Chapter 3

Synthesis and Assessment of Structure of Alkali-metal and Ammonium Oxodiperoxofluorovanadates(V),
\[ A_2 \sqrt{\text{VO}_2 F_2} \] (A = Na, K, Rb, Cs or NH\(_4\))

Although there has been a continued interest in the study of peroxovanadium(V) chemistry,\(^1\)\(^-\)\(^7\) the synthesis, characterisation and structural assessment of peroxo and heteroligand peroxovanadium(V) compounds have received much less attention. This is presumably owing to the uncertain nature of peroxovanadium(V) in solutions of varying pH. In view of this and as a sequel of studies involving fluorocompounds of vanadium (Chapters 1 and 2), the synthesis of peroxofluorovanadium(V) compounds was undertaken.

The present Chapter (Chapter 3) reports first general synthesis of alkali-metal and ammonium:

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oxodiperoxo fluoro vanadates(V), $A_2 \sqrt{\text{VO}(O_2)_2 F}$

$(A = \text{Na, K, Rb, Cs or NH}_4)$ along with their characterization and structural assessment.

**Experimental**

Vanadium pentoxide, alkali-metal and ammonium fluorides and hydrogen peroxide were all reagent grade products (B.D.H., E. Merck, S.D., IDPL and Sarabhai Chemicals).

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

Magnetic susceptibility measurements were carried out by Gouy method using Hg $\sqrt{\text{Co(NCS)₄}}$ as a calibrant.

**Elemental Analyses.** Vanadium, Fluoride, sodium, potassium, rubidium, cesium and nitrogen estimations were accomplished by the methods described in Chapter 1.

**Active Oxygen (Peroxo-oxygen):** (1) Permanganometry:

An accurately weighed amount of the peroxovanadium(V) compound was dissolved in 7(N) sulphuric acid containing about 5 g of boric acid (to prevent loss of active oxygen through the formation of peroxoboric acid). The solution was then titrated with a standard potassium
permanganate solution

1ml (N) KMnO₄ solution = 0.01701 g H₂O₂

This method is suitable for peroxovanadium(V) compounds. The presence of fluoride does not effect the result.

(ii) Iodometry⁹: In this method an accurately weighed amount of the compound is added to a freshly prepared 2(N) sulphuric acid solution containing an appropriate amount of potassium iodide. The solution is maintained under a CO₂-atmosphere, and the liberated iodine is then titrated with a standard sodium thiosulphate solution.

The amount of iodine liberated in this process is equivalent to the amount of active oxygen (peroxide) plus the amount of vanadium(V) present in the compound. On subtraction of the contribution from vanadium(V), the contribution of active oxygen is found out.

1ml (N) Na₂S₂O₃ solution = 0.01701 g H₂O₂

(iii) Ceric (Ce⁴⁺) Sulphate Method.¹⁰ Peroxide content of a compound is determined directly by titration of an acidified solution of the peroxovanadium compound with a standard ceric sulphate solution. Vanadium(V), F⁻ or Cl⁻ do not interfere.
Synthesis of Alkali-metal and Ammonium Oxodiperoxo-fluorovanadates(V), $A_2 \left[ \text{VO}(O_2)_2 F \right]$ ($A = \text{Na, K, or NH}_4$).

A finely mixed powder of vanadium pentoxide, $V_2O_5$, (5.5 m mol) and alkali-metal or ammonium fluoride, AF, (11 m mol) was dissolved in 9% hydrogen peroxide (79.4 m mol) by slightly warming over a steam-bath, and a red solution was obtained. A concentrated solution of the corresponding alkali or ammonium hydroxide (50 m mol) was slowly added with constant stirring whereupon the solution became yellow. An excess of ethyl 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 diphosphorus pentoxide. The yields of $(\text{NH}_4)_2 \left[ \text{VO}(O_2)_2 F \right]$, $\text{Na}_2 \left[ \text{VO}(O_2)_2 F \right]$ and $K_2 \left[ \text{VO}(O_2)_2 F \right]$ were 1.6 g (78%), 1.8 g (84%) and 2.1 g (84%) respectively.

The $\text{Rb}_2 \left[ \text{VO}(O_2)_2 F \right]$ and $\text{Cs}_2 \left[ \text{VO}(O_2)_2 F \right]$ compounds were prepared in a manner analogous to that described above, however, the solution of $V_2O_5$ (5.5 m mol) and AF ($A = \text{Rb or Cs}$) (11 m mol) in 9% hydrogen peroxide (79.4 m mol) was made alkaline by the addition of 25% solution of ammonium hydroxide (50 m mol). The yield of
Rb$_2$ $\text{VO(O}_2\text{)}_2\text{F}^-$ was 2.6 g (74%) and that of Cs$_2$ $\text{VO(O}_2\text{)}_2\text{F}^-$ was 3.5 g (77%).

The analytical data, and the structurally significant i.r. bands of $\text{A\ VO(O}_2\text{)}_2\text{F}^-$ ($\text{A} = \text{Na, K, Rb, Cs or NH}_4$) compounds are set out in Table 1.

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**Results and Discussion**

It has long been recognised that vanadium forms yellow diperoxovanadate(V) in an alkaline medium$^{11}$, and is converted to a red monoperoxovanadium species in acidic solutions.$^6$ We observed that a similar yellow colour could be developed by performing a reaction of vanadium pentoxide, V$_2$O$_5$ and H$_2$O$_2$ in the presence of alkali-metal or ammonium fluoride, AF, in an alkaline medium, and thought that a heteroligand fluoroperoxovanadate(V) complex species must be responsible for this colour. Accordingly in line with our contention of synthesising heteroligand peroxo-vanadium compounds, we carried out the reactions among V$_2$O$_5$, alkali-metal or ammonium fluoride, AF, and hydrogen peroxide in the presence of an alkaline medium. The complex ion responsible for the yellow colour was isolated from the reaction medium as its alkali-metal or ammonium salt in
a very high yield. A report on the synthesis of $K_2 \left[ VO(O_2)_{2}F \right]_2$ appeared$^{12}$ while our work was in progress. However, the reaction condition of the present synthesis is different from the one previously reported.$^{12}$ We found that alkaline condition was more conducive to the synthesis of the $\Lambda_2 \left[ VO(O_2)_{2}F \right]_2$ compounds.

Alkali-metal and ammonium oxodiperoxofluoro-

vanadate(V) compounds are all yellow coloured microcrystalline products. They are soluble in water, in which they decompose slowly, thereby precluding their molar conductance measurements. The compounds can be stored undecomposed in sealed containers, and their stability can be ascertained by the periodic estimation of peroxide content of the products. Estimation of peroxide content, in such compounds, is considered to be of extreme importance in order to fix the number of $O_2^{2-}$ groups bound to the metal centre. The estimation of peroxide in the present case showed the presence of two peroxy groups per vanadium atom in each of the newly synthesised compounds. This result and the diamagnetic nature of the compounds, as evidenced by their magnetic susceptibility measurements, suggest that the complex ion contains two peroxy groups per vanadium
atom, and that the vanadium in each compound has oxidation state of +5.

The infrared spectra of the compounds are similar to each other, and show absorptions in the three characteristic regions, viz., at ca 880, ca 950 and ca 475 cm\(^{-1}\). The occurrence of sharp vibrations around 880 cm\(^{-1}\) (Table 1) imply the presence of triply bonded peroxy ligands \((\text{C}_2\text{v})\) and in keeping this there are two readily identifiable \(\nu_{\text{v}-\text{o}}\) bands at ca 895 and at ca 870 cm\(^{-1}\) \(^{7,13}\) another characteristic feature of the spectra is the absorption at 935-970 cm\(^{-1}\). This has been assigned to the \(\nu_{\text{v}-\text{o}}\) mode of terminal \(\text{v}-\text{o}\) multiple bonds.\(^{14,15}\) The strong absorption at 470-480 cm\(^{-1}\) in each spectrum, has been assigned as the \(\nu_{\text{v}-\text{f}}\) mode owing to the presence of a \(\text{F}^-\) ligand bonded to the vanadium(V) centre, and compare very well with those observed for many fluorovanadate species.\(^{16,17}\)

Thus, it is evident that heteroligand fluoroperoxo-vanadium(V) complex of the type \(\text{\(\nu\text{o}(O_2)^{2}\text{F}^{-}\)}\) can be synthesised from the reaction of \(\text{V}_2\text{O}_5\) with \(\text{H}_2\text{O}_2\) in an alkaline medium in the presence of alkali-metal or ammonium fluoride, \(\text{AF}\). The peroxy groups are bonded to the vanadium(V) centre in a triangular bidentate manner.
The complex species $\left[ VO(O_2)_{\frac{2}{2}} \right]^2-$ may be a hexa-coordinated monomer or it may have a polymeric structure through a weak V-O-V or a weak V-F-V bridging.

References


9 Ref. 8, p. 363.

10 Ref. 8, p. 325.


