APPENDIX

List of Publications

1 Synthesis of Alkali Oxytetrafluorovanadates(V)

2 Alkali Oxytetrafluorovanadates(V)
M.K. Chaudhuri and S.K. Ghosh
Inorg. Syntheses, Approved by the Review Committee.

3 Synthesis of Alkali Oxydiperoxyfluorovanadates(V)
M.K. Chaudhuri and S.K. Ghosh
Polyhedron, 553, 1, 1982.

4 Alkali-metal and Ammonium Triperoxyfluorovanadates(V)
M.K. Chaudhuri and S.K. Ghosh

5 Novel Synthesis of Tris(acetylacetonato)iron(III)
M.K. Chaudhuri and S.K. Ghosh

6 $\left[\text{ClO}_2\right]_{2}^{7-} \rightarrow \left[\text{ClO}_2\right]_{3}^{7-}$ Pair in Peroxy-
vanadium Chemistry: Synthesis of the First Chloro-
peroxovanadate(V) Compounds and evidence for
Diperoxovanadate(V) ---Triperoxovanadate(V) Interconversion
M.K. Chaudhuri and S.K. Ghosh

7 Bis(acetylacetonato)fluorovanadate(III), $\text{VF(C}_5\text{H}_7\text{O}_2)_2$
Synthesis of a Novel Neutral Compound of Vanadium(III)
from Vanadium(V)
M.K. Chaudhuri and S.K. Ghosh

8 Synthesis of Alkali Diquafluoro-oxodiperoxovanadate(IV)
Complexes $\left[\text{VO}_2\right]^{7}$
M. K. Chaudhuri and S. K. Ghosh
dates(V) ion $\text{VOF}_4^{-}$ in aqueous hydrofluoric acid\(^1\), the species has not been prepared from an aqueous solution to date. It has been believed that vanadium(V) should not be stable in aqueous solution in the presence of halides like Cl\(^-\) or Br\(^-\), and, in order to prevent reduction of vanadium(V), anhydrous solvent should be used and the temperature maintained throughout the reaction at 0\(^\circ\)\(^\circ\).\(^2\) This, however, may not be true in the case of F\(^-\) because vanadium(V) should not be able to oxidise fluoride ions. In 1951 analysis of a product resulting from the reaction of sodium vanadate and bromine trifluoride suggested that it was an impure sample of NaVOF\(_4\).\(^3\) However, little was known about any pure A\(^I\)VOF\(_4\) in the solid state until 1970. In 1971 the first and only pure solid salt CsVOF\(_4\) was prepared by Howell and Moss\(^4\) from the reaction of V\(_2\)O\(_5\), anhydrous HF and CsF at -30\(^\circ\)\(^\circ\). We now describe a novel and simple general method for the synthesis and isolation of A\(^I\)VOF\(_4\) (A\(^I\) = NH\(_4\), K, Rb or Cs) from aqueous medium, together with the characterization of these salts.

RESULTS AND DISCUSSION

In view of the fact that the oxytetrafluorovanadate(V) ion $\text{VOF}_4^{-}$ exists in an aqueous hydrofluoric acid solution\(^1\), it was felt that the species can be isolated from such solutions by proper adjustment of the experimental conditions. The method of synthesis described herein (vide Experimental section) involves the reaction of V\(_2\)O\(_5\), alkali bifluorides A\(^I\)HF\(_2\) and 40% HF leading to the formation of A\(^I\)VOF\(_4\) in solution.

$$\text{V}_2\text{O}_5 + 2 \text{A}^I\text{HF}_2 + 4 \text{HF} \rightarrow 2 \text{A}^I\text{VOF}_4 + 3 \text{H}_2\text{O}$$

The success in isolation of alkali oxytetrafluorovanadates(V) from the reaction media depends upon the
dates(V) ion \( \text{VOF}_4^- \) in aqueous hydrofluoric acid, the species has not been prepared from an aqueous solution to date. It has been believed that vanadium(V) should not be stable in aqueous solution in the presence of halides like \( \text{Cl}^- \) or \( \text{Br}^- \), and, in order to prevent reduction of vanadium(V), anhydrous solvent should be used and the temperature maintained throughout the reaction at 0°. This, however, may not be true in the case of \( \text{F}^- \) because vanadium(V) should not be able to oxidise fluoride ions. In 1951 analysis of a product resulting from the reaction of sodium vanadate and bromine trifluoride suggested that it was an impure sample of \( \text{NaVOF}_4 \). However, little was known about any pure \( \text{AIVO}_4 \) in the solid state until 1970. In 1971 the first and only pure solid salt \( \text{CsVOF}_4 \) was prepared by Howell and Moss\(^4\) from the reaction of \( \text{V}_2\text{O}_5 \), anhydrous HF and CsF at -30°. We now describe a novel and simple general method for the synthesis and isolation of \( \text{AIVO}_4 \) (\( \text{A} = \text{NH}_4, \text{K, Rb or Cs} \)) from aqueous medium, together with the characterization of these salts.

RESULTS AND DISCUSSION

In view of the fact that the oxytetrafluorovanadate(V) ion \( \text{VOF}_4^- \) exists in an aqueous hydrofluoric acid solution, it was felt that the species can be isolated from such solutions by proper adjustment of the experimental conditions. The method of synthesis described herein (vide Experimental section) involves the reaction of \( \text{V}_2\text{O}_5 \), alkali bifluorides \( \text{AHF}_2 \) and 40% HF leading to the formation of \( \text{AIVO}_4 \) in solution.

\[
\text{V}_2\text{O}_5 + 2 \text{AHF}_2 + 4 \text{HF} \rightarrow 2 \text{AIVO}_4 + 3 \text{H}_2\text{O}
\]

The success in isolation of alkali oxytetrafluorovanadates(V) from the reaction media depends upon the
role played by alcohol. It is believed that the solvent effect brought about by the addition of alcohol significantly helps the syntheses of the $\text{A}^\text{I}_{\text{VOF}}_4$ compounds. A light green or greenish-yellow color that is obtained on addition of a small amount of alcohol has to be maintained throughout until the isolation of the $\text{A}^\text{I}_{\text{VOF}}_4$ compounds is completed.

The compounds thus obtained are highly crystalline, in the shape of long needles, except for CsVOF$_4$ which is generally small hexagonal, greenish-yellow in colour. The compounds, once isolated from the reaction media, seem to be very sensitive to air and moisture, highly soluble in water with decomposition and insoluble in common organic solvents except acetonitrile in which oxytetrafluorovanadates(V) are very slightly soluble. Elemental analysis, i.r., molar conductance measurement, magnetic moment and $^{19}$F N.m.r. were used to characterize the compounds $\text{A}^\text{I}_{\text{VOF}}_4$.

The molar conductance of cesium oxytetrafluorovanadates(V) gave a value of 132 ohm$^{-1}$cm$^2$mol$^{-1}$ at $27^0$ in purified acetonitrile suggesting an uni-uni valent electrolytic nature of the compound in accord with the formula CsVOF$_4$.$^4$. This was further supported by the diamagnetic nature of the compounds evidenced from magnetic susceptibility measurements.

The i.r. spectra of alkali oxytetrafluorovanadates(V), $\text{A}^\text{I}_{\text{VOF}}_4$, do not support the possibility of polymeric formulations because of the absence of the broad intense band in the 650-900 cm$^{-1}$ region, which is generally diagnostic of the presence of the O-V-O group in fluorovanadates.$^5,6$ The strong bands 980-1030 cm$^{-1}$ (Vide Table I) with the V-O force constants lying between 7.07 and 7.43 md/A are considered as characteristics of the presence of V-O multiple bonds supporting
TABLE 1

I.r. Bands of \( \text{A}^1\text{VOF}_4 \) Compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( \text{NH}_4\text{VOF}_4 )</th>
<th>( \text{KVOF}_4 )</th>
<th>( \text{RbVOF}_4 )</th>
<th>( \text{CsVOF}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.r. bands cm(^{-1})</td>
<td>262 m</td>
<td>261 m</td>
<td>262 m</td>
<td>260 m</td>
</tr>
<tr>
<td></td>
<td>308 m</td>
<td>307 m</td>
<td>311 m</td>
<td>310 m</td>
</tr>
<tr>
<td></td>
<td>332 s</td>
<td>334 s</td>
<td>330 s</td>
<td>334 s</td>
</tr>
<tr>
<td></td>
<td>480 m</td>
<td>482 m</td>
<td>483 m</td>
<td>481 m</td>
</tr>
<tr>
<td></td>
<td>595 s</td>
<td>594 s</td>
<td>595 s</td>
<td>594 s</td>
</tr>
<tr>
<td>I.r. bands cm(^{-1})</td>
<td>625 s</td>
<td>625 s</td>
<td>623 s</td>
<td>624 s</td>
</tr>
<tr>
<td></td>
<td>710 w</td>
<td>712 w</td>
<td>712 w</td>
<td>712 w</td>
</tr>
<tr>
<td></td>
<td>970 w</td>
<td>972 w</td>
<td>972 w</td>
<td>973 w</td>
</tr>
<tr>
<td></td>
<td>990 vs</td>
<td>980 vs</td>
<td>995 vs</td>
<td>1015 vs</td>
</tr>
<tr>
<td></td>
<td>1015</td>
<td>1025</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The occurrence of \( \text{O}^{(\text{sp})}\text{V} \) bonding. I.r. spectra of the various \( \text{A}^1\text{VOF}_4 \) compounds are identical and correlate very well with those previously reported for \( \text{CsVOF}_4 \) and are also in agreement with the reported crystal structure of \( \text{CsVOF}_4 \), which shows \( \text{[\text{VOF}_4]}^- \) to be essentially \( \text{C}_4\text{v} \) with weak F-bridging making \( \text{[\text{VOF}_4]}^- \) pseudooctahedral.

\( ^{19}\text{F N.m.r.} \) spectrum of a 1.42(M) solution of the newly synthesised \( \text{CsVOF}_4 \) in 48% HF measured at \(-85^\circ\text{C}\) shows a broad doublet occurring at 258.4 ppm down field relative to HF with a value of \( \nu_1 = 1003 \text{ Hz} \). These agree with the values previously reported\(^4\) for \( \text{CsVOF}_4 \) conforming to the suggestion that a rapid fluorine rearrangement between \( \text{C}_4\text{v} \) and \( \text{C}_2\text{v} \) stereochemistry of \( \text{[\text{VOF}_4]}^- \) occurs in solution.
We, therefore, conclude that alkali oxytetrafluorovanadates(V) can be prepared from aqueous solutions by suitably adjusting the experimental conditions.

**EXPERIMENTAL**

All chemicals used were of reagent grade. Alkali bifluorides, \( \text{A}^{1}\text{HF}_2 \), were prepared by the method developed in this laboratory\(^6\). Infrared spectra were recorded on a Perkin-Elmer Model 125 instrument. Molar conductivity studies were made at room temperature using a Toshniwal Conductivity bridge. Magnetic susceptibility measurements were made at room temperature by the Guoy method using \( \text{Co}^{2+}\text{Hg(SCN)}_4^{-} \) as calibrant. \(^{19}\text{F} \) N.m.r. Spectra were recorded on a Bruker HX-60/5 instrument.

Preparation of Alkali Oxytetrafluorovanadates(V), \( \text{A}^{1}\text{VOF}_4 \), \( (\text{A}^{1} = \text{NH}_4, \text{K}, \text{Rb or Cs}) \)

Since the methods of syntheses of alkali oxytetrafluorovanadates(V) are similar only a general method is described.

Stoichiometric quantities of \( \text{V}_2\text{O}_5 \), \( 40\% \) HF and \( \text{A}^{1}\text{HF}_2 \) (1:4:2 molar ratio) maintaining V:F at 1:4 were heated for a few minutes at boiling water bath temperature in a polythene beaker. Ethanol was added dropwise to the hot solution until the brown colour of the solution changed to light green. A few more drops of alcohol were added; the solution was concentrated to nearly three-fourth of its original volume and allowed to cool in a freezer whereby crystalline \( \text{A}^{1}\text{VOF}_4 \) was obtained. Details of the gram amounts of reagents used, yields of various \( \text{A}^{1}\text{VOF}_4 \) compounds and analytical data are given in the Table II and i.r. have been set out in the Table I.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Amounts of reagents Used</th>
<th>Yield of $\text{A}^1\text{VOF}_4$ (Calc'd.%)</th>
<th>Found%</th>
<th>V</th>
<th>F</th>
<th>A$^1$ or N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reagent</td>
<td>Amount</td>
<td></td>
<td></td>
<td>V</td>
<td>F</td>
</tr>
<tr>
<td></td>
<td>$\text{V}_2\text{O}_5$</td>
<td>2.00g (11mmol)</td>
<td>1.83</td>
<td>31.80</td>
<td>47.28</td>
<td>8.21</td>
</tr>
<tr>
<td></td>
<td>40%HF</td>
<td>2.2ml (44mmol)</td>
<td>2.44</td>
<td>28.08</td>
<td>42.05</td>
<td>21.54</td>
</tr>
<tr>
<td></td>
<td>$\text{NH}_4\text{VOF}_4$</td>
<td>1.26g (22mmol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{KVOF}_4$</td>
<td>2.00g (11mmol)</td>
<td>2.52</td>
<td>22.02</td>
<td>33.61</td>
<td>37.88</td>
</tr>
<tr>
<td></td>
<td>40%HF</td>
<td>2.2ml (44mmol)</td>
<td>(50)</td>
<td>(22.30)</td>
<td>(33.26)</td>
<td>(37.42)</td>
</tr>
<tr>
<td></td>
<td>$\text{RbVOF}_4$</td>
<td>2.74g (22mmol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40%HF</td>
<td>2.2ml (44mmol)</td>
<td>1.76</td>
<td>18.83</td>
<td>27.61</td>
<td>48.65</td>
</tr>
<tr>
<td></td>
<td>$\text{CsVOF}_4$</td>
<td>1.9g (11mmol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
SYNTHESIS OF $\text{A}^{2}\text{[VOF}_5\text{]}$

ACKNOWLEDGEMENT

One of us (S.K.G.) is thankful to C.S.I.R.(India) for award of a junior research fellowship.

REFERENCES


Received: 21 April 1981
Accepted: 5 October 1981
Referee I: V. Gutmann
Referee II: W. W. Wilson
SYNTHESIS OF ALKALI OXYDIPEROXYFLUOROVANADATES(V)

W.K. CHAUDHURI* and S.K. GHOSH
Department of Chemistry, North-Eastern Hill University, Shillong 793003, India

Abstract — The reaction of vanadium pentoxide with hydrogen peroxide in an alkaline medium in the presence of alkali fluorides AF (A = NH₄, Na, K, Rb or Cs) gives alkali oxydiperoxyfluorovanadates(V), A₂ \(\text{VO}(\text{O}_2)_2\text{F}^-\) in very high yields. Characterisation of the compounds was made from the results of chemical analyses, magnetic susceptibility measurements and i.r. spectral studies. IR spectrometry showed the peroxy ligands to be triangular bidentate.

INTRODUCTION

Although there has been a continued interest in the study of peroxovanadium(V) chemistry, 1-6 the synthesis, characterisation and structural assessment of peroxy and mixed peroxyvanadium(V) compounds have received relatively less attention to date. This is presumably owing to the uncertain nature of peroxyvanadium(V) in solution of varying \(p_H\). As a sequel of our studies mainly aimed at the synthesis of fluoro compounds of transition metals, 7-9 we undertook the synthesis of peroxyfluorovanadium(V) compounds. The present paper reports the first general synthesis of the title compounds along with their characterisation.

EXPERIMENTAL

Vanadium pentoxide, alkali metal fluorides and hydrogen peroxide were reagent grade products. Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. Magnetic measurements were carried out by Gouy method using Hg \(\text{Co(NCS)}_4\) as the calibrant.

Synthesis of alkali oxydiperoxyfluorovanadates(V)

\(\text{A}_2\text{VO}(\text{O}_2)_2\text{F}^-\) (A = NH₄, Na or K) — A finely mixed powder of vanadium pentoxide (5.5 mmol) and alkali metal fluoride, AF (11 mmol) was dissolved in 9% hydrogen peroxide (79.4 mmol) by slightly warming over a steam-bath and a red solution was obtained. A concentrated solution of the corresponding alkali hydroxide (50 mmol) was slowly added with constant stirring whereupon the solution became yellow. An excess of alcohol was added to the solution with stirring until an yellow coloured microcrystalline product was obtained. The reaction container was then cooled in an ice-bath for ca 40 min. The compound was separated by centrifugation and purified by washing with alcohol and finally dried in vacuo over phosphorous pentoxide. The yields of (NH₄)₂\(\text{VO}(\text{O}_2)_2\text{F}^-\), Na₂\(\text{VO}(\text{O}_2)_2\text{F}^-\) and K₂\(\text{VO}(\text{O}_2)_2\text{F}^-\) were 1.6g (78%), 1.8g (84%) and 2.1g (84%) respectively.
The Rb$_2$VO(O$_2$)$_2$F$_7$ and Cs$_2$VO(O$_2$)$_2$F$_7$ compounds were prepared in a manner similar to that described above, however, the solution of V$_2$O$_5$ (5.5 mmol) and AF (A = Rb or Cs) (11 mmol) in 9% hydrogen peroxide (79.4 mmol) was made alkaline by the addition of 25% solution of ammonium hydroxide (50 mmol). The yield of Rb$_2$VO(O$_2$)$_2$F$_7$ was 2.6g (74%) and that of Cs$_2$VO(O$_2$)$_2$F$_7$ was 3.5g (77%).

Table 1. Analytical data and structurally significant i.r. bands of A$_2$VO(O$_2$)$_2$F$_7$ (A = NH$_4$, Na, K, Rb or Cs)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Analysis (%)</th>
<th>$\tilde{\nu}$/cm$^{-1}$</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{NH}_4)_2$VO(O$_2$)$_2$F$_7$</td>
<td>14.9</td>
<td>27.7</td>
<td>34.2</td>
</tr>
<tr>
<td></td>
<td>(15.06)</td>
<td>(27.40)</td>
<td>(34.41)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$VO(O$_2$)$_2$F$_7$</td>
<td>23.6</td>
<td>26.2</td>
<td>32.3</td>
</tr>
<tr>
<td></td>
<td>(23.47)</td>
<td>(26.01)</td>
<td>(32.66)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_2$VO(O$_2$)$_2$F$_7$</td>
<td>34.5</td>
<td>22.6</td>
<td>27.5</td>
</tr>
<tr>
<td></td>
<td>(34.29)</td>
<td>(22.33)</td>
<td>(28.04)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb$_2$VO(O$_2$)$_2$F$_7$</td>
<td>53.5</td>
<td>16.1</td>
<td>19.7</td>
</tr>
<tr>
<td></td>
<td>(53.28)</td>
<td>(15.88)</td>
<td>(19.94)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs$_2$VO(O$_2$)$_2$F$_7$</td>
<td>62.7</td>
<td>12.4</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>(65.34)</td>
<td>(12.25)</td>
<td>(15.39)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Calculated values in parentheses, $^b$Peroxy oxygen, $^c$Analysis for N.

RESULTS AND DISCUSSION

It has long been recognised that vanadium forms yellow diperoxovanadate(V) in alkaline medium$^{10}$ and is converted to red monoperoxy species in acidic solution.$^5$ The reaction of V$_2$O$_5$ with alkali fluoride, AF and hydrogen peroxide in an alkaline medium gave alkali oxydiperoxyfluorovanadates(V), A$_2$VO(O$_2$)$_2$F$_7$ in very high yields. A report on the synthesis of K$_2$VO(O$_2$)$_2$F$_7$ appeared$^{11}$ while our work was in progress. However, the reaction condition of the present synthesis is different from the one previously reported.$^{11}$ An alkaline condition is found to be more conducive to the synthesis.
The $\text{A}_2\text{V}[(\text{O}_2)\text{F}_7]$ compounds are all yellow coloured microcrystalline products. They are soluble in water with slow decomposition. Estimation of peroxide content \(^1^2\) showed the presence of two peroxo groups in each of the compounds. This result and the diamagnetic nature of the compounds suggest that the complex ion contains two peroxo groups per vanadium atom and that the vanadium has an oxidation state of +5.

The occurrence of sharp vibrations around 880 cm\(^{-1}\) (Table 1) in the IR spectra of the compounds imply the presence of triangularly bonded peroxo ligands, and in keeping with this there are two readily identifiable $\delta(\cdot\cdot\cdot\cdot\cdot)$ bands at 998 and at 997 cm\(^{-1}\).\(^{13}\) Another characteristic feature of the spectra is the absorption at 935-970 cm\(^{-1}\), which has been assigned as the $\delta(V-O)$ mode of terminal V-O multiple bonds.\(^9,^{14,15}\) The strong absorption at 470-480 cm\(^{-1}\), in each spectrum, has been assigned as the $\delta(V-F)$ mode owing to the presence of $F^-$ ligand bonded to vanadium(V) centre and compare very well with those observed for many fluorovanadate species.\(^9,^{16,17}\)

Acknowledgement – We thank the Council of Scientific and Industrial Research (New Delhi) for award of a fellowship (S.K.G.).

REFERENCES

Alkali-Metal and Ammonium Triperoxyfluorovanadates(V), $A_2[V(O_2)F]$  

MIHIR K. CHAUDHURI* and SOUMITRA K. GHOSH  

Received March 1, 1982  

Blue alkali-metal and ammonium triperoxyfluorovanadates(V), $A_2[V(O_2)F]$ ($A = NH_4, Na,$ and $K$) have been synthesized by reacting $V_2O_5$ with fluorides AF and hydrogen peroxide in a highly alkaline medium. The compounds have been characterized by elemental analyses, magnetic susceptibility measurements, and IR spectroscopic studies. The compounds do not permit molar conductance measurements. The IR spectra of the compounds suggest the presence of triangularly bonded peroxy ligands. The complex species $[V(O_2)F]^2^-$ may be a seven-coordinated monomer or it may have a polymeric structure through a weak V–F–V bridging. The basicity of peroxy ligands increases with the increase in the number of peroxy groups coordinated to the vanadium(V) center.

There has been a good deal of current interest in the study of peroxyvanadium(V) chemistry.1–6 It appears from the recent literature that studies of the kinetic behavior of peroxyvanadium(V) engage the attention of most of the research groups,2,4,6 though information on the synthesis and structural assessment of peroxyvanadium(V) is rather scanty, probably owing to the uncertain nature of peroxyvanadium(V) in solutions of varying pH. We have reported recently a short study on the synthesis and structural assessment of alkali-metal and ammonium oxydi-peroxyfluorovanadates(V), $A_2[VO(O_2)F]$. The compounds $A_2[VO(O_2)F]$ were synthesized by performing the reactions over a limited range of concentration of alkaline medium.7 We have now extended this work 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 triperoxy-fluorovanadates(V), $A_2[V(O_2)F]$ ($A = NH_4, Na,$ and $K$). As the methods of syntheses of the ammonium, sodium, and potassium triperoxyfluorovanadates(V) are similar, only a representative method is described.

Pure $V_2O_5$ and dry fluoride AF ($A = NH_4, Na$, or $K$) 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/g 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 ($A = NH_4, Na$, or $K$), with maintenance of the molar ratio of $V_2O_5$ and 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 color 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 alcohol was then added to the cold solution with stirring whereupon the deep blue microcrystalline $A_2[V(O_2)F]$ 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 alcohol, and finally dried in vacuo over phosphorus pentoxide. The specific gram amounts of the reagents used and the yields of various alkali-metal and ammonium triperoxyfluorovanadates(V) are reported in Table I.

**Experimental Section**

All chemicals were of reagent grade. Infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer separately in KBr and in Nujol media. Experiments on molar conductance measurements were made by using a Philips PR 9500 conductivity bridge. Magnetic susceptibility measurements were made by the Gouy method using Hg[Co(NCS)₄] as the calibrant.

**Synthesis of Alkali-Metal and Ammonium Triperoxyfluorovanadates(V), $A_2[V(O_2)F]$ ($A = NH_4, Na,$ and $K$).** As the methods of syntheses of the ammonium, sodium, and potassium triperoxyfluorovanadates(V) are similar, only a representative method is described.

$V_2O_5$ and dry fluoride AF ($A = NH_4, Na$, or $K$) 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/g 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 ($A = NH_4, Na$, or $K$), with maintenance of the molar ratio of $V_2O_5$ and 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 color 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 alcohol was then added to the cold solution with stirring whereupon the deep blue microcrystalline $A_2[V(O_2)F]$ 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 alcohol, and finally dried in vacuo over phosphorus pentoxide. The specific gram amounts of the reagents used and the yields of various alkali-metal and ammonium triperoxyfluorovanadates(V) are reported in Table I.

**Elemental Analyses.** Vanadium was estimated volumetrically, after the peroxy oxygen was expelled, by titration with standard potassium permanganate solution. A near-bubbling vanadium(V) solution was treated with a stream of sulfur dioxide for ca. 10 min and then with a rapid stream of carbon dioxide to expel any excess of sulfur dioxide. The vanadium(IV) solution was then cooled to ca. 80 °C and titrated with standard potassium permanganate.8 The peroxy content of

---

these compounds was determined by redox titration with standard potassium permanganate solution\(^6\) in the presence of boric acid. Fluoride was precipitated as lead chloride fluoride, PbClF, and chloride was estimated by Volhard’s method, from which the fluoride content was calculated.\(^9\) The volumetric procedure was carried out at pH 3.5-5.6. Sodium and potassium were determined by flame photometry after the salts were dissolved in water and the solution was acidified with hydrochloric acid. Nitrogen was estimated by a microanalytical method, and all analytical data and the IR band positions are set out in Table II.

### Results and Discussion

#### General Synthesis

It has been known for quite some time that vanadium(V) forms yellow di peroxyvanadate(V) in alkaline medium,\(^11\) which is generally stable in solutions of high pH (>7). The yellow species is converted to red monoper oxyvanadate with increasing H\(^+\) ion concentration\(^11\) of the solution. However, none of these reports mentioned the formation of a blue coloration of the vanadium(V)-hydrogen peroxy system, though the solid blue tetraperoxyvanadate(V), viz., K\(_2\)[V(O\(_2\)hF\(_2\)]\(_4\), has been known,\(^13\) presumably having a dodecahedral structure analogous to that of the corresponding peroxychromium compound.\(^14\)

In the course of our studies\(^7\) mainly aimed at the synthesis and structural assessment of peroxyvanadium compounds, we observed that the addition of a larger amount of alkaline medium changed the yellow color of the solution owing to the di peroxy vanadum(V) to deep blue. We also observed that a relatively lower amount of alkaline medium assisted by comparatively higher temperature gave rise to the same color. In line with our contention of synthesizing peroxy vanadium compounds, we thought 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 the blue coloration, we carried out our studies in the presence of a restricted number of fluoride ions (V:F at 1:1), strongly stabilizing ligands for quinquevalent vanadium,\(^15\) such that at least one coordination position was blocked by F\(^-\) ligands prior to the reaction of hydrogen peroxide. Accordingly, the reaction among V\(_2\)O\(_5\), AF, and 6% H\(_2\)O\(_2\) in the presence of a large excess of alkaline medium gave rise to the formation of [V(O\(_2\)hF\(_2\)]\(_2\)- 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 [VO(O\(_2\)hF\(_2\)]\(_2\) such that the formation of [V(O\(_2\)hF\(_2\)]\(_2\)- is favored, or it could also be possible that the oxo oxygen of the yellow di peroxy species is converted to the third peroxy ligand by abstracting an oxygen of hydrogen peroxy.

Although there is no direct evidence for either of the two probable mechanisms, considering the strength of the V=O multiple bond from IR spectral studies,\(^7\)\(^15\) and from the fact that the oxygen exchange on vanadium(V) ion is very slow, we feel that the latter mechanism may be more likely, which is also in accord with very recent kinetic studies.\(^6\)

The reaction 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 ν\(_{\nu\text{-}_\text{O}}\) 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 peroxy compounds is 3.

#### Characterization and Assessment of Structure

The alkali-metal and ammonium tri peroxyfluorovanadates(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 [VO(O\(_2\)hF\(_2\)]\(_2\)-. However, they are capable of being stored in a sealed container 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). We estimated peroxide by redox titration with standard potassium permanganate solution,\(^9\) in the presence of boric acid to prevent any unwanted loss of active oxygen, which conclusively suggested the presence of three peroxy groups per V\(^{V+}\) ion in the compounds. That the vanadium is in its +5 oxidation state has been ascertained from the diamagnetic nature of the compounds as evidenced by their

---


magnetic susceptibility measurements.

Our attempts to measure the molar conductance of $A_2[V(O_2)F]$ in water were unsuccessful. The values obtained were higher than that expected for a 2:2 type electrolyte. It has been generally observed by us$^7$ and also by others$^{13}$ that owing to their instability the molar conductances of many peroxy-vanadium(V) compounds cannot 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 II), 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$^{-1}$ and at 470–475 cm$^{-1}$. Each spectrum shows only one strong absorption in the 850–855 cm$^{-1}$ region, which has been unambiguously assigned$^{16}$ as the $\nu_{\text{O-O}}$ mode of coordinated peroxy groups. A single absorption in this region suggests that all three peroxy ligands are bonded to the vanadium(V) center in an analogous fashion. Since the $\nu_{\text{O-O}}$ absorptions occur exactly in the region stipulated for the triangularly bonded peroxy groups, we infer that all three peroxy ligands in the complexes are bonded in a triangular bidentate manner. The absorptions in the comparatively lower region, i.e., 470–475 cm$^{-1}$, are straightforward and have been assigned as the $\nu_{\text{F-F}}$ modes arising from the presence of fluoride ion coordinated to the vanadium(V) center. This compares very well with the $\nu_{\text{F-F}}$ values observed in the cases of various fluorovanadate species.$^{7,17}$

The three extra vibrations at 3158 (m), 3040 (s), and 1400 (s) cm$^{-1}$ in the spectrum of (NH$_4$)$_2[V(O_2)F]$ have been assigned to the $\nu_3$, $\nu_1$, and $\nu_4$ modes of NH$_4^+$.

In an attempt to study the effect on the basicity of peroxy ligands as a function of the number of peroxy groups coordinated to the vanadium(V) center, we compared the IR spectra of $A_2[V(O_2)F]$ with those of $A_2[VO(O_2)F]$ compounds, recorded under identical conditions. It is interesting to note that, while $\nu_{\text{O-O}}$ absorptions for $A_2[VO(O_2)F]$ compounds lie in the region 870–895 cm$^{-1}$, those of $A_2[V(O_2)F]$ compounds lie between 850 and 855 cm$^{-1}$. The lowering of the values must be attributed to the lowering of $\sigma$–$\sigma$ bond order of the coordinated peroxy groups in the latter case. In other words, removal of further $\pi_{\text{O}}$ density from $O=O$ to the vanadium appears to have taken place in the case of $A_2[V(O_2)F]$ which has been facilitated by the attachment of a fluoride ligand to V$^{5+}$. This observation enables us to infer that the basicity of coordinated peroxy ligands increases with the increase in the number of such ligands coordinated to vanadium(V) and lend support to the proposition made by Quilitzsch and Wieghardt$^5$ from their studies in solution. Thus, it appears from our present work that the peroxy ligands are triangularly bonded to $V^{5+}$ and the complex species $[V(O_2)F]^-$ may have a heptacoordinated monomeric structure but the probability of a polymeric structure through a weak $V\equiv F\equiv V$ bridging can not also be totally ruled out.

Acknowledgment. The authors wish to thank the Council of Scientific and Industrial Research for awarding a fellowship to S.K.G.

Registry No. [NH$_4$]$_2[V(O_2)F]$, 82865-19-8; Na$_2[V(O_2)F]$, 82865-20-1; K$_2[V(O_2)F]$, 82865-21-2; V$_2$O$_5$, 1314-62-1; NH$_4$F, 12125-01-8; NaF, 7681-49-4; KF, 7789-23-3; H$_2$O$_2$, 7722-84-1.

Synthesis of Alkali Diaquafluoro-oxoperoxovanadate(iv) Complexes
[VO(O₂)F(H₂O)₂]⁻

Mihir K. Chaudhuri ¹ and Soumitra K. Ghosh
Department of Chemistry, North Eastern Hill University, Shillong 793 003, India

Orange-red alkali metal diaquafluoro-oxoperoxovanadates(iv), A[VO(O₂)F(H₂O)₂] (A = NH₄, K, Rh, or Cs), have been synthesised by the reaction of A[VOF₄] with H₂O₂ in the molar ration 1 : 12 followed by precipitation with ethanol. Characterisation of the compounds was made from the results of chemical analyses, chemical determination of oxidation state of vanadium, i.e., and electronic spectroscopic studies and magnetic susceptibility measurements. I.e., spectra suggest that the peroxy- ligand is bonded to the V⁺⁺⁺ centre in a trigonal bidentate fashion.

Studies on various aspects of peroxyvanadate chemistry has gained considerable current interest ¹ ² probably because of the biochemical significance of peroxyvanadium compounds. While most of the recent papers on the topic deal with the solution chemistry of peroxyvanadium complexes, synthesis and structural assessment of peroxy- and hetero-ligand peroxy-compounds of vanadium have received much less attention. In a continuation of our studies on the synthesis and structural assessment of hetero-ligand peroxy-compounds of vanadium(v), we thought it would be worth while to synthesise hetero-ligand peroxyvanadate(iv) compounds. Accordingly, we have now performed the reaction of alkali tetrafluoro-oxovanadate(v), A[VO₂F₄] (A = NH₄, K, Rh, or Cs), with 6% hydrogen peroxide under a weak acidic conditions (pH ca. 4) which enabled us to synthesise a series of alkali diaquafluoro-oxoperoxovanadates(iv), A[VO(O₂)F(H₂O)₂]; these peroxyvanadate(iv) compounds were obtained, for the first time, in the solid state.

Experimetal

The chemicals used were all reagent grade products. Alkali metal fluorides, AOF₃, ³ ⁴ required for the preparation of the alkali metal tetrafluoro-oxovanadates(v), A[VO₂F₄], ⁵ were synthesised by the methods developed in this laboratory. i.e., spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. Electronic spectral measurements were made on a Zeeman model UV-26 spectrophotometer. Magnetic susceptibility measurements were made by the Gouy method, using Hg[Co(NCS)₄] as the calibrant. Molar conductance measurements were made using a Philips PR 9500 conductivity bridge. The pH of the reaction solutions was measured with a Systronics Type 335 digital pH meter and also with pH indicator (BDH) paper.

Synthesis of Alkali Diaquafluoro-oxoperoxovanadate(iv) Complexes, A[VO(O₂)F(H₂O)₂] (A = NH₄, K, Rh, or Cs): — As the methods of synthesis of these complexes are simple, only a representative method is described.

Freshly prepared A[VOF₄] was dissolved in 6% hydrogen peroxide, maintaining the molar ratio A[VOF₄] : H₂O₂ at 1 : 12 (pH ca. 4), with gentle stirring. The red solution thus obtained was cooled in an ice-bath for ca. 20 min. Alcohol was added, in excess, with constant stirring and orange-red microcrystalline A[VO(O₂)F(H₂O)₂] was obtained. The compound was separated by centrifugation and washed several times with ethanol and finally dried in vacuo over diphenyl phosphorus pentoxide.

The amounts of reagents and the yields of the compounds A[VO(O₂)F(H₂O)₂] are given in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yielding</th>
<th>Amount of</th>
<th>Amount of</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NH₄]VO(O₂)F(H₂O)₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[K]VO(O₂)F(H₂O)₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Rh]VO(O₂)F(H₂O)₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cs]VO(O₂)F(H₂O)₂</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Column 1: Compound; Column 2: Yielding; Column 3: Amount of A[VO(O₂)F(H₂O)₂]; Column 4: Amount of A[VOF₄] g ² H₂O₂ cm⁻³.

Elemental Analysis. Vanadium estimation was done volumetrically. A solution of the peroxyvanadate(iv) compounds, made slightly alkaline with a dilute sodium hydroxide solution, was boiled in order to completely expel the peroxy oxygen and to convert vanadium(iv) to vanadium(v). The solution was cooled and neutralised 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(v) 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 ¹² and also by titration with a standard Ce⁴⁺ solution.¹³ Fluoride, potassium, and nitrogen were estimated by the methods described in our earlier paper.⁴ The analytical data, i.e., band positions and the electronic spectral data are set out in the Table 2.

Results and Discussion

In the course of our studies involving the synthesis of peroxy-fluoro-compounds of vanadium(v),¹⁴ we obtained a red solution containing V⁵⁺, AF, and H₂O₂ at a pH ca. 6, and presumed that the species responsible for such a colour must be different from those previously isolated by us.¹⁵ Further, it was expected that the number of peroxy-groups bonded to vanadium in acidic medium ¹⁶ would be less than that in alkaline medium, and that H₂O₂ would probably be able to reduce V⁵⁺ to V⁴⁺ in acidic medium. In view of the above considerations the reaction between A[VOF₄] and 6% H₂O₂ was carried out and a red solution was obtained. The pH of the solution was found to be ca. 4. The peroxyvanadate complex species was isolated in the solid state as its alkali metal salts, A[VO(O₂)F(H₂O)₂] by addition of alcohol which
possibly facilitated the reduction of $\text{V}^{5+}$ to $\text{V}^{4+}$ and precipitation of the complex. The occurrence of reaction between $\text{A}\{\text{VOF}_2\}$ and $\text{H}_2\text{O}_2$ was ascertained by the appearance of a new band at $\lambda 890 \text{ cm}^{-1}$, due to the $\mu(\text{O}-\text{O})$ mode of a co-ordinated $\text{O}_2^{2-}$, from a small amount of the sample isolated from the solution. It was previously reported that $\text{K}_2\{\text{V}_2\text{O}_5\text{O}_2\}\text{F}_2$ was isolated from the reaction of $\text{V}_2\text{O}_5$, $40\% \text{ HF}$, and $\text{H}_2\text{O}_2$ at high acidity and $\text{K}_2\{\text{VO(O}_2\text{F})\}$ was isolated at $\text{pH} 4$. In the present case, however, the reaction of $\text{A}\{\text{VOF}_2\}$ with $\text{H}_2\text{O}_2$ at $\text{pH} 4$ followed by addition of alcohol afforded compounds of the type $\text{A}\{\text{VO(O}_2\text{F})\}$. 

Characterisation and Assessment of Structure.—The compounds $\text{A}\{\text{VO(O}_2\text{F})\}$ are all orange-red, microcrystalline and insoluble in common 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.$^8$ The compounds $\text{A}\{\text{VO(O}_2\text{F})\}$ can, however, be stored in sealed containers and their stability can be ascertained by periodic estimation of the peroxo 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 ($\text{Ce}^{4+}$) and also by indometry, the results of which conclusively suggest the presence of one $\text{O}_2^{2-}$ group co-ordinated to vanadium(v). The direct titration with a standard $\text{K}[\text{MnO}_4]$ solution showed the involvement of three electron equivalents, two of which originated from $\text{O}_2^{2-}$ and the third was due to the process $\text{V}^{5+} \rightarrow \text{V}^{4+} + e$. The magnetic moment values of the compounds ($295 \text{ K}$), lying between 1.70 and 1.75 B.M. ($1 \text{ B.M.} \approx 9.27 \times 10^{-6} \text{ J/T}$) are consistent with the presence of vanadium(v) and are in excellent agreement with those reported in the literature for $\text{V}^{4+}$ systems.$^7$

The optical spectra of $\text{A}\{\text{VO(O}_2\text{F})\} \text{F}_2\text{H}_2\text{O}_2$ ($\text{A} = \text{NH}_4$, $\text{K}$, $\text{Rb}$, or $\text{Cs}$) recorded immediately after preparing solutions in cold dilute $\text{H}_2\text{O}_2$, showed three absorptions at $\lambda 11700$, $\lambda 1768$, and $\lambda 21400 \text{ cm}^{-1}$, with the last being obscured by strong charge-transfer transitions. The first two bands have been assigned to $\epsilon \rightarrow \delta$ and $\delta \rightarrow \delta$ transitions respectively and agree very well with the reported spectra of oxovanadium(v) complexes,$^9$ giving strong evidence for the presence of vanadium(v) in the orange-red peroxovanadium compounds. Our observations also support the very recent report$^8$ concerning the existence of peroxovanadium(v) in solutions.

The i.r. spectra (Table 2) of the series of four salts are similar, showing absorptions at $\lambda 3160 \text{ br}$, $\lambda 1630 \text{ br}$, $\lambda 1530$, $\lambda 1090$, and $\lambda 615 \text{ cm}^{-1}$. The band at $\lambda 890 \text{ cm}^{-1}$ has been assigned to the $\nu(\text{O}-\text{O})$ mode of the terminal bonded $\text{V}^2\text{O}_5\text{O}_2$ group,$^5$ while those at $\lambda 890$ and $\lambda 615 \text{ cm}^{-1}$ have been attributed to $\nu(\text{O}-\text{O})$ and $\nu(\text{V}-\text{O})$ respectively of the co-ordinated peroxide.$^8$ The absorptions at $\lambda 3160 \text{ br}$ and $\lambda 1630 \text{ br}$ cm$^{-1}$ have been attributed to $\nu(\text{O}-\text{H})$ and $\nu(\text{H}^\prime\text{O}-\text{H})$ modes of co-ordinated water. The lowering of the $\nu(\text{O}-\text{H})$ frequencies and broadening of $\nu(\text{H}^\prime\text{O}-\text{H})$ bands relative to those of free water suggest the possibility of intramolecular hydrogen bonding.$^{11}$ The band at $\lambda 475 \text{ cm}^{-1}$ is attributed to a $\nu(\text{V}-\text{O})$ stretching mode: its position suggests the presence of bridging rather than terminal$^1$ bond. The $\nu(\text{O}-\text{O})$ and the complementary $\nu(\text{V}-\text{O})$ fall in the regions expected for the triangular bonded $\text{O}_2^{2-}$ ligands.$^8,10,14,15$ We infer that the peroxide group is bonded to the $\text{V}^{4+}$ centre in a triangular bidentate manner. Two extra vibrations at $\lambda 140$ and $\lambda 140 \text{ cm}^{-1}$ in the case of the ammonium salt have been attributed to the $\nu_1$ and $\nu_2$ modes of $\text{NH}_4^+$. The $\nu_2$ mode of $\text{NH}_4^+$ could not be identified due to its overlap with the broad $\nu(\text{O}-\text{H})$ mode of water.

It thus appears that the complex ion has the formula $\{\text{VO(O}_2\text{F})\}_2\text{H}_2\text{O}_2$, containing a triply bonded peroxide ligand. The complex species may have a polymeric structure...
through V-F-V bridging; however, the possibility of a weak V-O-V interaction cannot be ruled out completely.

Acknowledgements

We thank the C.S.I.R. (New Delhi) for award of a fellowship (to S. K. G.).

References

14 Ref. 13, p. 325.
17 Ref. 16, p. 517.

Received 9th March 1983; Paper 3/376
Known methods of the synthesis of tris(acetylacetonato)-
iron(III), [Fe(acac)₃], have some limitations in scope. The
reaction between metallic iron and acetylacetone (Hacac) in
the presence of oxygen is extremely slow. The aqueous
reaction between iron(III) chloride and acetylacetone in
the presence of a large amount of sodium acetate as buffer 1,3 may
contaminate the product. The synthesis due to Dunne and Cotton 4 involving the reaction between [Fe(CO)₅] and
acetylacetone requires the preparation and handling of the
toxic air-sensitive metal carbonyl. The present report describes
a novel synthesis of [Fe(acac)₃] directly from iron(III)
hydroxide and acetylacetone, without the use of any buffer,
and characterization of the compound [equation (1)].

\[ \text{Fe(OH)}_3 + 3 \text{Hacac} \rightarrow \text{Fe}^{3+} + 3 \text{acac}^- + 3\text{H}_2\text{O} \quad (1) \]

**Experimental**

Reagent-grade iron(III) chloride and acetylacetone were used.
Infrared spectra were recorded on a Perkin-Elmer model 125
spectrophotometer. Magnetic susceptibility measurements
were made by the Gouy method using Hg[Co(NCS)₄] as the
calibrant. Molar conductance measurements were made
using a Philips PR 9500 conductivity bridge.

The mass spectra were recorded on a Varian MAT CH-5
mass spectrometer using a direct insertion probe. The opera­tion conditions were electron energy, 70 eV (1 eV = 1.6 × 10⁻¹⁹ J); source temperatures of 50, 100, and 150 °C; resolution,
1 000; and accelerating voltage, 8 kV. The mass spectrometric
observations were made with the field of ionising
current sufficiently strong to trap primary ions.

**Synthesis of Tris(acetylacetonato)iron(III)**, [Fe(C₅H₇O₂)₃]—Anhydrous iron(III) chloride (4.0 g, 24.7 mmol) was
dissolved in water (6 cm³) with gentle warming. Ammonia
solution (specific gravity 0.890, 9 cm³, excess) was added slowly
with constant stirring. The mixture was heated on a
steam-bath for 15–20 min, and the precipitate of iron(III)
hydroxide was then filtered off and washed with water until
free from chloride.

The moist iron(III) hydroxide and acetylacetone (12.0 g,
120 mmol) were placed in a small conical flask, the neck of
which was plugged with cotton wool, and the whole was heated
on a steam-bath for 35 min. On cooling, large red crystals of
[Fe(acac)₃] were obtained which were dried on filter paper and
recrystallised from ethanol. Yield, 7.8 g (90%), m.p. 175 °C
[Found: M (mass spectrometer), 353; C, 51.2; Calc. for C₆H₇O₂-
₃FeO: M, 353; C, 51.0%]. Molar conductance (H₂O):
Ω cm⁻¹ mol⁻¹. Magnetic moment (295 K): 5.92 B.M.

Acknowledgements

Our thanks are due to C.S.I.R. (New Delhi) for the award of
a fellowship (to S. K. G.).

**Results and Discussion**

Recently [Mn(acac)₃] was synthesised by the reaction of
[MnO₄]⁻ with acetylacetone 5 by exploiting the electron-transfer reaction between them. The weak acidity of Hacac in
a polar medium and the absence of any reaction of water with
[Fe(acac)₃] constitute the basis of the present synthesis. The
method described leads to the rapid synthesis of [Fe(acac)₃]
in a very high yield. Analogous methods have been used with
success for the synthesis of [Co(acac)₃] from CoO(OH) and
[Mn(acac)₃] from MnO(OH). The pH of the solution recorded
immediately after the formation of the compound was found
to be ca. 5 which concurs with that maintained by using a large
amount of sodium acetate 1,3 in the synthesis of [Fe(acac)₃]
from FeOCl₂.

The i.r. spectrum of the compound is unambiguous and
exhibits the typical pattern of chelated acetylacetonates
(acac⁻) in agreement with those of various [M(acac)₃] compounds. The mass spectra were obtained using a direct
insertion probe to introduce the sample into the ionisation
chamber without prior heating. The other conditions, except
the source temperatures, were similar to those maintained in
our earlier experiments. 7

The spectrum run at 150 °C parallels those previously
reported 5,9 showing the molecular ion at m/z 353 (intensity 16%) and the most dominant peak at m/z 254 assigned to
[Fe(acac)₃]⁺ with the major fragmentation pathway being
[Fe(C₅H₇O₂)₂]⁺ → [Fe(C₂H₅O₂)₂]⁺ → [Fe(C₆H₇O₂)-
(C₅H₇O₂)]⁺ → [Fe(C₅H₇O₂)]⁻ → Fe⁺. The metastable peaks at m/z 182.7, 224.9, 100.8, and 126.5 support the fragmentation path. The two additional,
metastable-supported signals at m/z 170 and 71 have been
assigned to the fragment ions [Fe(CH₃)(C₅H₇O₂)]⁺ and
[Fe(CH₃)]⁺ respectively, providing evidence for easy methyl
migration from carbon to metal presumably favoured by the
formation of a new bond between the metal atom and CH₃.

**References**

3. D. Nicholls, 'The Chemistry of Iron, Cobalt, and Nickel' in
   'Pergamon Texts in Inorganic Chemistry,' Pergamon Press,

Received 29th April 1982; Paper 2/708
Peroxyvanadates(V) have received considerable current interest, partly owing to the special biochemical significance of peroxo-transition-metal complexes. Whereas most of the recent reports on peroxovanadium chemistry deal with the studies in solutions, the synthesis and structural assessment of such compounds have received only scant attention. Moreover, only a few heteroligand peroxo complexes of vanadium are known, in contrast to many such reported examples for other trivalent metals. Our interest in this area involving the synthesis, characterization, and study of the chemistry of peroxyvanadium compounds has led to the synthesis of chloroperoxy compounds of vanadium(V). In this paper we wish to report the synthesis of two series of chloroperoxyvanadates(V), viz., the yellow alkali-metal and ammonium chloroperoxyvanadates(V), A2[V2O5Cl2](A = Na, K, or NH₄), and the blue alkali-metal and ammonium salts of triperoxychlorovanadates(V), A2[V3O8Cl2](A = Na, K, or NH₄), the first chloroperoxy compounds of vanadium. Also reported in this paper are a set of internally consistent data regarding the effect on the redox mode of O₂⁻ ligands with the increase in the number of such ligands in going from [V2O5Cl2]⁷⁻ to [V2O5OCl⁶]⁷⁻ and the facile interconversion [V2O5Cl2]⁷⁻ + [V2O5OCl⁶]⁷⁻, evidencing the ability of such compounds to undergo a basic formation reaction and an acidic dissociation reaction.

**Experimental Section**

The chemicals used in the present work were all reagent grade products (B.D. H. Merck, or Sardhath M. Chemicals). Infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer separately in KBr and in Nujol media. Molar conductances measurements were made by using a Phillips PR 9550 conductivity bridge. Magnetic susceptibility measurements were made by the Gouy method.

The compound Hg[Co(VCS₄)]₉ was the calibrant.

**Synthesis of** A2[V2O5Cl2](A = Na, K, or NH₄)

Vanadium pentoxide and dry alkali chloride, ACl, taken in the molar ratio 1:2, were intimately mixed by powdering them together in an agate mortar.

A concentrated solution of the corresponding alkali hydroxide, AOH, was then added to the mixed powder while the molar ratio V₂O₅ : AOH was maintained at 1:1.0, and the resulting mixture was stirred at room temperature for ca. 10 min. Hydrogen peroxide (3% solution) was slowly added to this solution with constant stirring, with the molar ratio of V₂O₅ : H₂O₂ rising ultimately to 1:1.4. Stirring was continued at room temperature for another 15 min, followed by filtration to remove any undissolved residue. The clear solution was cooled at ice-bath temperatures for ca. 20 min. An excess of ethyl alcohol was then added to the cold solution with stirring until yellow-colored microcrystals A2[V2O5Cl2] was obtained. The reaction container was allowed to cool at ice-bath temperatures for ca. 10 min. The compound was then treated by centrifugation, washed several times with ethyl alcohol until it was free from alcohol, and finally dried in vacuo over phosgene pentoxide. The yields of (NH₄)₂[V2O5Cl2], Na₂[V2O5OCl]₂, and K₂[V2O5Cl2] were 77%, 83%, and 77%, respectively.

**Synthesis of** A₂[V3O8Cl2](A = Na, K or NH₄)

The blue alka-
The synthesis of a new triaminocobalt(III) chloride complex was achieved through the reaction of CoCl₂ with the corresponding ammonium salt. The resulting complex was characterized by its unique magnetic properties and its potential use in various applications.

The complex was further studied in solution, where it showed excellent stability and solubility. The magnetic susceptibility measurements confirmed the proposed structure, and the infrared spectrum exhibited characteristic bands for the triaminocobalt(III) chloride moiety.

The potential of this complex as a catalyst in various chemical reactions was also explored, and promising results were obtained. Overall, the study highlighted the importance of this new complex in expanding the knowledge of cobalt chemistry and its potential applications.
The IR spectra of the three salts of the yellow \( [VO(O_2Cl)_2] \) ion resemble each other very closely (Table I), indicating that the compounds are similar both structurally and stoichiometrically. The absorptions occurring in the four characteristic regions, viz. at 915-920, 870-890, 770-790, and 530-545 cm\(^{-1}\)
1. The spectra of the three salts of the $[\text{VO}(\text{Cl})_2]^2$ anion also resemble each other very strongly, showing absorptions in the regions 855-860, 615-620, and 410-450 cm$^{-1}$, respectively, owing to the presence of coordinated peroxide and chloride ligands and the peaks are assigned to the $\nu_{\text{PC}}, \nu_{\text{PC}},$ and $\nu_{\text{PC}}$ modes. The three extra modes for the $\text{NH}_4^+$ ion in the case of the ammonium salt were also observed in their usual positions. The spectral pattern and the band positions resemble those of the analogous $[\text{VO}(\text{Cl})_2]^2$ compounds, suggesting that both the tripersychlorovanadate(V) and tripersychlorovanadate(VI) probably have structural similarity.

2. Conversion of $[\text{VO}(\text{Cl})_2]^2$ to $[\text{VO}(\text{Cl})_2]^2$ and the Reversal. Evidence for Facile Diper oxyvanadate(V)-Triper oxyvanadate(V) Interconversion. Having obtained the yellow oxytripersychlorovanadate(V), $[\text{VO}(\text{Cl})_2]^2$, and the blue tripersychlorovanadate(VI), $[\text{VO}(\text{Cl})_2]^2$, we thought it would be interesting to study the conversion of $[\text{VO}(\text{Cl})_2]^2$ to $[\text{VO}(\text{Cl})_2]^2$ and vice versa. We chose the sodium salts of the anions for such studies because of their stabilities. It was observed that under suitable conditions (vide Experimental Section) Na$_3[\text{VO}(\text{Cl})_2]$ can be easily converted to Na$_3[\text{VO}(\text{Cl})_2]^2$, which again can be converted to Na$_3[\text{VO}(\text{Cl})_2]^2$. The oxytripersychlorovanadate(V)-tripersychlorovanadate(V) interconversion reactions were found to be quite facile, thereby affording a very good example of a process involving a basic formation reaction and an acidic dissociation reaction. Although both compounds are formed in the presence of alkali medium and an excess of hydrogen peroxide, it is the large excess of alkali medium that favors the formation of the tripersychlorovanadate(VI) species. The peroxide uptake and the deperoxigenation reactions can be best monitored by IR spectroscopy. The complete conversion of the $[\text{VO}(\text{Cl})_2]^2$ to $[\text{VO}(\text{Cl})_2]^2$ is ascertained by observing the complete disappearance of the $\nu_{\text{PC}}$ band at ca. 950 cm$^{-1}$ in a small amount of the compound isolated from the solution.

3. It may be concluded that under the conditions described above, the complex species responsible for yellow and blue colors are $[\text{VO}(\text{Cl})_2]^2$ and $[\text{VO}(\text{Cl})_2]^2$, respectively. In each of the compounds the peroxide ligands are bonded to a tetrahedral vanadium(V) center. The complex species $[\text{VO}(\text{Cl})_2]^2$ may be a hexacoordinated monomer or it may as well be a polymer through a weak $\text{V}-\text{O}-\text{V}$ or a...
weak $V$–$Cl$–$V$ bridging. Similarly, the complex species $[V$
\((O_{2}Cl)_{3}]^{2-}$ may be a tetracoordinated monomer or it may have a
polymeric structure through a weak $V$–$Cl$–$V$ interaction.

The $[VO(O_{2}Cl)_{3}]^{2-}$ to $[V(O_{2}Cl)_{3}]^{2-}$ interconversion provides a
good example of a process that involves a basic formation reaction and an acidic dissociation reaction of peroxo-
vanadium($V^{IV}$) compounds.

Acknowledgment. Our thanks are due to C.S.I.R. (New
Delhi) for awarding a fellowship to S K G

References


The number of words in this manuscript is 2950.

The manuscript type is A.

Running Heads:

Chloroperoxovanadate($V$ IV) compounds.
Chaudhuri and Ghosh.

Author Index - Bhattacharya, P.
Ghosh, S. K.

Text Page Size Estimate = 0.6 Pages
Graphic Page Size Estimate = 0.5 Pages
Total Page Size Estimate = 0.1 Pages

Table 1. Analytical Data and Structurally Significant IR Bands of $A_i[VO(O_2)_iCl]$ and $A_i[VO_2Cl]$ ($A = Na, K, or NH_4$)

<table>
<thead>
<tr>
<th>compd</th>
<th>A or N</th>
<th>V</th>
<th>O$_x$</th>
<th>Cl</th>
<th>IR, cm$^{-1}$</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>% found (%)</td>
<td>calc</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(NH_4)_2[VO(O_2)_2Cl]$</td>
<td>13.21</td>
<td>24.82</td>
<td>32.13</td>
<td>17.72</td>
<td>970 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td>(13.84)</td>
<td>(23.16)</td>
<td>(31.64)</td>
<td>(17.81)</td>
<td>870 (2)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td>$Na_2[VO(O_2)_2Cl]$</td>
<td>22.21</td>
<td>24.34</td>
<td>31.33</td>
<td>16.28</td>
<td>955 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td>(21.65)</td>
<td>(23.99)</td>
<td>(30.14)</td>
<td>(16.69)</td>
<td>875 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td>$K_2[VO(O_2)_2Cl]$</td>
<td>31.57</td>
<td>20.21</td>
<td>26.88</td>
<td>14.38</td>
<td>970 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td>(31.97)</td>
<td>(20.83)</td>
<td>(26.17)</td>
<td>(14.49)</td>
<td>875 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>885 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td>$NH_4[VO_2Cl]$</td>
<td>12.87</td>
<td>22.79</td>
<td>44.66</td>
<td>16.72</td>
<td>855 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td>(12.97)</td>
<td>(23.32)</td>
<td>(43.94)</td>
<td>(16.23)</td>
<td>620 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>410 (s)</td>
<td>ν_O-CI</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3155 (m)</td>
<td>ν_O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3040 (v)</td>
<td>ν_O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1460 (s)</td>
<td>ν_O</td>
</tr>
<tr>
<td>$Na_2[VO_2Cl]$</td>
<td>20.92</td>
<td>22.85</td>
<td>42.93</td>
<td>15.22</td>
<td>860 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td>(20.15)</td>
<td>(22.31)</td>
<td>(42.04)</td>
<td>(15.52)</td>
<td>615 (s)</td>
<td>ν_v-O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>400 (s)</td>
<td>ν_O-CI</td>
</tr>
<tr>
<td>$K_2[VO_2Cl]$</td>
<td>30.82</td>
<td>20.31</td>
<td>36.13</td>
<td>12.25</td>
<td>855 (s)</td>
<td>ν_O-O</td>
</tr>
<tr>
<td></td>
<td>(30.06)</td>
<td>(19.58)</td>
<td>(36.00)</td>
<td>(13.63)</td>
<td>620 (s)</td>
<td>ν_v-O</td>
</tr>
</tbody>
</table>

*Proxy oxygen.
SYNTHESIS OF ALKALI OXYTETRAFLUOROVANADATES(V)

Mihir K. Chaudhuri*, Himadri S. Dasgupta and Soumitra K. Ghosh
Department of Chemistry, North-Eastern Hill University,
Shillong 793 003, INDIA

Darlando T. Khathing
Department of Physics, North-Eastern Hill University,
Shillong 793 003, INDIA

ABSTRACT

I.R. and $^{19}$F N.m.r. spectroscopy, molar conductance, magnetic moments and chemical analyses show that alkali oxytetrafluorovanadates(V), $\text{A}^I\text{VOF}_4^-$, are the principal products of the reactions of $\text{V}_2\text{O}_5$ with 40% HF and alkali bifluorides $\text{A}^I\text{HF}_2$ in presence of a small amount of alcohol at steam bath temperature. While the i.r. spectra suggest square pyramidal $C_4^V$ structures for solid $\text{A}^I\text{VOF}_4^-$, the $^{19}$F N.m.r. spectrum shows stereochemical non-rigidity owing to rapid fluorine rearrangement between $C_4^V$ and the trigonal bipyramidal $C_2^V$ stereochemistry of $\text{A}^I\text{VOF}_4^-$ in solution.

INTRODUCTION

Although there is $^{19}$F N.m.r. spectroscopic evidence for the existence of the oxytetrafluorovanadate(V) structures, the stereochemical non-rigidity observed in the N.m.r. spectrum indicates the presence of a rapid fluorine rearrangement between the square pyramidal and trigonal bipyramidal structures.

Copyright © 1982 by Marcel Dekker, Inc.