Chapter 4

Alkali-metal and Ammonium Triperoxofluorovanadates (V), $A_2 \sqrt{\text{VO}(O_2)_{3}F}$ ($A = \text{Na, K or NH}_4$). Synthesis and Structural Assessment*

There has been a good deal of current interest in the study of peroxovanadium(V) chemistry.\(^1\text{-}^3\) It appears from the recent literature that studies of the kinetic behaviour of peroxovanadium(V) engage the attention of most of the research groups,\(^1\text{-}^3\text{,}\text{8}\) though information on the synthesis and structural assessment of peroxovanadium(V) and heteroligand peroxovanadium(V) is rather scanty, probably owing to the uncertain nature of peroxovanadium(V) in solutions of varying pH. A short study on the synthesis and structural assessment of alkali-metal and ammonium oxodiperoxofluorovanadates (V), $A_2 \sqrt{\text{VO}(O_2)_{2}F}$ has been reported in chapter 3. The compounds $A_2 \sqrt{\text{VO}(O_2)_{2}F}$ were synthesised by performing the reactions over a limited range of concentration of alkaline medium.\(^9\) This work has

*The work described in this chapter has been published:
been extended to an alkaline medium concentration region higher than that of the previously examined one, thus enabling us to synthesize a series of novel compounds, alkali-metal and ammonium triperoxofluorovanadates(V), $A_2 \left[\text{VO} \left(\text{O}_2\right)_{2} \text{F}_7\right] \ (A = \text{Na}, \text{K} \text{ or } \text{NH}_4)$, and to make some reasonable conclusions about the formation of various peroxo compounds of fluorovanadium(V). Also investigated are the IR spectra of these solid compounds in order to obtain a set of internally consistent data regarding the effect on the basicity of peroxo ligands by the increase in the number of peroxo groups coordinated to fluorovanadium(V).

**Experimental**

All chemicals were of reagent grade.

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

Experiments on molar conductance measurements were made by using a Philips PR9500 conductivity bridge.

Magnetic susceptibility measurements were made by the Gouy method using Hg $\left[\text{Co} (\text{NCS})_4 \right]$ as the calibrant.

Elemental Analyses. Vanadium, fluoride, peroxide, sodium, potassium and nitrogen were estimated by the methods already described in the previous Chapters.
Synthesis of Alkali-metal and Ammonium Triperoxo-
fluorovanadates(v), \( \lambda_2 \left[ V(O_2)_{3}F \right] \) \((\lambda = Na, K, or NH_4)\).
As the methods of syntheses of the ammonium, sodium and potassium triperoxo-
fluorovanadates(v) are similar, only a representative method is described.

Pure \( V_2O_5 \) and dry fluoride AF \((\lambda = Na, K, or NH_4)\) were taken with maintenance of the molar ratio of
\( V_2O_5 \) and AF at 1:2, and mixed thoroughly by powdering
together in an agate mortar. The finely mixed powder
was dissolved in 6% hydrogen peroxide, with use of
60.0 ml of hydrogen peroxide per gram of \( V_2O_5 \), by
stirring the solution magnetically. After dissolution
was complete, the solution became transparent red.
The solution was filtered to remove any undissolved
impurity. To the filtrate was slowly added, with
continuous stirring, an excess of hydroxide,
AOH \((\lambda = Na, K, or NH_4)\), with maintenance of the molar
ratio of \( V_2O_5 : AOH \) at 1:12. While the stipulated
amount of ammonium hydroxide was added in the form
of its 25% solution, sodium and potassium hydroxides
were added in their solid form. The colour of the
solution changed from red to yellow and ultimately
to blue with the progress of addition of the alkaline
medium. After the addition of alkali-metal or ammonium
hydroxide was over, the deep blue solution was cooled at ice-bath temperature for ca. 15 min. An excess of ethanol was then added to the cold solution with stirring whereupon the deep blue microcrystalline \( \text{A}_2 \sqrt[3]{\text{V(O}_2\text{)}}_3\text{F}_7 \) was obtained in a very high yield. The reaction container was allowed to cool for ca. 30 min, and the compound was then separated by centrifugation, washed several times with ethanol, and finally dried \textit{in vacuo} over diphosphorus pentoxide.

The specific gram amounts of the reagents used and the yields of various alkali-metal and ammonium triperoxyfluorovanadates(V) are reported in Table 1, while all analytical data and IR band positions are set out in Table 2.

Results and Discussion

General Synthesis. It has been known for quite some time that vanadium(V) forms yellow diperoxovanadate(V) in an alkaline medium\(^{10,11}\) which is generally stable in solutions of high pH (\(>7\)). The yellow species is converted to red monoperoxovanadate with increasing \(\text{H}^+\) ion concentration\(^{6,10,11}\) of the solution. However, none of these reports mentioned the formation of a blue colouration of the vanadium(V) --- hydrogen peroxide
system, though the solid blue tetraperoxovanadate(V), viz., \( K_3 \left[ \frac{\sqrt{V(\text{O}_2)}_4}{7} \right] \), has been known, presumably having a dodecahedral structure analogous to that of the corresponding peroxochromium compound,\(^\text{13}\)

In the course of our studies\(^\text{9}\) (Chapter 3) mainly aimed at the synthesis and structural assessment of heteroligand peroxovanadium compounds, it was observed that the addition of a larger amount of alkaline medium changed the yellow colour of the solution owing to the diperoxovanadium(V) to deep blue. It was also observed that a relatively lower amount of alkaline medium assisted by a comparatively higher temperature gave rise to the same colour. In line with the concentration of synthesizing heteroligand peroxovanadium compounds, it was expected that the higher temperature might not be a very conducive condition for achieving the goal. Thus, we preferred the enhanced alkalinity of the medium rather than a higher temperature for the reaction. In order to ascertain the minimum number of peroxo ligands responsible for the formation of blue colouration, the reactions were carried out in the presence of a restricted number of fluoride ions (V : F at 1 : 1), strongly stabilizing ligands for quinque valent vanadium,\(^\text{14}\) such that at least
one coordination position was blocked by $F^-$ ligands prior to the reaction of hydrogen peroxide. Accordingly, the reaction among $V_2O_5$, AF, and 6% $H_2O_2$ in the presence of a large excess of alkaline medium gave rise to the formation of $\left[\mathbf{V}O_2\right]_3F_7^-$ species in the solution. The complex ion was isolated as its alkali-metal or ammonium salt by the addition of alcohol, which facilitated precipitation of the solid compounds. A plausible interpretation of this result is that a very high alkalinity probably helps to remove the last oxygen from $\left[\mathbf{V}O_2\right]_2F_7^{2-}$ such that the formation of $\left[\mathbf{V}O_2\right]_3F_7^{2-}$ is favoured, or it could also be possible that the $\text{oxy}$ oxygen of the yellow diperoxo species is converted to the third peroxy ligand by abstracting an oxygen of hydrogen peroxide. Although there is no direct evidence for either of the two probable mechanisms, considering the strength of the $\nu$-O multiple bond from IR spectral studies$^9,14$ and from the fact that the oxygen exchange on vanadium(V) ion is very slow, it is believed that the latter mechanism may be more likely, which is also in accord with very recent kinetic studies.$^7$

The reaction, leading to the formation of the complex $\left[\mathbf{V}O_2\right]_3F_7^-$ ion, is best monitored by IR
spectroscopy. This was accomplished by isolating a small amount of the compound followed by recording its IR spectrum. The disappearance of the sharp band at ca 950 cm\(^{-1}\) owing to \(\nu_{\text{V-O}}\) indicated the completion of the reaction. It is evident that, at least under the present condition, the minimum number of peroxo ligands responsible for the formation of blue peroxo compounds is 3.

**Characterization and Assessment of Structure.**

The alkali-metal and ammonium triperoxofluorovanadates(V) are all deep blue microcrystalline products. They are generally hygroscopic, and this tendency seems to be more pronounced with the Na\(^+\) and K\(^+\) salts of \(\left[\overset{\text{V}}{\overset{\text{3}}{\overset{\text{F}}{\overset{\text{O}}{\text{2}}}}}\right]^{-}\)\(\overset{\text{2-}}{\text{7}}\). However, they are capable of being stored in sealed containers for prolonged periods and the stability can be checked by periodic estimation of the peroxide content. The estimation of peroxide content is considered to be of extreme importance in such compounds in order to decide about the number of such ligands attached to vanadium(V). The estimation of peroxide was done by redox titrations (vide Chapter 3), in the presence of boric acid to prevent any unwanted loss of active oxygen, which conclusively suggested the presence of three peroxo groups per \(\overset{\text{5+}}{\text{V}}\) ion in the compounds. That the
Table 1. Amounts of Reagents Used and Yields of $A_2 \sqrt{V(O_2)_3F}$ (A=Na, K or NH₄)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield in g (%)</th>
<th>Amount of $V_2O_5$ in g (mmol)</th>
<th>Amount of AF in g (mmol)</th>
<th>Amount of 6% $H_2O_2$ in ml (mmol)</th>
<th>Amount of AOH (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(NH_4)_2 \sqrt{V(O_2)_3F}$</td>
<td>1.9 (86)</td>
<td>1.0 (5.5)</td>
<td>0.4 (10.9)</td>
<td>60.0</td>
<td>9.2 ml (25% soln.)</td>
</tr>
<tr>
<td>Na$_2 \sqrt{V(O_2)_3F}$</td>
<td>2.0 (87)</td>
<td>1.0 (5.5)</td>
<td>0.46 (11)</td>
<td>60.0</td>
<td>2.6</td>
</tr>
<tr>
<td>K$_2 \sqrt{V(O_2)_3F}$</td>
<td>2.3 (85)</td>
<td>1.0 (5.5)</td>
<td>0.64 (11)</td>
<td>60.0</td>
<td>3.7</td>
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vanadium is in its +5 oxidation state has been ascertained from the diamagnetic nature of the compounds, as evidenced by their magnetic susceptibility measurements.

The attempts to measure the molar conductance of $A_2 \sum V(\text{O}_2)_{3\text{F}^{-}}$ in water was unsuccessful. The values obtained were higher than that expected for a 2:2 type electrolyte. It has been generally observed\textsuperscript{9,12} that owing to their instability the molar conductances of many peroxovanadium(v) compounds can not be measured. Thus, the higher conductance values in the present case are not too surprising.

The IR spectra of the series of three salts resemble each other very closely (Table 2), indicating that the compounds are similar both structurally and stoichiometrically. The spectra of the compounds showed absorptions in two characteristic regions, viz., at 850-855 cm\textsuperscript{-1} and at 470-475 cm\textsuperscript{-1}. Each spectrum shows only one strong absorption in the 850 - 855 cm\textsuperscript{-1} region, which has been unambiguously assigned\textsuperscript{15} as the $\sum_{\text{O}-\text{O}-\text{O}}$ mode of coordinated peroxy groups. A single absorption in this region suggests that all three peroxy ligands in the complexes are bonded to the vanadium(v) centre in an analogous fashion. Since the
Table 2. Analytical Data and Structurally Significant IR Bands of $A_2 \left[ V(O_2)_3F \right]$ ($A = \text{Na}, \text{K} \text{ or } \text{NH}_4$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Found (% Calcd.)</th>
<th>IR Bands cm$^{-1}$</th>
<th>Assignments</th>
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<tr>
<td></td>
<td>$A \text{ or } N$</td>
<td>$V$</td>
<td>$O_a$</td>
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<tr>
<td>$(\text{NH}_4)_2 \left[ V(O_2)_3F \right]$</td>
<td>13.81 (13.87)</td>
<td>25.22 (25.23)</td>
<td>46.97 (47.54)</td>
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<tr>
<td>$\text{Na}_2 \left[ V(O_2)_3F \right]$</td>
<td>21.56 (21.70)</td>
<td>24.12 (24.04)</td>
<td>44.87 (45.30)</td>
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<tr>
<td>$\text{K}_2 \left[ V(O_2)_3F \right]$</td>
<td>32.11 (32.03)</td>
<td>20.81 (20.87)</td>
<td>36.93 (39.32)</td>
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absorptions occur exactly in the region stipulated for the triangularly bonded peroxy groups, it may be inferred that all three peroxy ligands in the complexes are bonded in a C₂ᵥ i.e. triangular bidentate manner. The absorptions in the comparatively lower region, i.e., 470-475 cm⁻¹, are straightforward and have been assigned as the υᵥ-F modes arising from the presence of fluoride ion coordinated to the vanadium(V) centre. This compares very well with the υᵥ-F values observed in the cases of various fluorovanadate species.⁹,¹⁶-¹⁸ The three extra vibrations at 3158 cm⁻¹, 3040 cm⁻¹ and 1400 cm⁻¹ in the spectrum of (NH₄)₂[V(O₂)₃F⁻] have been assigned to the υ₃, υ₁ and υ₄ modes of NH₄⁺.

In an attempt to study effect on the basicity of peroxy ligands as a function of the number of peroxy groups coordinated to the vanadium(V) centre, the IR spectra of A₂[V(O₂)₃F⁻] with those of A₂[VO(O₂)₂F⁻] compounds, recorded under identical conditions. It is interesting to note that, while υ₋₋₋₋₋₋ absorptions for A₂[VO(O₂)₂F⁻] compounds lie in the region 870 - 895 cm⁻¹, those of A₂[V(O₂)₃F⁻] compounds lie between 850 and 855 cm⁻¹. The lowering of the values must be attributed to the lowering of ‐O‐O‐ bond order.
of the coordinated peroxo groups in the latter case. In other words, removal of further $\pi_2p$ density from $O_2^{2-}$ to the vanadium appear to have taken place in the case of $\Lambda_2 \sqrt{V(O_2)_3F}$ which has been facilitated by the attachment of a fluoride ligand to $V^{5+}$. It is thus possible to infer from this observation that the basicity of coordinated peroxyl ligands increase with the increase in the number of such ligands coordinated to vanadium(v) and lend support to the proposition made by Quilitzsch and Wieghardt$^6$ from their studies in solution.

Thus, it appears from our present work that the peroxo ligands are trianlyarly bonded to $V^{5+}$ and the complex species $\sqrt{V(O_2)_3F^{-}}$ may have a heptacoordinated monomeric structure but the probability of a polymeric structure through a weak $V-F-V$ bridging can not also be totally ruled out.

References


