mium–carbon bond in $Cr–CH_2C_6H_5^{2+}$[27] and the very low rate of homolysis of $Cr–CH(CF_3)OH^{2+}$.[5]

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**Registry No.** $Cr–CH(CH_3)_2^{2+}$, 60764-48-9; $Cr–C(CH_3)_2OH^{2+}$, 32108-93-3; $Cr–C(CH_3)_2CO_2H^{2+}$, 82494-81-3; $Cr–C(CH_3)_2CN^{2+}$, 82494-82-4; $Cr–CH_2CN^{2+}$, 76068-68-3; $Cr–CH_2CH_2CN^{2+}$, 76068-69-4; $Cr–CH(CH_3)CN^{2+}$, 82494-83-5; $Cr^{2+}(aq)$, 20574-26-9; $H_2O_2$, 7722-84-1.

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# Alkali-Metal and Ammonium Triperoxyfluorovanadates(V), $A_2[V(O_2)_3F]$

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Blue alkali-metal and ammonium triperoxyfluorovanadates(V), $A_2[V(O_2)_3F]$ (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 $[V(O_2)_3F]^{2-}$ 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,[2–6] 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 oxydiperoxyfluorovanadates(V), $A_2[VO(O_2)_2F]$. The compounds $A_2[VO(O_2)_2F]$ 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 triperoxyfluorovanadates(V), $A_2[V(O_2)_3F]$ (A = $NH_4$, Na, and K), and to make some reasonable conclusions about the formation of various peroxy compounds of fluorovanadium(V). We have also investigated the IR spectra of these solid compounds in order to obtain a set of internally consistent data regarding the effect on the basicity of peroxy ligands by the increase in the number of peroxy groups coordinated to fluorovanadium(V).

## 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), $A_2[V(O_2)_3F]$ (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 $A_2[V(O_2)_3F]$ 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-boiling 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 peroxide content of

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**Table I.** Amounts of Reagents Used and Yields of $A_2[V(O_2)_3F]$ (A = $NH_4$, Na, or K)

| compd | yield, g (%) | amt of $V_2O_5$, g (mmol) | amt of AF, g (mmol) | amt of 6% $H_2O_2$, mL (mmol) | amt of AOH (mmol) |
|---|---|---|---|---|---|
| $(NH_4)_2[V(O_2)_3F]$ | 1.9 (86) | 1.0 (5.5) | 0.4 (10.9) | 60.0 (105.8) | 9.2 mL (25% soln) (65.7) |
| $Na_2[V(O_2)_3F]$ | 2.0 (87) | 1.0 (5.5) | 0.46 (11.0) | 60.0 (105.8) | 2.6 g (65.0) |
| $K_2[V(O_2)_3F]$ | 2.3 (85) | 1.0 (5.5) | 0.64 (11.0) | 60.0 (105.8) | 3.7 g (65.9) |

**Table II.** Analytical Data and Structurally Significant IR Bands of $A_2[V(O_2)_3F]$ (A = $NH_4$, Na, or K)

| | % found (% calcd) | | | | | |
|---|---|---|---|---|---|---|
| compd | A or N | V | $O_A$[a] | F | IR, $cm^{-1}$ | assignts |
| $(NH_4)_2[V(O_2)_3F]$ | 13.81 (13.87) | 25.22 (25.23) | 46.97 (47.54) | 9.52 (9.41) | 850 (s)<br>475 (s)<br>3158 (m)<br>3040 (s)<br>1400 (s) | $\nu_{-O-O-}$<br>$\nu_{V-F}$<br>$\nu_3$<br>$\nu_1$<br>$\nu_4$ |
| $Na_2[V(O_2)_3F]$ | 21.56 (21.70) | 24.12 (24.04) | 44.87 (45.30) | 8.89 (8.97) | 855 (s)<br>470 (s) | $\nu_{-O-O-}$<br>$\nu_{V-F}$ |
| $K_2[V(O_2)_3F]$ | 32.11 (32.03) | 20.81 (20.87) | 38.93 (39.32) | 7.85 (7.78) | 855 (s)<br>470 (s) | $\nu_{-O-O-}$<br>$\nu_{V-F}$ |

[a] Peroxy oxygen.

these compounds was determined by redox titration with standard potassium permanganate solution[9] 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.[10] The volumetric procedure was carried out at pH 3.6–5.6. 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 diperoxyvanadate(V) in alkaline medium,[11,12] which is generally stable in solutions of high pH (>7). The yellow species is converted to red monoperoxyvanadate with increasing $H^+$ ion concentration[5,11,12] of the solution. However, none of these reports mentioned the formation of a blue coloration of the vanadium(V)–hydrogen peroxide system, though the solid blue tetraperoxyvanadate(V), viz., $K_3[V(O_2)_4]$, 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 diperoxyvanadium(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 synthsizing peroxyvanadium 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 peroxy 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 $V_2O_5$, AF, and 6% $H_2O_2$ in the presence of a large excess of alkaline medium gave rise to the formation of $[V(O_2)_3F]^{2-}$ 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 $[VO(O_2)_2F]^{2-}$ such that the formation of $[V(O_2)_3F]^{2-}$ is favored, or it could also be possible that the oxo oxygen of the yellow diperoxy 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 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 $\nu_{V-O}$ indicated the completion of the reaction. It is evident that, at least under the present condition, the minimum number of peroxy ligands responsible for the formation of blue peroxy compounds is 3.

**Characterization and Assessment of Structure.** The alkali-metal and ammonium triperoxyfluorovanadates(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 $[V(O_2)_3F]^{2-}$. 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 $V^{5+}$ 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

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magnetic susceptibility measurements.

Our attempts to measure the molar conductance of $A_2[V(O_2)_3F]$ 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 peroxyvanadium(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 $\nu_{-O-O-}$ 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 $\nu_{-O-O-}$ 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 $\nu_{V-F}$ modes arising from the presence of fluoride ion coordinated to the vanadium(V) center. This compares very well with the $\nu_{V-F}$ 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 $(NH_4)_2[V(O_2)_3F]$ 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 $A_2[V(O_2)_3F]$ with those of $A_2[VO(O_2)_2F]$ compounds, recorded under identical conditions. It is interesting to note that, while $\nu_{-O-O-}$ absorptions for $A_2[VO(O_2)_2F]$ compounds lie in the region 870–895 $cm^{-1}$, those of $A_2[V(O_2)_3F]$ 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 peroxy groups in the latter case. In other words, removal of further $\pi_{2p}$ density from $O_2^{2-}$ to the vanadium appears to have taken place in the case of $A_2[V(O_2)_3F]$ 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 $[V(O_2)_3F]^{2-}$ 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.

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**Registry No.** $[NH_4]_2[V(O_2)_3F]$, 82865-19-8; $Na_2[V(O_2)_3F]$, 82865-20-1; $K_2[V(O_2)_3F]$, 82865-21-2; $V_2O_5$, 1314-62-1; $NH_4F$, 12125-01-8; NaF, 7681-49-4; KF, 7789-23-3; $H_2O_2$, 7722-84-1.

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# Stereochemical Nonrigidity in Nine-Vertex Polyhedral Boranes: Dimethyl Sulfide Derivatives of Nonahydrononaborate(2−)[1]

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Reaction of nonahydrononaborate, $B_9H_9^{2-}$, with acetic anhydride/dimethyl sulfoxide yielded both isomers of $B_9H_8SMe_2^-$. Variable-temperature $^1H$ and $^{13}C$ NMR studies revealed these to exhibit the first example of intramolecular rearrangement of a nine-boron cluster. The activation barrier of this dynamic process has been found to be 22 kcal/mol. Disubstitution by prolonged reaction time followed by workup and recrystallization yielded a single isomer of $B_9H_7(SMe_2)_2$ identified by X-ray diffraction work as the 1,5-isomer. At ambient temperatures and above, dynamic behavior of this isomer was observed which suggested its equilibration with both the 4,5- and 1,8(9)-isomers. $^1H$ NMR (90 MHz) spectral data indicated coalescence at 130 °C due to rapid cage rearrangement with an activation barrier of 19 kcal/mol. This evidence for structural nonrigidity and the possible mechanism involved are discussed in light of known dynamic processes in cluster chemistry.

## Introduction

Structural nonrigidity in boron cluster compounds provides a useful model for fluxional behavior of coordination compounds in general and cluster compounds in particular.[2a,b] Especially appropriate is the family of polyhedral boranes, $B_nH_n^{2-}$, ranging in geometry from the six-vertex octahedron to the twelve-vertex icosahedron.[2c,d] An intriguing range of fluxionality exists. While $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ have high rearrangement barriers and are stereochemically rigid under normal conditions,[2c,d] $B_8H_8^{2-}$ has been shown to be nonrigid at 30 °C with an estimated activation barrier of only 12 kcal/mol.[3] More dramatically, $B_{11}H_{11}^{2-}$ has high fluxionality and its limiting solution spectrum was not observed even at −90 °C.[4] Although the intermediate $B_9H_9^{2-}$ species should

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