0.37, 0.60) 20ml</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₄(THF) (3c)</td>
<td>Yellow viscous mass, soluble in benzene, THF</td>
<td>Ta (26.13), Cl (10.05)</td>
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<tr>
<td>10</td>
<td>TaCl₅ + NaOC₆H₃Me₂-3,4, (2.12, 5.92) (2.56, 17.79) 40ml</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₃(THF) (3c)</td>
<td>Yellow-green viscous mass, soluble in benzene, THF</td>
<td>Ta (26.05), Cl (10.32)</td>
</tr>
<tr>
<td>11</td>
<td>TaCl₅ + NaOC₆H₃Me₂-3,4, (1.43, 4.00) (2.31, 16.05) 40ml</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl(THF) (3d)</td>
<td>Light-yellow viscous mass, soluble in benzene, THF</td>
<td>Ta (23.51), Cl (4.92)</td>
</tr>
<tr>
<td>12</td>
<td>TaCl₅ + NaOC₆H₃Me₂-3,4, (1.30, 3.65) (2.64, 18.37) 40ml</td>
<td>Ta(OC₆H₃Me₂-3,4)Cl₂(THF) (3e)</td>
<td>Light brown liquid, soluble in benzene; THF</td>
<td>Ta (21.02), Cl (21.07)</td>
</tr>
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</table>

(a) Calculated values are given in parenthesis, HOC₆H₃Me₂-3,4 = 3,4-dimethylphenol, THF = tetrahydrofuran, Py = pyridine.
(b) Tantalum and chloride were estimated gravimetrically (ref. 13).
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(C₆-H). The C₅-H appears as a doublet at δ 7.01 (J = 8.1 Hz).

The two methyl group protons are observed at δ 2.20(s) and 2.18(s) ppm because of their non-equivalent environments. These methyl group protons in aryloxo derivatives appear in the range δ 2.16-2.25, whereas aromatic protons at C-2,C-5 and C-6 are seen in the regions of δ 6.69-6.70, 6.92-7.10 and 6.36-6.79 ppm respectively. The α- and β-protons of coordinated THF in aryloxo derivatives are observed at δ 3.60 ± 0.20 and 1.80 ± 0.10 ppm respectively. As expected α-protons exhibit deshielding to the extent of δ 0.37 ppm.

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References