Synthesis and characterization of monooxovanadium(V)aryloxides

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The monooxovanadium(V)aryloxides of composition \( \text{VOCI}_3 \cdot n(\text{OAr}_1 \cdot 2)_n \) (where \( n = 1 \) to 3; \( \text{OAr}_1 = -\text{OC}_6\text{H}_2\text{Bu'}_2\cdot 2,6-\text{Me}-4 \) and \( \text{OAr}_2 = -\text{OC}_6\text{H}_4\text{N0}_\text{4r}_4 \)) have been synthesized by the reaction of \( \text{VOCI}_3 \) with 2,6-di-t-butyl-4-methylphenol and trimethylsilyl derivative of 4-nitrophenol respectively in CCl₄. The aryloxides have been characterized by IR, \(^1\text{H}-\text{NMR,UV-vis}\) spectral and elemental analysis.

Aryloxides and alkoxides have been the subject of significant interest and in fact phenolates are known to be the excellent ligands for vanadium providing not only stable complexes of the relatively rare \( \text{VO}^{3+} \) moiety\(^{13}\), but display interesting reactivity patterns such as the capability of dinitrogen fixation. Prompted by these observations and as part of comprehensive investigations on the preparation and properties of vanadyl aryloxides\(^{5-8}\), it was contemplated to synthesize a series of such complexes derived from 2,6-di-t-butyl-4-methylphenol (A) and 4-nitrophenol (B) with an aim to get an insight into the effects of substituent on the nature and properties of these complexes.

Vanadium in complexes was estimated as \( \text{V}_2\text{O}_3 \) and chlorine by Volhard's method. Carbon and hydrogen microanalyses were performed on a Coleman CHN analyzer. The IR spectra were recorded in KBr and Nujol mulls on a Beckmann IR 4250 spectrophotometer and \(^1\text{H}-\text{NMR}\) spectra on a Jeol JNM PMX 60 SI spectrometer using CDCl₃ as solvent. The monooxovanadium(V) 4-nitrophenoxides being insoluble in nature were made to dissolve by the addition of TFA. Electronic spectra were recorded on Beckmann Du-6 spectrophotometer using CH₃CN as solvent. Molecular weights were determined cryoscopically in nitrobenzene using Beckmann thermometer while conductance measurements in the same solvent were made on an Elíco conductivity bridge CM Type-82T using a 10⁻² M solution at 25°C.

Preparation of complexes \([\text{VOCI}_3 \cdot n(\text{OAr}_1 \cdot 2)_n]\) \((n = 1 \) to 3\)

To a solution of \( \text{VOCI}_3 \) (5.62 g, 0.032 mol) in dry CCl₄ (50 cm³) was added a solution of \( \text{Ar}_1\text{OH} \) (4.85 g, 0.032 mol; 9.71 g, 0.064 mol and 14.57 g, 0.096 mol respectively) in the same solvent in separate experiments. The reaction mixture was stirred for 2-3 h and then heated under reflux until no more evolution of HCl gas was observed. The resulting solution was filtered and the filtrate concentrated by distilling off the solvent was treated with pet. ether when black to shining black solids were obtained which were dried in vacuo (yield 78%).

Preparation of complexes \([\text{VOCI}_3 \cdot n(\text{OAr}_2 \cdot 2)_n]\)

A typical reaction procedure was as follows:

To a solution of \( \text{Me}_3\text{SiOAr}^2 \) (0.0212 mol) in CCl₄+MeCN was added a solution of \( \text{VOCI}_3 \) (3.68 g, 0.0212 mol) in CCl₄. The reaction mixture was stirred for 3-5 h followed by heating under reflux for another 2 h to ensure completion of reaction. The by-product \( \text{Me}_3\text{SiCl} \) and the solvents were distilled off and the resulting concentrated solution was treated with light petroleum when a fine solid separated out and was dried in vacuum. The yield of \( \text{VOCI}_3(\text{OAr}^2) \) by this method was 82%. Complexes of compositions \( \text{VOCI}(\text{OAr}^2)_2 \) and \( \text{VO}(\text{OAr}^2)_3 \) were prepared by the similar procedure using two and three equivalents of \( \text{Me}_3\text{SiOAr}^2 \).

Results and discussion

Complexes of compositions \([\text{VOCI}_3 \cdot n(\text{OAr}_1 \cdot 2)_n]\) \((n = 1 \) to 3\) have been successfully obtained in fairly
good yield (70-80%) by the direct reaction of VOCl₃ with 2,6-di-t-butyl-4-methylphenol (Ar¹OH) taken in appropriate molar ratios using CCl₄ as solvent medium, while preparation of VOCl₃·n(OAr²)ₙ involved the interaction of VOCl₃ with Me₃SiOAr² in CCl₄+CH₃CN solvent mixture according to the reactions:

$$\text{VOCl}_3 + n \text{HOAr}^1 \rightarrow \text{VOCl}_3 \cdot n(\text{OAr}^1)_n + n \text{HCl}$$

$$\text{VOCl}_3 + n \text{Me}_3\text{SiOAr}^2 \rightarrow \text{VOCl}_3 \cdot n(\text{OAr}^2)_n + n \text{Me}_3\text{SiCl}$$

The formation of complexes was readily discerned from elemental analyses. The complexes do not exhibit sharp melting points. Interestingly, monooxovanadium(V) 2,6-di-t-butyl-4-methylphenoxides were air stable, soluble in most common organic solvents while analogous 4-nitrophenoxides were found to be insoluble. Accordingly, the molecular weight and molar conductance determinations of VOCl₃·n(OAr¹)ₙ showed their monomeric and non-electrolytic nature. The similar studies of VOCl₃·n(OAr²)ₙ, however, had to be precluded because of their insolubility in suitable solvents.

The most important diagnostic and characteristic bands of the IR spectra of monooxovanadium(V) aryl oxide derivatives are V Cv=Ol, V Cv-O and V Cv-O).9 stretching vibrations. The V Cv=Ol for VOCl₂(OAr¹) (I), VOCl(OAr¹)₂ (II) and VO(OAr¹)₃ (III) have been observed at 978, 962 and 984 cm⁻¹ while for the 4-nitrophenoxides this band appeared at 972, 977 and 995 cm⁻¹. The V Cv=Ol stretch in vanadyl salts is known to occur between 1035 and 935 cm⁻¹ (ref. 10) and has also been found to be sensitive11 to the donor ability of the ligand which coordinates the vanadium atom at the position opposite to the oxygen atom. The displacement of V Cv=Ol stretch to lower frequencies in the complexes under investigation, compared to the terminal V=O stretch of VOCl₃ implies substantial weakening of the bond upon strong σ and π-electron donation by the phenoxide ions. This lowering further seems to suggest that more weakly associated complex will exhibit the higher energy V=O stretch12. The V Cv=Ol stretching vibration has been observed at 1152, 1140 and 1145 cm⁻¹ for I, II and III while the bands at 1125, 1136 and 1158 cm⁻¹ have been attributed to V Cv=Ol mode in monooxovanadium(V)-nitrophenoxides VOCl₂(OAr²) (IV), VOCl(OAr²)₂ (V) and VO(OAr²)₃ (VI) respectively. The observed pattern of lowering in V Cv=Ol mode coupled with V Cv-O stretch can be rationalized for 2,6-di-t-butyl-4-methylphenoxide complexes as a sum of electronic and steric effects while only electronic effects seem to play a role in monooxovanadium(V)nitrophenoxide derivatives.

Table I — Analytical data of monooxovanadium(V) aryl oxides

<table>
<thead>
<tr>
<th>Complex (colour)</th>
<th>Found (Calcld), %</th>
<th>Ω mol⁻¹ cm² cm⁻¹</th>
<th>M. wt in PhNO₂ mol⁻¹</th>
<th>M. wt in Phenol (Calcld)</th>
</tr>
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<tbody>
<tr>
<td>VOCl₂(OAr¹)</td>
<td>14.31</td>
<td>20.01</td>
<td>48.97</td>
<td>6.88</td>
</tr>
<tr>
<td>Black</td>
<td>(14.28)</td>
<td>(19.89)</td>
<td>(50.42)</td>
<td>(6.44)</td>
</tr>
<tr>
<td>VOCl(OAr¹)₂</td>
<td>10.01</td>
<td>7.11</td>
<td>65.81</td>
<td>8.92</td>
</tr>
<tr>
<td>II</td>
<td>(9.44)</td>
<td>(6.56)</td>
<td>(66.65)</td>
<td>(8.51)</td>
</tr>
<tr>
<td>Shining Black</td>
<td>7.27</td>
<td>—</td>
<td>75.13</td>
<td>9.69</td>
</tr>
<tr>
<td>VO(OAr¹)₃</td>
<td>(7.04)</td>
<td>—</td>
<td>(74.59)</td>
<td>(9.53)</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purple Black</td>
<td>19.13</td>
<td>26.08</td>
<td>26.94</td>
<td>2.08</td>
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<tr>
<td>VOCl₂(OAr²)</td>
<td>(18.47)</td>
<td>(25.72)</td>
<td>(26.09)</td>
<td>(1.45)</td>
</tr>
<tr>
<td>IV</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dull Green</td>
<td>13.94</td>
<td>10.09</td>
<td>39.86</td>
<td>2.93</td>
</tr>
<tr>
<td>VO(OAr²)₂</td>
<td>(13.47)</td>
<td>(9.38)</td>
<td>(38.04)</td>
<td>(2.11)</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>11.12</td>
<td>—</td>
<td>45.36</td>
<td>3.17</td>
</tr>
<tr>
<td>Black</td>
<td>(10.60)</td>
<td>(44.91)</td>
<td>(2.49)</td>
<td></td>
</tr>
</tbody>
</table>

(OAr¹ = OC₆H₄C₂H₅-2,6-Me-4; OAr² = OC₆H₄NO₂-4)
nature of the substituent in aromatic ring and in the present study, following order of complexing ability in two different series of complexes has been observed:

\[ \text{VOCI(OAr}^1\text{)}_2 > \text{VOCI}_2(\text{OAr}^1) > \text{VO(OAr}^1\text{)}_3 \]

\[ \text{VOCI}_2(\text{OAr}^2) > \text{VOCI}_2(\text{OAr}^2) > \text{VO(OAr}^2\text{)}_3 \]

The bands -590 cm\(^{-1}\) have been assigned to \(v_{(\nu O)}\) mode in these complexes while bands -360 cm\(^{-1}\) have been attributed to \(v_{\nu CH}\) mode in their respective chloroaryloxides.

In the room temperature \(^1\)H NMR spectra of the complexes VOCI\(_{3-n}\)(OAr)\(_n\), the complete absence of a signal at \(\delta 4.78\) due to phenolic -OH proton in free 2,6-di-t-butyl-4-methylphenol has confirmed the deprotonation of this group. The complexes have displayed three resonances at \(\delta 8.1\) (S, 18H, Ar-C(CH\(_3\))\(_2\)-2,6; \(\delta 2.2\) (S, 3H, Ar-CH\(_3\)) and \(\delta 7.14\) - 7.31(S, 2H, CH (aromatic) attributed to t-butyl, methyl and m-aromatic ring protons respectively. These resonances indicate that there is a significant downfield shift for m-aromatic protons only while the other remain almost unaltered. These have appeared at \(\delta 7.28, \delta 7.31\) and \(\delta 7.14\) for I, II and III respectively compared to that of uncoordinated phenol at \(\delta 6.8\). Interestingly, a larger downfield shift in the case of complex VOCI(OAr\(_1\))\(_2\) suggests a larger donation of electron density towards vanadium metal. This observation is in conformity with the infrared spectral studies as well.

The \(^1\)H NMR spectrum of the complexes VOCI\(_{3-n}\)(OAr\(_2\)) have displayed two resonances in the ranges \(\delta 8.2-8.5\) (d, Ar-H\(_m\)) and \(\delta 7.0-7.3\) (d, Ar-H\(_o\)) for meta and ortho protons respectively. The corresponding proton resonances in Me\(_3\)SiOAr\(_2\) appeared at \(\delta 8.0\) and \(\delta 6.76\) respectively. These downfield shifts may be ascribed to the deshielding of these protons due to electron withdrawing \(-\text{NO}_2\) substituent in the aromatic ring.

The UV-vis spectra of the complexes (10\(^{-3}\) mol dm\(^{-3}\) solutions) examined in the region 200-700 nm have displayed a single intense band in the range 372-500 nm (Table 1). The lack of d-electrons of vanadium(V) and the magnitude of the extinction coefficients (2400-3200 M\(^{-1}\) cm\(^{-1}\)) suggest that these must be either due to ligand to metal charge-transfer excitation or internal transition. Intense charge-transfer spectra are known to be observed for monooxovanadium(V) phenolates\(^{13,14}\). Interestingly, the position of the energy bands appears to be highly sensitive to the nature of the substituent associated with the coordinated phenoxy group and therefore it seems reasonable to assign this as a LMCT transition since electron withdrawing groups are expected to lower the energy of phenolate oxygen orbitals resulting in an increasing ligand to metal energy gap.

To conclude, an interesting trend has, apparently emerged with regard to the solubility of the newly synthesised complexes. The complexes derived from sterically bulky 2,6-di-t-butyl-4-methylphenol are soluble in organic solvents while the analogous 4-nitrophenoxy oxovanadium(V) complexes are insoluble. This behaviour has been rationalised in terms of electronic and steric effects, due to the substituents in the phenyl ring of the phenols.

References

9 Nakamoto K, Infrared spectra of inorganic and coordination compounds (John Wiley, NY) 1963, 221.