Chapter 6

Synthesis and Assessment of Structure of Alkali-metal and Ammonium Diaquofluoro-peroxovanadate(IV) Complexes $\left[\text{VO(O}_2\text{)}\text{F (H}_2\text{O)}_2\right]^{-}$

Studies on various aspects of peroxovanadium chemistry has gained considerable current interest\(^1\)\text{--}^6 probably because of the biochemical significance of peroxovanadium compounds.\(^7\) While most of the recent papers on the topic deal with the solution chemistry of peroxovanadium complexes, synthesis and structural assessment of peroxo- and hetero-ligand peroxo compounds of vanadium have received much less attention. In a continuation of studies on the synthesis and structural assessment of hetero-ligand peroxo-compounds of vanadium(V)\(^8\),\(^9\) (Chapters 3 to 5), it was thought worthwhile to synthesise hetero-ligand peroxovanadate(IV) compounds

* The work described in this Chapter has been accepted for publication:

Accordingly the reaction of alkali-metal and ammonium tetrafluoro-oxovanadates (V), $A \sqrt{\text{VOF}_4\text{F}}_4$ ($A = K, Rb, Cs$ or $NH_4$), with 6% hydrogen peroxide under a weak acidic conditions ($pH \lesssim 4$) was performed which enabled the synthesis of a series of alkali-metal and ammonium diaquo-fluoro-oxoperoxovanadates(IV), $A \sqrt{\text{VO(O}_2\text{F(H}_2\text{O)}_2\text{F}}_4$; these peroxovanadate(IV) compounds were obtained, for the first time, in the solid state.

The present chapter describes the synthesis and structural assessment of alkali-metal and ammonium diaquo-fluoro-oxoperoxovanadate(IV) complexes, $A \sqrt{\text{VO(O}_2\text{F(H}_2\text{O)}_2\text{F}}_4$ ($A = K, Rb, Cs$ or $NH_4$).

Experimental

The chemicals used were all reagent grade products (E. Merck, B.D.H., IDPL and Sarabhai M. Chemicals).

Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer.

Electronic spectral measurements were made on a BECKMAN model UV-26 spectrophotometer.

Magnetic susceptibility measurements were made by the Gouy Method, $\sqrt{\text{Co(NCS)}_4\text{F}}_4$ was the calibrant.
Molar conductance measurements were made using a Philips PR9500 conductivity bridge.

The pH of the reaction solutions was measured with a Systronic Type 335 digital pH meter and also with pH indicator (B.D.H.) paper.

**Preparation of Alkali-metal and Ammonium Difluorides, AHF\(_2\) (A= K, Rb, Cs or NH\(_4\)).** These compounds were prepared by the methods developed in this laboratory (described in Chapter 1).

**Preparation of Alkali-metal and Ammonium Tetrafluoro-oxovanadates(V), A\(\overset{\circ}{\text{V}}\text{O}_4\)\(_7\) compounds were prepared by the methods already described in Chapter 1.

**Synthesis of Alkali-metal and Ammonium Diaquo-fluoro-oxoperoxovanadate(IV) complexes, A\(\overset{\circ}{\text{V}}\text{O}(\text{O}_2)\text{F}(\text{H}_2\text{O})_2\)\(_7\) (A = K, Rb, Cs or NH\(_4\)).** As the methods of synthesis of these complexes are similar, only a representative method is described.

Freshly prepared alkali-metal or ammonium tetrafluoro-oxovanadate(V), A\(\overset{\circ}{\text{V}}\text{O}_4\)\(_7\) was dissolved in 6% hydrogen peroxide, maintaining the molar ratio A\(\overset{\circ}{\text{V}}\text{O}_4\)\(_7\) : \(\text{H}_2\text{O}_2\) at 1 : 12 (pH ca 4), with gentle stirring. The red solution thus obtained was cooled in an ice-bath for ca 20 min. Ethyl alcohol was added,
in excess, with constant stirring and orange-red microcrystalline alkali-metal or ammonium diaquofluorooxocperoxovanadate(IV), $\frac{A}{\sum VO(O_2)F(H_2O)_2}$ was obtained. The compound was separated by centrifugation and washed several times with ethanol, and finally dried over diphosphorus pentoxide.

The amounts of reagents used and the yields of the compounds $\frac{A}{\sum VO(O_2)F(H_2O)_2}$ are given in Table 1.

Table 1. Amounts of Reagents Used and Yields of
$\frac{A}{\sum VO(O_2)F(H_2O)_2}$ (A = K, Rb, Cs or NH$_4$) compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield in g (%)</th>
<th>Amount of $A/\sum VOF_4$ in g(mmol)</th>
<th>Amount of 6% H$_2$O in ml(mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4/\sum VO(O_2)F(H_2O)_2$</td>
<td>0.4 (75)</td>
<td>0.5 (3.1)</td>
<td>22.0 (38.5)</td>
</tr>
<tr>
<td>K/\sum VO(O_2)F(H_2O)_2</td>
<td>0.3 (57)</td>
<td>0.5 (2.8)</td>
<td>19.0 (33.5)</td>
</tr>
<tr>
<td>Rb/\sum VO(O_2)F(H_2O)_2</td>
<td>0.5 (68)</td>
<td>0.7 (3.1)</td>
<td>22.0 (38.5)</td>
</tr>
<tr>
<td>Cs/\sum VO(O_2)F(H_2O)_2</td>
<td>0.5 (69)</td>
<td>0.7 (2.5)</td>
<td>17.0 (30)</td>
</tr>
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</table>
**Elemental Analyses.** Vanadium estimation was done volumetrically. A solution of the peroxovanadate(IV) compounds, made slightly alkaline with a dilute sodium hydroxide solution, was boiled in order to completely expel the peroxo oxygen and to convert vanadium(IV) to vanadium(V). The solution was cooled and neutralized with dilute sulphuric acid. A near-boiling solution of vanadium(V) was treated with a stream of sulphur dioxide for 10-15 min, and then with a rapid stream of carbon dioxide to expel any excess of sulphur dioxide. The vanadium(IV) solution thus obtained was then cooled to ca 80°C, and titrated with a standard potassium permanganate solution.\(^{12}\)

The peroxide content in each of the compounds was determined by iodometry,\(^{13}\) and also by titration with a standard Ce\(^{4+}\) solution\(^{14}\) (vide Chapter 3).

Fluoride, potassium and nitrogen were estimated by the methods already described in Chapter 1.

The analytical data, magnetic moment values, IR band positions and electronic spectral data are set out in the Table 2.
Results and Discussion

In the course of the earlier studies (Chapters 3 and 4) involving the synthesis of peroxofluoro-compounds of vanadium(V), a red solution was obtained containing V\(^{5+}\), alkali-metal or ammonium fluoride, AF, and H\(_2\)O\(_2\) at a pH ca 4, and presumed that the species responsible for such a colour must be different from those isolated previously (Chapters 3 and 4). Further, it was expected that the number of peroxo-groups bonded to vanadium in acidic medium\(^5,12\) would be less than that in alkaline medium, and that H\(_2\)O\(_2\) would probably be able to reduce CV\(^{5+}\) to V\(^{4+}\) in an acidic medium. In view of the above considerations the reaction between \(\text{A} \left[\text{VOF}_4\right]^-\) and 6% hydrogen peroxide was carried out and a red solution was obtained. The pH of the solution measured immediately after the formation of the red colouration was found to be ca 4. The complex species responsible for the red colouration was isolated in the solid state as its alkali-metal and ammonium salts, \(\text{A} \left[\text{VO(O}_2\text{P(H}_2\text{O})_2\right]^-\), by addition of alcohol which possibly facilitated the reduction of V\(^{5+}\) to V\(^{4+}\), and precipitation of the complex. The occurrence of reaction between alkali-metal or ammonium...
tetrafluoro-oxovanadate(V), $\text{A}^{\text{VOF}_4\text{F}}$ and $\text{H}_2\text{O}_2$ was ascertained by the appearance of a new band ca 890 cm$^{-1}$, due to the $\text{D}_{\text{O-O}}$ mode of a coordinated peroxide, $\text{O}_2^{2-}$, from a small amount of the sample isolated from the solution. It was previously reported$^{15}$ that $\text{K}_2^{\text{V}_2\text{O}_3\text{(O}_2\text{)}_2\text{F}_2\text{F}}$ was isolated from the reaction of $\text{V}_2\text{O}_5$, 4% hydrofluoric acid, and $\text{H}_2\text{O}_2$ at high acidity and $\text{K}_2^{\text{VO(O}_2\text{)}_2\text{F}}$ was isolated at pH 4. In the present case, however, the reaction of $\text{A}^{\text{VOF}_4\text{F}}$ with $\text{H}_2\text{O}_2$ at pH 4 followed by addition of ethanol afforded compounds of the type $\text{A}^{\text{VO(O}_2\text{)}\text{F(H}_2\text{O)}_2\text{F}}$.

Characterization and Assessment of Structure. The alkali-metal and ammonium diaquofluoro-oxodiperoxo-oxovanadates(IV), $\text{A}^{\text{VO(O}_2\text{)}\text{F(H}_2\text{O)}_2\text{F}}$, are all orange-red, microcrystalline products. The compounds are insoluble in organic solvents. They decompose in water thus precluding their molar conductance measurements. In fact, owing to their instability, most of the peroxovanadium compounds do not permit molar conductance measurements.$^{8,9,16}$ The compounds $\text{A}^{\text{VO(O}_2\text{)}\text{F(H}_2\text{O)}_2\text{F}}$ can, however, be stored in sealed containers and their stability can be ascertained by periodic estimation of the peroxide content. The estimation of peroxide is crucial in order to determine the number of $\text{O}_2^{2-}$ ligands bonded to the
metal centre. The peroxide content was estimated by 
cerimetry (Ce⁴⁺), and also by iodometry, the results 
of which conclusively suggest the presence of one 
O₂²⁻ group coordinated to vanadium(IV). The direct 
titration with a standard KMnO₄ solutions showed the 
involution of three electron equivalents, two of 
which originated from O₂²⁻ and the third was due to 
the process V⁴⁺ → V⁵⁺ + e. The room temperature 
magnetic susceptibility measurements gave the magnetic 
moment values of the compound (295K), lying between 
1.70 and 1.75 B.M. (1 B.M. = 9.27 × 10⁻²⁴ JT⁻¹) 
are consistent with the presence of vanadium(IV) 
and are in excellent agreement with those reported 
in the literature for V⁴⁺ systems.¹⁷

The optical spectra of potassium and ammonium 
diaquafluoro-oxoeperoxovanadates(IV), A[VO(O₂)F(H₂O)₂]⁻⁻ 
(A = K or NH₄), recorded immediately after preparing 
solutions in cold dilute H₂O₂, showed three absorptions 
at ca. 11,700, ca. 17,699, and > 21,400 cm⁻¹, 
with the last being obscured by strong charge-transfer 
transitions. The first two bands have been assigned 
to e ← b₂ and b₁ ← b₂ transitions respectively and 
agree very well with the reported spectra of oxovanadium(IV) 
complexes,¹⁸ giving strong evidence for the presence of
vanadium(IV) in the orange-red peroxovanadium compounds. These observations also support the very recent report\(^6\), concerning the existence of peroxovanadium(IV) in solutions.

The infrared spectra (Table 2) of the series of four salts are similar, showing absorptions at ca 3160 m, br, ca. 1,630 w, br, ca. 960 s, ca. 890 s, ca. 615 s, and ca. 475 s cm\(^{-1}\). The band at ca 960 cm\(^{-1}\) has been assigned to the \(\nu\)\(_{\text{v-o}}\) mode of the terminally bonded \(\nu = 0\) group,\(^{18}\) while those at ca 890 and ca 615 cm\(^{-1}\) have been assigned to \(\nu\)\(_{-\text{0-0-}}\) and \(\nu\)\(_{\text{v-o}}\)^2 respectively of the coordinated peroxide.\(^8,9,19,20\) The absorptions at ca 3,160 m, br and ca. 1,630 w, br cm\(^{-1}\) have been attributed to \(\nu\)\(_{\text{0-h}}\) and \(\delta\)\(_{\text{H-0-H}}\) modes of coordinated water. The lowering of the \(\nu\)\(_{\text{0-h}}\) frequencies and broadening of \(\delta\)\(_{\text{H-0-H}}\) bands relative to those of free water suggest the possibility of intramolecular hydrogen bonding.\(^{21,22}\) The band at ca 475 cm\(^{-1}\) is attributed to a \(\nu\)\(_{\text{F}}\) stretching mode; its position suggests the presence of bridging rather than terminal \(\text{F}\). Since the \(\nu\)\(_{-\text{0-0-}}\) and the complementary \(\nu\)\(_{\text{v-o}}\) fall in the regions expected for the triply bonded \(\text{O}_2\)\(^{2-}\) (\(C_{2v}\) symmetry) ligands,\(^8,9,19,20\) it is inferred that the peroxide group is bonded to the \(\text{V}^{4+}\).
Table 2. Analytical data, Magnetic moments, Structurally Significant In and Electronic Spectral bands of $\sum [\mathrm{V}(O_2)]^2(\mathrm{H}_2\mathrm{O})_2$ ($A = \mathrm{K}, \mathrm{Rb}, \mathrm{Cs}$ or $\mathrm{NH}_4$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{\text{eff}}$/BM</th>
<th>% Found (% Calcd.)</th>
<th>In</th>
<th>Assignments</th>
<th>Electronic Absorption (cm$^{-1}$)</th>
<th>Transition</th>
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<tbody>
<tr>
<td></td>
<td>295$^\circ$K</td>
<td>$A$ or $N$ V $O$ F</td>
<td></td>
<td></td>
<td>(cm$^{-1}$)</td>
<td></td>
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<tr>
<td>$\mathrm{NH}_4[\mathrm{V}(O_2)]^2(\mathrm{H}_2\mathrm{O})_2$</td>
<td>1.73</td>
<td>8.3 30.2 10.8 19.3</td>
<td>955s</td>
<td>0-0</td>
<td>11,628</td>
<td>$e \leftrightarrow b_1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8.15) (29.6) (18.6)</td>
<td>890s</td>
<td>$0-0-0$</td>
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<td></td>
<td></td>
<td></td>
<td>610s</td>
<td>$0-0-0$</td>
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<td>$\mathrm{K}[\mathrm{V}(O_2)]^2(\mathrm{H}_2\mathrm{O})_2$</td>
<td>1.75</td>
<td>20.8 25.9 17.0 10.4</td>
<td>950s</td>
<td>0-0</td>
<td>11,905</td>
<td>$e \leftrightarrow b_1$</td>
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<td></td>
<td></td>
<td>(20.25) (26.4) (16.55)</td>
<td>880s</td>
<td>$0-0-0$</td>
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<td>610s</td>
<td>$0-0-0$</td>
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<td>$\mathrm{Rb}[\mathrm{V}(O_2)]^2(\mathrm{H}_2\mathrm{O})_2$</td>
<td>1.70</td>
<td>21.7 13.9 7.6 9.3</td>
<td>970s</td>
<td>0-0</td>
<td>17,999</td>
<td>$b_1 \leftrightarrow b_2$</td>
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<tr>
<td></td>
<td></td>
<td>(21.25) (13.35) (7.95)</td>
<td>880s</td>
<td>$0-0-0$</td>
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<td>610s</td>
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<tr>
<td>$\mathrm{Cs}[\mathrm{V}(O_2)]^2(\mathrm{H}_2\mathrm{O})_2$</td>
<td>1.73</td>
<td>18.3 11.8 6.8 9.6</td>
<td>965s</td>
<td>0-0</td>
<td>17,999</td>
<td>$b_1 \leftrightarrow b_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(17.75) (11.15) (6.6)</td>
<td>895s</td>
<td>$0-0-0$</td>
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<td></td>
<td></td>
<td></td>
<td>610s</td>
<td>$0-0-0$</td>
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Note: A = ferrox-oxygen
centre in a triangular bidentate manner. Two extra vibrations at 3,140 and 1,440 cm\(^{-1}\) in the case of the ammonium salt have been assigned to the \(\tilde{\nu}_1\) and \(\tilde{\nu}_4\) modes of NH\(_4^+\). The \(\tilde{\nu}_3\) mode of NH\(_4^+\) could not be identified due to its overlap with the broad \(\nu\)\(_{\text{O-H}}\) mode of water.

It thus appears that the complex ion has formula \(\sqrt{\nu\text{O}(\nu\text{O})\left(\text{H}_2\text{O}\right)\nu_2}\), containing a triangularly bonded peroxide ligand. The complex species may have a polymeric structure through \(\nu\)\(\text{V-F-V}\) bridging; however, the possibility of a weak \(\nu\)-O-V interaction can not be ruled out completely.

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