SOME CONTRIBUTIONS
TO
THE CHEMISTRY OF OXOFLUORO AND HETEROLIGAND PEROXO COMPOUNDS OF VANADIUM (V) AND (IV)
AND
SYNTHESIS AND STRUCTURAL ASSESSMENT OF BIS (ACETYLACETONATO)-FLUOROVANADATE (III) AND A NOVEL SYNTHESIS OF TRIS (ACETYLACETONATO)-IRON (III)

Abstract

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A THESIS
SUBMITTED IN FULFILMENT OF THE REQUIREMENT OF THE DEGREE OF
DOCTOR OF PHILOSOPHY

To

NORTH-EASTERN HILL UNIVERSITY
SHILLONG 793001
INDIA

JANUARY, 1984

Chem
(Thesis)

Abstract

Chapter 1 of the thesis describes the synthesis, characterization and structural assessment of alkali-metal and ammonium oxotetrafluorovanadates(V), $A[VOF_4]$ ($A = K$, Rb, Cs or NH_4). I.R. and ^{19}F N.m.r. spectroscopy, molar conductance, magnetic moments and chemical analyses show that $A[VOF_4]$ are the principal products of the reactions of V_2O_5 with 40% HF and alkali-metal and ammonium bifluorides AHF_2 in presence of a small amount of ethanol at steam-bath temperature. While the i.r. spectra suggest square pyramidal C_{4v} structures for the solid $A[VOF_4]$ compounds, the ^{19}F N.m.r. spectrum shows stereochemical non-rigidity owing to rapid fluorine rearrangement between C_{4v} and the trigonal bipyramidal C_{2v} stereochemistry of the $[VOF_4]^-$ ion in solution.

Synthesis and spectroscopic studies of a new oxofluorovanadate(IV) complex, $[VOF_3]^-$, constitute the subject matter of Chapter 2. Blue crystalline hydrazonium oxotrifluorovanadate(IV), $N_2H_5[VOF_3]$, has been synthesised by the reaction of V_2O_5 with an excess of 99% hydrazine hydrate in the presence of 40% HF. The alkali-metal and ammonium salts, of the complex anion, $A[VOF_3]$ ($A = Na$, K or NH_4), have been prepared by metatheses between $N_2H_5[VOF_3]$ and an excess of AF

in an aqueous medium. Characterization of the compounds was made from the results of chemical analyses, chemical determination of the oxidation state of vanadium, molar conductance and magnetic susceptibility measurements, infrared, electronic and esr spectroscopic studies. The molar conductance values of the hydrazonium, and alkali-metal and ammonium salts of $[VOF_3]^-$ ion suggest a 1:1 electrolytic nature of each of them, and their i.r. spectra show the multiple nature of the V-O bond and the absence of water. The magnetic moments of the compounds lie between 1.51 and 1.53 B.M. The solution electronic spectrum of $N_2H_5[VOF_3]$ shows absorptions at 11,950 and 16,000 cm^{-1}, without exhibiting any notable change with the addition of an excess of F^- ions, owing to the two d-d transitions characteristic of an oxovanadium(IV) species. The esr spectra of $N_2H_5[VOF_3]$ in an aqueous solution at 100K indicate that the complex species, $[VOF_3]^-$, has a distorted octahedral structure in solutions, through the coordination of two H_2O molecules to the oxovanadium(IV) centre in addition to the three coordinated fluoride ions. In the solid state, the complex ion, $[VOF_3]^-$ may have a polymeric structure through weak V-O...V and V-F...V interactions.

Chapter 3 describes the results of studies on alkali-metal and ammonium oxodiperoxofluorovanadates(V), $A_2[VO(O_2)_2F]$ (A = Na, K, Rb, Cs or NH_4). It has been shown that the reaction of vanadium pentoxide, V_2O_5, with hydrogen peroxide in an alkaline medium in the presence of alkali-metal and ammonium fluorides, AF (A = Na, K, Rb, Cs or NH_4) gives alkali-metal and ammonium oxoperoxofluoro-vanadates(V), $A_2[VO(O_2)_2F]$, in very high yields. Characterization of the compounds was made from the results of chemical analyses, magnetic susceptibility measurements and infrared spectroscopic studies. IR spectrometry showed the peroxo ligands to be bonded to the vanadium(V) centre in a triangular bidentate(C_{2v}) manner. The complex species $[VO(O_2)_2F]^{-}$ may be a hexacoordinated monomer, or it may have a polymeric structure through a weak V-O...V or a weak V-F...V bridging.

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been characterised 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 chelated peroxo 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 peroxo ligands increases with the increase in the number of peroxo groups coordinated to the vanadium(V) centre.

Synthesis, and assessment of structures of the first chloroperoxovanadate(V) compounds, and evidence for diperoxovanadate(V) —— triperoxovanadate(V) interconversion constitute the basis of Chapter 5. Alkali-metal and ammonium salts of yellow oxodiperoxochlorovanadates(V), $A_2[VO(O_2)_2Cl]$, and blue triperoxochlorovanadates(V), $A_2[V(O_2)_3Cl]$ (A = Na, K or NH_4), have been synthesised, for the first time, by reacting V_2O_5 with alkali chloride, ACl, and hydrogen peroxide in varying concentrations of alkaline media. The three salts of the anion $[VO(O_2)_2Cl]^{2-}$ are comparatively more stable than those of the complex anion $[V(O_2)_3Cl]^{2-}$. Characterization of the compounds have been made from the results of elemental analyses,

magnetic susceptibility measurements and infrared spectroscopic studies. The IR spectra suggest that the peroxo groups are bonded to vanadium(V) in a triangular bidentate manner, and that the O-O bond order of peroxo ligands decreases with the increase in the number of peroxo groups coordinated to the metal centre. The conversion of $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$, and the reverse provide good evidence for the facile diperoxovanadate(V) ——— triperoxovanadate (V) interconversion. The complex species $[VO(O_2)_2Cl]^{2-}$ may be a hexacoordinated monomer or it may as well be a polymer through a weak V-O-V or a weak V-Cl-V bridging. Similarly the complex species $[V(O_2)_3Cl]^{2-}$ may be a heptacoordinated monomer or it may have a polymeric structure through a weak V-Cl-V interaction.

Chapter 6 of the thesis reports the synthesis, characterization and structural assessment of alkali-metal and ammonium diaquofluoro-oxoperoxovanadate(IV) complexes, $A[VO(O_2)F(H_2O)_2]$ (A = K, Rb, Cs or NH_4). These compounds are the first peroxovanadate(IV) compounds to be obtained in the solid state. Orange-red alkali-metal and ammonium diaquofluorooxoperoxovanadates(IV), $A[VO(O_2)F(H_2O)_2]$, have been synthesised by the reaction of alkali-metal and ammonium tetrafluorooxovanadate(V), $A[VOF_4]$

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Chapter 7 describes the synthesis and assessment of structure of bis(acetylacetonato) fluorovanadate(III), $VF(acac)_2$, a novel neutral compound of vanadium(III). It has been shown that vanadium pentoxide, V_2O_5, undergoes a ready reaction with an excess of hydrazine hydrate in the presence of 40% HF to give $N_2H_5[VOF_3]$, which on being treated with acetylacetone affords blue-green crystalline bis(acetylacetonato) fluorovanadate(III), $VF(C_5H_7O_2)_2$, in a very high yield. The compound $VF(C_5H_7O_2)_2$ has been characterized on the basis of the results of chemical analyses, chemical determination of oxidation state of vanadium, magnetic susceptibility measurement, infrared

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The work described in Chapters 1, 3, 4 and 8 have been published, while those of Chapters 5, 6 and 7 are in press.

Chapter 1

Synth. React. Inorg. Met.-Org. Chem., 63, 12, 1982.

Chapter 3

Polyhedron, 553, 1, 1982.

Chapter 4

Inorg. Chem., 4020, 21, 1982.

Chapter 5

Inorg. Chem., in press.

Chapter 6

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Chapter 7

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Chapter 8

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Chem
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DEPARTMENT OF CHEMISTRY
Laitumkhrah, SHILLONG- 793003 (Meghalaya)

Phone : 26593
Grams : NEHU

Dr. Mihir Kanti Chaudhuri
Reader in Chemistry

I certify that the thesis entitled ". Some Contributions to The Chemistry of Oxofluoro and Heteroligand Peroxo Compounds of Vanadium(V) and (IV) and Synthesis and Structural Assessment of Bis(acetylacetonato) Fluorovanadate(III) and a Novel Synthesis of Tris (acetylacetonato) Iron(III). submitted by Mr. Soumitra Kumar Ghosh for the degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the Award of the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

Date. 18 Jan. 1984
Place: Shillong.

Mihir Kanti Chaudhuri
Signature of the Supervisor

North-Eastern Hill University

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December 12, 1983

This is to certify that Sri Soumitra Kumar Ghosh has satisfactoraly completed the following Pre-Ph. D. courses as prescribed by this university:

1. CHEM 640 - CHEMICAL KINETICS
2. CHEM 608 - BIO-INORGANIC CHEMISTRY

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C O N T E N T S

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Soumitra Kumar Ghosh.

(Soumitra Kumar Ghosh)

Shillong.
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Summary

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Introduction

The highest oxidation state of vanadium is + (V). Vanadium (V) forms two oxo-species, the VO^{3+} and VO_2^+ ions, and none of these disproportionates because of their being better oxidants. The VO^{3+} unit occurs in the oxyhalides VOX_3 (X = F, Cl or Br) in which the V-O stretching frequencies are at 1058, 1035 and 1025 cm^{-1} respectively. In addition, however, a number of complexes of the types $VOCl_3.L$ and $VOCl_3.2L$, in which L can be an oxygen-donar or a nitrogen-donar ligand, have been characterized.[1,2] The complexes appear to be either five - or six coordinate monomers.

Vanadium oxychloride, $VOCl_3$, has been shown to react[1] with ligands containing replaceable hydrogen atoms to give rise to substitution products of the type $VO(OMe)_3$, $VOCl_2(OMe)$, $VOCl_2(OEt)$, $VOCl(OEt)_2$, $VOCl_2(acac)$, $VOCl(acac)_2$ (Hacac = acetylacetone). Very little structural information is available for these complexes. The structure of the alkoxide $VO(OMe)_3$ has, however, been determined, and it has been shown that the molecule is a linear polymer, with a dimeric repeat unit and alkoxide bridging.[3]

The second oxovanadium(V) species, the VO_2^+ ion, is not very much characterized, but it is believed to occur discretely in the complexes $VO_2(NO_3)$, VO_2F and $VO_2(SbF_6)$, and as a cis-VO_2 unit in the complexes[4] $K_3[VO_2(C_2O_4)_2]$ and $K_3[VO_2F_4]$. The other example of complex compounds formed under non-aqueous conditions include the salts of $VOCl_4^-$ and VOF_4^- (Ref 5).

The complex species, VOF_4^-, is particularly interesting because this exhibits fluxional behaviour[5] in solution. However, no simple method is available for the synthesis of oxotetrafluorovanadate(V) complexes. The only compound $CsVOF_4$ was prepared by Howell and Moss[5] under non-aqueous conditions and carrying out the reaction at -30°C.

Chapter 1 of the present thesis describes a new and simple general method for the synthesis, and isolation in the solid state, of $AVOF_4$ (A = K, Rb, Cs or NH_4) compounds from aqueous media, together with the characterization of these compounds.

The chemistry of vanadium(IV) is largely dominated by the formation of oxo species, and a wide range of compounds with VO^{2+} groups is known. Although many oxometal species have been characterized to date, the

diatomic ion VO^{2+} is thought to be the most stable ion known. The ion VO^{2+} forms a wide variety of complexes which may be cationic, neutral or anionic.[6,7]

The oxovanadium(IV) complexes are generally of the type[3,8] $[VOL_5]^{n\pm}$, $[VOL_4]^{n\pm}$, $[VOL_xL'_{5-x}]^{n\pm}$ or $[VOL_xL'_{4-x}]^{n\pm}$ e.g. $A_3[VOF_5]$, $A_2[VOF_4]$, $VOCl_2$, 3DMSO (DMSO = Dimethylsulphoxide) and $VOCl_2.2C_5H_5N$. The VO^{2+} entity bonds most effectively to the most electronegative atoms, e.g. F, Cl, O, or N, although bonds to S and P are also known.

The structures of several oxovanadium(IV) species have been determined by X-ray crystallography. The characteristic coordination polyhedron is the tetragonal pyramid, in which the axial V=O bond has a length of 1.57 - 1.68 A°, the equatorial V-O bonds are $\sim$ 0.4A° longer, the O=V-O angles are $\sim$ 106°, and the vanadium atom lies $\sim$ 0.55 A° above the plane formed by the four singly-bonded oxygen atoms. In some complexes, octahedral coordination is completed by the formation of a further relatively long bond trans to the V=O bond. Some of the structures are of particular interest. The complex $VO(H_2O)_5SO_4$ occurs in three forms, one monoclinic and two orthorhombic. The structure of the monoclinic form indicates that the VO^{2+} group is bound

to four water molecules and to one of the oxygen atoms of the sulphate group.[9] The latter is in the cis-position to the VO^{2+} group, and not the trans-position.

The most characteristic feature of the infrared spectra of oxovanadium(IV) complexes is the very strong, sharp band at 985 ± 50 cm^{-1}. This band is assigned to the V=O stretching frequency[6], and, as expected lies near the upper frequency limit for those complexes which are known from X-ray work to have the shortest V=O bonds. Coordination of ligand to the sixth octahedral position, i.e. the position trans to the V=O bond, brings about a drop of ~50 cm^{-1} in the V=O stretching frequency of the parent complex.

The magnetic moments of oxovanadium(IV) complexes lie almost invariably in the range 1.70 - 1.73 B.M. This result is to be expected since the ligand field around the vanadium(IV) ion (d^1 configuration) is strongly axial, and hence all the orbital contribution to the moment is quenched.[3] The magnetic moments of discrete oxovanadium(IV) complexes should thus be, and indeed are, independent of temperature.

The e.s.r. g_{av} values for oxovanadium(IV) complexes occur in the range 1.95 - 2.00, i.e. close to the

spin-only value of 2.00.[23] Both these results and the fact that the anisotropy of the g-values is small in comparison with that for the magnetically similar d^9 complexes, indicates that the axial component to the ligand field is high. The unpaired electron lies in an orbital of b_2 symmetry.[8]

The optical spectra[6] of oxovanadium(IV) complexes are characterized by three d-d transitions ($5 < E < 100$) in the range 8000-32,000 cm^{-1}. The first band lies in the range 11,00 - 14,700 cm^{-1}, the second in the range 14,800 - 20,400 cm^{-1}, and the third in the range 21,000 - 31,250 cm^{-1} and are assigned to $e \leftarrow b_2$, $b_1 \leftarrow b_2$ and $a_1 \leftarrow b_2$ transitions respectively. The third band is frequently obscured by strong charge transfer transitions, and the first band in the spectra of some complexes shows vibrational structure ($\sim$ 700 cm^{-1} spacings, corresponding to the V=O stretching frequency in the excited state).

A number of attempts have been made at detailed interpretations of the ligand field spectra of oxovanadium(IV) complexes. The most successful of these is the molecular orbital treatment of the $VO(H_2O)_5^{2+}$ ion by Ballhausen and Gray.[10] The bonding scheme in the

Ballhausen-Gray treatment is described as follows:

> a strong σ-bond of a_1 symmetry between the sp_σ oxygen hybrid orbital and the $(4s + 3dz^2)$ hybrid orbital on the vanadium atom;
>
> two π bonds of e symmetry between the $2p_x$ and $2p_y$ oxygen orbitals and the $3d_{xz}$ and $3d_{yz}$ vanadium orbitals;
>
> four σ-bonds between the four equivalent sp_σ (water) oxygen hybrid orbitals and the $(4s - 3dz^2)$ (a_1), $4p_x$, $4p_y(e)$ and $3d_{x2-y2}(b_1)$ vanadium orbitals;
>
> the fifth water molecule is bound to the $4p_z(a_1)$ vanadium orbital, leaving the $3d_{xy}(b_2)$ orbital non-bonding and free to hold the single d-electron of vanadium(IV).

The order of the energy levels is thus $b_2 < e\pi^* < b_1^* < a_1^*$. Thus, the π-bonding in the ion $VO(H_2O)_5^{2+}$ is essentially axial, giving rise to a triple bond between the vanadium and the unique oxygen atom.

Our interest in the field of fluorometalate chemistry led us to synthesise the hitherto unreported oxotrifluorovanadate(III) complexes, VOF_3^-. We were particularly interested on the VOF_3^- species because

such a species has no reported evidence in the literature, although the corresponding $VOCl_3^-$ ion has been known.[11] Further we were interested in the structure and chemistry of oxotrifluorovanadate(IV) complexes.

Chapter 2 of the thesis presents the synthesis of the VOF_3^- ion and its isolation in the solid state as hydrazonium and alkali-metal salts. The Chapter 2 also reports the results of structural assessment of the newly synthesised compounds.

It has been known[12] for over a century that characteristic colour reactions may take place when hydrogen peroxide is added to solutions of transition metal derivatives, and many peroxy transition metal compounds have been isolated in the solid state. Peroxy derivatives of metals, besides having an intrinsic interest of their own, are of considerable and growing importance particularly in relation to the catalysis of oxidations involving hydrogen peroxide or oxygen gas, the catalytic decomposition of H_2O_2 itself, and the storage and transport of oxygen in biological systems.[13,14]

Although the term molecular oxygen refers only to the free uncombined O_2 molecule with the ground state

$^3\Sigma_g^-$, the term dioxygen has been used as a generic designation for the O_2 moiety in any of its several forms, and can refer to O_2 in either a free or combined state.[15] For use of this term it is essential that a covalent bond has to exist between the oxygen atoms. Thus, a metal-dioxygen complex refers to a metal containing O_2 group coordinated to the metal centre, and no distinction is made between neutral dioxygen or dioxygen in any of its reduced forms. Accordingly, a metal-peroxide complex is one in which the coordinated dioxygen resembles a peroxide (O_2^{2-}) anion.[13] The incorporation of O_2 into a metal complex to form a metal-dioxygen compound is called <u>oxygenation</u>, and the reverse is known as <u>deoxygenation</u>.

Simple peroxo compounds of transition metals are the ones which contain peroxides, hydroperoxides and water molecules, whereas heteroligand peroxo complexes are mixed ligand metal complexes containing one to three coordinated peroxo groups, and one or more monodentate or polydentate ligands. Heteroligands range from monodentate halide ions to bulky porphyrin[14] (F, Cl, NH_3, C_2O_4, NTA, EDTA, dipy, O-phen, oxine, porphyrin, pyridine-2,6-dicarboxylate etc.) The stability of peroxo complexes is generally enhanced by

specific heteroligand combinations. Thus, many simple transition metal peroxides often explode spontaneously; some are sensitive to shock or decompose above 0°C and several do not exist at all as stoichiometric compounds.[12] Many heteroligand peroxo complexes, on the other hand, survive recrystallisation from boiling aqueous solutions, heating in vacuo, and remain unchanged for prolonged periods in closed containers.[16]

The biochemical significance of peroxo-metal complexes has been emphasized recently in the literature.[17-20] The reactivity of peroxides and the lability of metal-oxygen bonds in special heteroligand environments in solutions are of particular interest to biochemistry, but are not easy to measure directly.

A comparison between the peroxo and unreduced dioxygen heteroligand complexes reveals that the chemistry of the two is very different owing to the presence of two extra electrons in the antibonding O-p π^* orbitals of the peroxide ion. The electron rich O_2^{2-} ion therefore preferably forms complexes with metal ions of low d^n electron configuration, while the neutral dioxygen molecule favour higher d^n metal acceptors. However, there are at least two things that these two oxygen species have in common: both are

stabilised by specific heteroligand spheres, and both are of importance in biochemistry.

The importance of neutral dioxygen complexes in biochemistry is well known, but the biochemical connection of the metal peroxo complexes with biological processes is not very well understood. The transition metals, Sc, Ti, V, Cr, Y, Zr, Nb, Mo, La, Hf, Ta, W, form stable heteroligand peroxo complexes, and there is increasing evidence that vanadium has a significant biological role.[21] It is reasonable to assume that the participation of vanadium will depend upon parameters such as pH, and the availability of inorganic or organic molecules that can act as heteroligands.

Molecular oxygen is a paramagnetic molecule, having a triplet $^3\Sigma_g^-$ ground state. A molecular orbital description of $^3\Sigma_g^-$ level is

$$O_2\ KK(2s\,\sigma_g)^2\ (2s\,\sigma_u^*)^2\ (2p\,\sigma_g)^2\ (2p\,\pi_u)^4(2p\,\pi_g^*)^1(2p\,\pi_g^*)^1$$

where the KK term indicates that the K shells of the two oxygen atoms are filled. The two unpaired electron in the $^3\Sigma_g^-$ ground state are found in the two degenerate antibonding $2p\,\pi_g^*$ orbitals (Fig.1), leaving O_2 with a formal bond order of two.

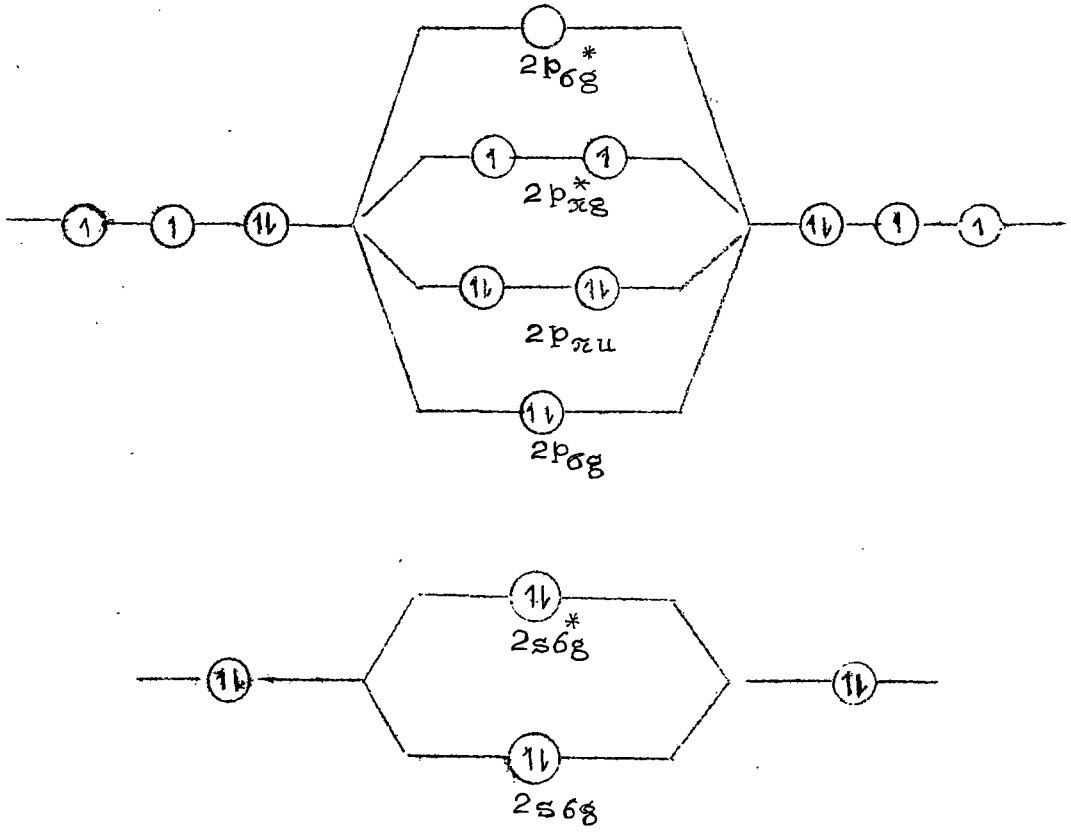

Fig. 1.

The MO description of O_2 ($^3\Sigma_g^-$) shows a vacancy for the addition of a single electron in both of $2p_g$ orbitals. The addition of one or two electron to

a neutral O_2 results in formation of the superoxide (O_2^-) and peroxide (O_2^{2-}) species, respectively, leaving O_2^- with a bond order of 1.5, and the peroxide O-O link with a normal bond order of one. Some of the salient features for O_2, O_2^- and O_2^{2-} are summarized in Table 1.

Table 1. Some Properties of O_2, O_2^- and O_2^{2-}

	Bond order	Compound	O-O distance(A°)	Bond energy(Kcal/mol)	O-O cm^{-1}
O_2	2	O_2	1.207[22]	117.2	1554.7[24]
O_2^-	1.5	KO_2	1.28	-	1145[25]
O_2^{2-}	1	Na_2O_2	1.49[23]	48.8	842[26]

The way in which a peroxo group is expected to coordinate to metals (Fig. 2) can range from a symmetrical bidentate to a terminal monodentate position, including all the possible angles in between.

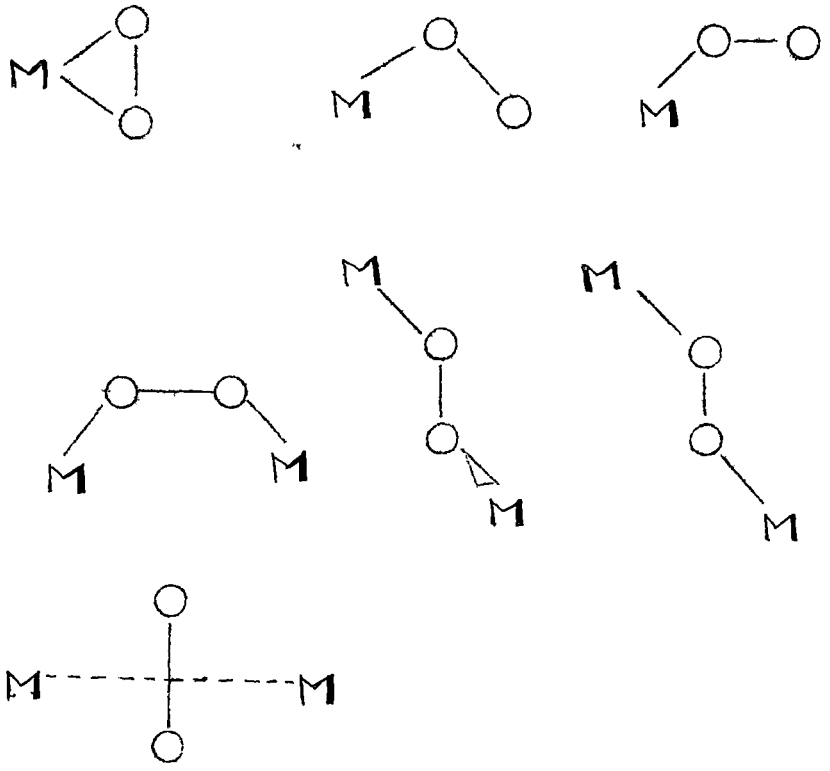

Fig. 2.

The bridging μ -peroxo could vary from cis-planar and trans-planar to trans-nonplanar configurations. An unusual symmetrical double bridging was also found.[27] Deviations from the ideal symmetry are common. In the cases of heteroligand fields they are due to the inherent symmetry of different donar atoms. Additional p π^* electron delocalization to the metal ion is

anticipated, which would therefore favour d^0 or low d^n metal ion configurations.

The stereochemical polyhedra in heteroligand peroxo complexes are fairly predictable. For the second row elements Nb and Mo, coordination number 8 with dodecahedral (D_{2d}) symmetry has invariably been observed in the absence of oxo groups. In oxoperoxo heteroligand surroundings, the pentagonal bipyramidal arrangement is the most common, usually with two coordinated peroxogroups in the cis positions and one oxo group in an axial position. There is an interesting non-octahedral example of coordination number 6 for a vanadium complex.[28]

Infrared spectra are essential for the characterisation of complexes containing coordinated peroxo groups. For a bidentate peroxide, regarded as a C_{2v} unit, three i.r. active modes are expected:[29] the peroxo stretching (A_1), and symmetric assymmetric $M-O_2$ stretchings (A_1 and B_2). The ν(O-O-) band is the most sensitive and intense one and characteristrically occurs between 800 and 900 cm^{-1}. The frequency of this band remains fairly independent of the heteroligand environment, but is affected by the mass of the metal

ion, indicating coupling of the ν(-O-O-) with M-O_2 vibrations. This most familiar way of bonding of O_2^{2-} groups, in a triangular bidentate manner, is similar to that proposed by Griffith[30] for the bonding of O_2 in oxyhemoglobin, and the ν(-O-O-) values, which are similar to those observed for free O_2^{2-} ion.

The dimeric peroxo complex is often more stable than the monomeric complex and will generally form unless its formation is inhibited. (e.g. $[(NH_3)_5Co-O_2-Co(NH_3)_5]^{4+}$). These complexes are diamagnetic with the oxygen being viewed as "peroxide-like" with a concomitant oxidation of the metal centres to low-spin d^6 (Co^{3+}). The ν(-O-O-) for such complexes span a range of 790-844 cm^{-1} with an avarage value of 810 cm^{-1} (c.f. μ-peroxo).[13]

Heteroligand complexes of Nb and Ta are rather easily formed. Structural analysis of some such niobium complexes show that the coordination polyhedron is dodecahedral.[31] Vanadium, however, presents a different story. Several peroxo and oxoperoxo vanadium(V) species occur,[12] but only few heteroligand complexes are known.[28,32] Unlike Nb and Ta, vanadium has a strong tendency to form oxoperoxo species.

The reaction of concentrated alkali hydroxide with concentrated solutions of V_2O_5 in H_2O_2 at $>0^oC$ gives blue solutions which contain the ion $V(O_2)_4^{3-}$. The salts of $V(O_2)_4^{3-}$ can also be obtained by addition of alcohol to such solutions. The salts are stable only at low temperatures, the stability decreasing with increasing cation size.[12] The potassium salt which is isomorphous with $K_3[Cr(O_2)_4]$, has a magnetic moment of 0.6B.M., consistent with the presence of vanadium(V). The i.r. spectra of the $(NH_4)_3[V(O_2)_4]$ and $K_3[V(O_2)_4]$ contains bands in the region 800-900 cm^{-1} that have been assigned to ν(-O-O-) modes of peroxy groups.[33]

It is suggested that slight excess of a base causes the destruction of the tetraperoxy species and the formation of the yellow triperoxy anion $VO(O_2)_3^{3-}$:

$$V(O_2)_4^{3-} + OH \rightleftharpoons V(O)(O_2)_3^{3-} + HO_2^-$$

which is stable at room temperature.

The yellow colour produced by addition of H_2O_2 to a dilute solution of a metavanadate has been shown to be due to be a diperoxy anion by cryoscopy and spectrophotometry[34] as well as by thermochemical studies.[35] There is, however, some controversy as to how the anion should be formulated, although the results of cryoscopic

and spectrophotometric studies have been interpretated in terms of the monobasic anion $[VO(O_2)_2]^-$.

The addition of H_2O_2 to V_2O_5[36], to an acid solution of a metavanadate,[37] to a vanadium (V) salt in weakly acid solution,[38] and to a decavanadate[39] produces a red colour due to the monomeric monoperoxyvanadate cation $VO(O_2)^+$. The red colour is stable in moderately acid media. In excess H_2O_2 the red cation is converted to the yellow peroxy anion $VO(O_2)_2^-$ (Ref. 38,39). It has been concluded[12] that,

(i). the number of peroxy groups per vanadium atom increases with alkalinity;

(ii). increasing acidity increases polymerisation and decreases the number of peroxy groups per vanadium atom;

(iii). increasing the concentration of H_2O_2 decreases the degree of polymerization.

Vanadium peroxo complexes are of special interest because of the function of V in living cell is unknown,[40] and is selectively toxic in mammals. From biochemical point of view, the most interesting aspect of peroxo-vanadium chemistry remains the experimental approach to measuring the reactivity of the coordinated peroxo group in an environment of various heteroligand fields.

The reactivity of coordinated peroxo groups means essentially the ease of electron-transfer to and from the dioxygen anion (O_2^{2-}). Thus, studies involving heteroligand peroxo complexes of vanadium requires an immediate attention. The chemistry of these compounds embraces a fascinating, rewarding and worthwhile area of investigation.

Chapters 3-6 of the present thesis describe syntheses, characterization structural assessment and some chemistry of a number of heteroligand (viz., fluoro and chloro) peroxo complexes of vanadium(V) and (IV).

Complexes of vanadium (III) are usually prepared by direct reaction between the vanadium trihalide and the ligand, all operations being carried out on a vacuum line.[8] The complexes are unstable towards air and moisture. All three types of complexes viz., cationic, anion and neutral have been known. The magnetic moments of octahedral vanadium (III) complexes ($^3T_{1g}$ ground term) are expected to be $\sim$ 2.8 B.M. at room temperature and to fall appreciably with a lowering of temperature.[41] In practice, however, the temperature dependence of these magnetic moments is less pronounced than is expected for an orbital triplet ground term; indeed, it is

consistent with a splitting of the ground triplet by some 500 - 2000 cm^{-1}. The splitting is most obviously brought about by a non-equivalence of all six ligands.

Tetrahedral vanadium(III) complexes, with a $^3A_2$ ground term, are expected to show a temperature independent magnetic moment of $\sim$ 2.7 B.M. and do so in practice.[8]

The electronic structure and spectra of octahedrally coordinated vanadium(III) (d^2) complexes have been interpreted satisfactorily in terms of the ligand-field model, although in general it has been found necessary to take account of the effects of a trigonal distortion (to D_{2d}) of the octahedral field.[42]

Vanadium trihalides form various neutral complexes, and the known examples can be classified into VL_3X_3 and VL_2X_3 types.[8] No example of neutral complex of the type $V(L\text{-}L')_2X$ (where L-L' is a bidentate uninegative ligand and CX is a halide) is known. Moreover, no report has been available on the synthesis of a neutral complex of vanadium(III) from a higher valent vanadium species through electron-transfer reactions.

Chapter 7 presents an account of the synthesis of bis(acetylacetonato) flurovanadate(III) complex achieved by an electron-transfer reaction between a

vanadium(IV) compound and acetylacetone (Hacac). This Chapter also reports the results of various physico-chemical studies, including mass spectrometry, of the newly synthesised neutral complex of vanadium(III).

As part of a programme of the laboratory, in which the whole work was done, a new method of synthesis of tris (acetylacetonato) iron(III), $Fe(C_5H_7O_2)_3$, has been developed. This compound has been known for quite sometime, but the methods used for its synthesis suffer from many difficulties. For example, the reaction between metallic iron and Hacac in the presence of oxygen[43] is extremely slow. The reaction between iron(III) chloride and Hacac in the presence of a large amount of sodium acetate as buffer[44,45] may contaminate the product. The reaction between $Fe(CO)_5$ and Hacac[46] requires the preparation and handling of the toxic air-sensitive metal carbonyl.

Chapter 8, indeed the last Chapter of this thesis, reports a novel synthesis and mass spectrometric studies of tris(acetylacetonato) iron(III), $Fe(C_5H_7O_2)_3$. Advantages of the new synthesis have been discussed.

Attempts have been made to make each Chapter a self-contained one. Thus, every Chapter has been provided with a brief introduction, experimental section, results and discussion section, and the relevant bibliography.

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Chapter 1

Synthesis. Characterization and Structural Assessment of Alkali-metal and Ammonium Oxotetrafluorovanadates(V), A $[VOF_4]$ (A = K, Rb, Cs or NH_4)*

Although there is ^{19}F N.m.r. spectroscopic evidence for the existence of the oxotetrafluorovanadate(V) ion, $[VOF_4]^-$ in aqueous hydrofluoric acid[1], the species has not been prepared from an aqueous solution. 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°C.[2] This, however, may not be true in the case of fluoride (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

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* The work described in this Chapter has been published: Synth. React. Inorg. Met.-Org. Chem., 63, 12, 1982.

it was an impure sample of $NaVOF_4$.[3] However, little was known about any pure A $[VOF_4]^4$ in the solid state until 1970. In 1971 the first and only pure solid salt Cs $[VOF_4]$ was prepared by Howell and Moss[4] from the reaction of V_2O_5, anhydrous HF and CsF at - 30°C. In view of this it appeared worthwhile to develope a method for the synthesis of A $[VOF_4]$ compound from aqueous media.

Chapter 1 of the thesis describe a novel and simple general method for the synthesis and isolation of alkali-metal and ammonium oxotetrafluorovandates(V), A $[VOF_4]$ (A = K, Rb, Cs or NH_4) from aqueous media, together with the characterization and assessment of structure of these compounds.

Experimental

All chemicals used were of reagent grade (B.D.H., E. Merck, IDPL, Sarabhai M. Chemicals).

Infrared spectra of the A $[VOF_4]$ compounds were recorded on a Perkin-Elmer model 125 spectrophotometer.

Molar conductivity studies were made at room temperature using a Philips PR9500 conductivity bridge.

Magnetic susceptibility measurements were made at room temperature by the Gouy method using Hg $[Co(NCS)_4]$ as the calibrant.

^{19}F N.m.r. spectra were recorded on a Brucker HX-60/5 instrument.

Alkali-metal and Ammonium Bifluorides, AHF_2.

The AHF_2 compounds were prepared by the methods developed by Chaudhuri and Chaudhury.[5] In an example representative of the general procedure, powdered alkali-metal or ammonium fluoride was dissolved in 40% hydrofluoric acid maintaining the molar ratio of AF:HF at 1:4. To the clear solution pyridine was added slowly with constant stirring until the precipitation was complete, and then allowed to settle. The white crystalline compound was separated by decantation and washed freefrom hydrofluoric acid by pyridine and then the adhered pyridine was removed by washing with acetone and finally dried in vacuo.

Elemental Analyses. Vanadium[6]: Vanadium was estimated volumetrically by titration with a standard potassium permanganate solution. A near boiling solution of an accurately weighed amount of the vanadium(V) compound 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 a standard potassium permanganate solution.[6]

Fluoride[7]: The determination of fluoride was made by precipitating fluoride from a solution, of the known amount of a compound, as lead chloride fluoride, PbClF, and estimating chloride by Volhard's method, from which the fluoride content was calculated.[7]

From a solution of an accurately weighed amount of the compound, fluoride was quantitatively precipitated as lead chloride fluoride, PbClF, by following the usual procedure.[7]

The precipitated PbClF was washed once with water and then 4 - 5 times with a saturated solution of PbClF. The pure PbClF was treated with a 5% nitric acid solution. An accurately known amount of a 0.1 (N) silver nitrate solution (excess) was added to the above solution and the whole was heated on a steam-bath for ca 15 min under stirring. The solution was then filtered, and the clear filtrate (containing silver nitrate) was titrated with a standard 0.1 (N) potassium thiocyanate solution using Fe^{3+} (ferric ammonium sulphate) as the indicator. The

amount of silver nitrate utilised in the process is equivalent to the amount of fluoride present in the amount of the sample taken.

1 ml (N) $AgNO_3 \equiv 0.0190$ g F

Potassium : Potassium content was determined by flame photometry after the salt was dissolved in water and acidified with hydrochloric acid.

Rubidium and Cesium[8]: Rubidium and Cesium were estimated gravimetrically as their perchlorates $RbClO_4$ and $CsClO_4$, from the solutions of accurately weighed amounts of the rubidium and cesium salts.

Nitrogen: Nitrogen was estimated by a microanalytical method.

Synthesis of Alkali-metal and Ammonium Oxotetrafluorovanadates(V), $A[VOF_4]$ (A = K, Rb Cs or NH_4). Since the methods of syntheses of alkali-metal and ammonium oxotetrafluorovanadates(V) are similar, only a general method is described.

Stoichiometric quantities of V_2O_5, 40% HF and AHF_2 (A = K, Rb, Cs or NH_4) (1 : 4 : 2 molar ratio) maintaining V : F at 1 : 4 were heated for a few minutes at ca 100°C in a polyethylene beaker. Ethanol

Table 1. Amounts of Reagents Used, Yields and Analytical Data of A $[VOF_4]$ compounds

Compound	Amount of reagent used		Yield of A$[VOF_4]$ in g(%)	% Found (% Calcd.)		
	Reagent	Amount in g (in mol)		V	F	A or N
$NH_4[VOF_4]$	V_2O_5	2.0 (11)				
	40%HF	2.2 (44)	1.83 (52)	31.8 (31.64)	47.28 (47.21)	8.21 (8.70)
	NH_4HF_2	1.26 (22)				
$K[VOF_4]$	V_2O_5	2.0 (11)				
	40%HF	2.2 (44)	2.44 (61)	28.1 (27.98)	42.1 (41.75)	21.54 (21.48)
	KHF_2	1.72 (22)				
$Rb[VOF_4]$	V_2O_5	2.0 (11)				
	40%HF	2.2 (44)	2.52 (50)	22.1 (22.30)	33.61 (33.26)	37.88 (37.42)
	$RbHF_2$	2.74 (22)				
$Cs[VOF_4]$	V_2O_5	1.0 (5.5)				
	40%HF	1.1 (22)	1.76 (58)	18.83 (18.47)	27.61 (27.55)	48.65 (48.18)
	$CsHF_2$	1.9 (11)				

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, and the solution was then concentrated to nearly three-fourth of its original volume. The concentrated solution was allowed to cool in a freezer and crystalline A $[VOF_4]$ was obtained.

Details of the gram amounts of reagents used, yields of various A $[VOF_4]$ compound and analytical data are given in Table 1, and the i.r. band positions and their assignments have been set out in Table 2.

Results and Discussion

It has been shown, by Hatton and his coworkers[1], from the results of N.m.r. spectroscopic studies that the complex species oxotetrafluorovanadate(V), $[VOF_4]^-$, may exist in an aqueous hydrofluoric acid. In view of this it was expected that the complex $[VOF_4]^-$ ion could be isolated from such solutions by proper adjustment of the experimental conditions. Since vanadium pentoxide is soluble in 40% hydrofluoric acid without any difficulty, it was thought that dissolving V_2O_5 in an aqueous HF solution, made rich with respect to F^- ions by the addition of alkali-metal or ammonium

bifluoride, AHF_2, to a 40% HF solution, may give rise to a condition conducive to the formation of $[VOF_4]^-$ species. The role of AHF_2, as envisaged, was not only to increase the F^- ion concentration in the reaction medium, but also to provide with counter cation A^+. Accordingly, the reaction of V_2O_5 with alkali-metal or ammonium bifluoride, AHF_2, and 40% HF gave rise to the formation of $A[VOF_4]$ in solution.

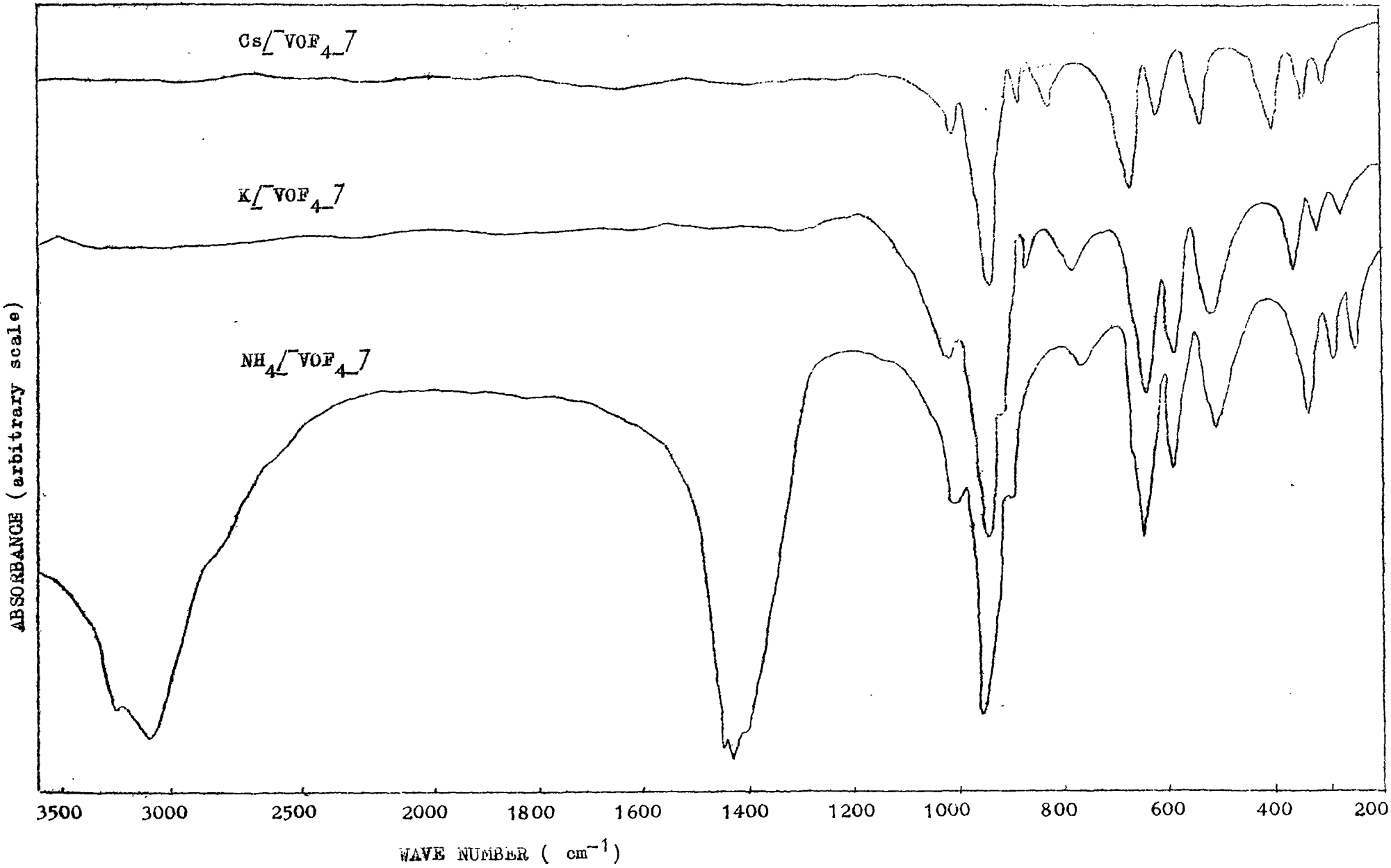
$$V_2O_5 + 2\ AHF_2 + 4HF \longrightarrow 2\ AVOF_4 + 3H_2O$$

The success in isolation of alkali-metal and ammonium oxotetrafluorovanadates(V) from the reaction media depends upon the roles played by ethanol. It is believed that the solvent effect brought about by the addition of alcohol significantly helps the syntheses of the $A[VOF_4]$ compounds. It must be noted that a light-green or greenish-yellow colour that is obtained on addition of a small amount of ethanol has to be maintained throughout until the isolation of the alkali-metal and ammonium oxotetrafluorovanadates(V) is completed. The scope of the method is justified by the syntheses of a number of $A[VOF_4]$ compounds.

The A $[VOF_4]$ (A = K, Rb, Cs or NH_4) compounds thus obtained are highly crystalline, in the shape of long needles, except for Cs $[VOF_4]$ which is generally hexagonal. The compounds are greenish-yellow in colour. The compounds, once isolated from the reaction media, seem to be very sensitive to air and moisture. They are highly soluble in water and the dissolution is accompained by decomposition. The A $[VOF_4]$ compounds are insoluble in common organic solvents, except acetonitrile in which the oxotetrafluorovanadates(V) are very slightly soluble. Chemical analysis, i.r., molar conductance measurement, magnetic moment and ^{19}F N.m.r. were used to characterize and make structural assessment of the compounds A $[VOF_4]$.

The molar conductance of cesium oxotetrafluoro-vanadate(V) was found to be 132 $ohm^{-1}cm^2mol^{-1}$ at 27°C in purified acetonitrile suggesting an uni-uni valent electrolytic nature of the compounds in complete accord with the formula Cs $[VOF_4]$. The room temperature magnetic susceptibility measurements show that the compounds are all diamagnetic which extends further support to the formulation of the compounds.

The infrared spectra of alkali-metal and ammonium salts of the oxotetrafluorovanadates(V) anion resemble


Cs[VOF4]
K[VOF4]
NH4[VOF4]
ABSORBANCE (arbitrary scale)
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVE NUMBER (cm-1)

each other very closely, showing that compounds are similar both structurally and stoichiometrically (Table 2). The strong absorptions in the region 980-1030 cm^{-1}

Table 2. Infrared Bands of A $[VOF_4]$ compounds

$NH_4[VOF_4]$	K $[VOF_4]$	Rb $[VOF_4]$	Cs $[VOF_4]$	Assignments[4]
-	-	-	-	ν_4
262m	261m	262m	260m	$\nu_7 - \nu_3$
-	-	-	-	ν_5
308m	307m	311m	310m	ν_9
332s	334s	330s	334s	ν_3
-	-	-	-	ν_6
480m	482m	483m	481m	ν_8
595s	594s	595s	594s	ν_7
625s	625s	623s	624s	ν_2
710w	712w	712w	712w	$\nu_1 - \nu_9$
990vs 1015	980vs	995vs	1015vs 1025	ν_1
970w	972w	972w	973w	$2\nu_2$ or $\nu_2 + \nu_3$

have been assigned to the ν V-O mode. The ν V-O positions, and the V-O force constants, lying between 7.07 and 7.43 md/Å, are considered as characteristics of the presence of V-O multiple bonds. This also supports the occurence of $O_{(p\pi)} \longrightarrow (d\pi)V$ bonding in the compounds. Moreover, the absence of the broad intense band in the 650-900 cm^{-1} region suggest that the possibility of a polymeric structure of the complex ion $[VOF_4]^-$ through a V-O...V interaction[9,10] is practically ruled out. The complex ion $[VOF_4]^-$ may have either a C_{4v} symmetry with the four F atoms occupying the four corners of a square, and the V and O atoms lying on the 4-fold axis normal to the plane of the square, or a C_{2v} symmetry (trigonal bipyramid) with two apical fluorine atoms normal to the two equatorial fluorine atoms and the equatorial oxygen atom. The C_2-axis thus contains the oxygen and the vanadium atoms and bisects the angle between the equatorial fluorine and vanadium atoms. It has been shown earlier[4] that should $[VOF_4]^-$ have a C_{4v} symmetry, there must be 6 i.r. active vibrations. Whereas for $[VOF_4]^-$ having a C_{2v} symmetry, 11 i.r. active bands must be present. It is evident from the i.r. spectral pattern (Table 2) of the compounds synthesised now that the $[VOF_4]^-$ in each of the compounds

has a C_{4v} symmetry. This correlates very well with those previously reported for Cs $[VOF_4]$[4] and is also in agreement with the reported crystal structure of Cs $[VOF_4]$[11], which shows that the $[VOF_4]^-$ is essentially C_{4v} with a weak F - bridging making $[VOF_4]^-$ pseudooctahedral.

^{19}F N.m.r. spectrum of a 1.42 (M) solution of the newly synthesised Cs $[VOF_4]$ in 48% hydrofluoric acid recorded at - 85°C shows a broad doublet occuring at 258.4 ppm down field relative to HF with a value of $W_{\frac{1}{2}} = 1003$ H_z. These agree with the values previously reported[4] for Cs $[VOF_4]$ and conform to the contention that a rapid fluorine rearrangement between C_{4v} and C_{2v} stereochemistry of $[VOF_4]^-$ occurs in solution.

Thus, it may be concluded that alkali-metal and ammonium oxotetrafluorovanadates(V), A $[VOF_4]$, can be synthesised from aqueous solutions by suitably adjusting the experimental conditions. The complex ion $[VOF_4]^-$ has a square pyramidal C_{4v} structure in the solid state, while it shows stereochemical non-rigidity owing to rapid fluorine rearrangement between C_{4v} and the C_{2v}(tbp) stereochemistry of $[VOF_4]^-$ in solution.

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Chapter 2

Hydrazonium, Alkali-metal and Ammonium Oxotrifluoro-vanadates(IV). Synthesis and Spectroscopic Studies of a New Oxofluorovanadate(IV) Complex, $[VOF_3]^-$

The extraordinary stability of VO^{2+} unit has been emphasised in the literature.[1,2] The VO^{2+} unit has been shown to combine with F^- species to form stable complexes[1,2] $[VOF_5]^{3-}$ and $[VOF_4]^{2-}$. There is, however, no reported evidence for the formation of oxotrifluorovanadate(IV), $[VOF_3]^-$, to date. The corresponding oxotrichlorovanadate(IV), $[VOCl_3]^-$, has been known.[3] The salts of the complex ion $[VOCl_3]^-$ were synthesised by precipitating from an aqueous alcoholic medium.[3] The basis of $[VOCl_3]^-$ synthesis was the facile electron-transfer reaction between V^{5+} and Cl^-. This philosophy cannot, however, be applied to the synthesis of $[VOF_3]^-$ complex because fluoride (F^-) cannot reduce V^{5+} (vide Chapter 1), rather it stabilises pentavalent vanadium.[4] It was expected that the reduction of V^{5+} in the presence of F^- ions would probably be a good strategy for the

synthesis of $[VOF_3]^-$.

Chapter 2 of the thesis presents the synthesis of hydrazonium, alkali-metal and ammonium salts of the complex ion $[VOF_3]^-$, and the results of spectroscopic studies involving the newly synthesised compounds.

Experimental

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

Molar conductance measurements were done with a Philips PR9500 conductivity bridge.

Magnetic susceptibility measurements were made by the Gouy method. Hg $[Co(NCS)_4]$ was the calibrant.

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

Electronic spectra were recorded on a BECKMAN UV-26 spectrophotometer.

Esr spectra of aqueous solutions of $N_2H_5[VOF_3]$ were recorded on a Varian E109, X-band Esr spectrometer with 100 Kc field modulator.

Elemental Analyses. Vanadium, fluoride, sodium (flame photometry), potassium and nitrogen were estimated by the methods described in Chapter 1.

Chemical Determination of the Oxidation States of Vanadium in A $[VOF_3]$ (A = Na, K or NH_4) compounds. The oxidation state of vanadium in each of the A $[VOF_3]$ compounds was estimated chemically by dissolving a known amount of it followed by the direct titration with a standard potassium permanganate solution.

Synthesis of Hydrazonium Oxotrifluorovanadate(IV), $N_2H_5[VOF_3]$. An amount of 2.0g (11 mmol) vanadium pentoxide (in about 10 ml of water) was dissolved by the addition of 2.2 ml (44 mmol) of 40% hydrofluoric acid by slightly warming over a steam-bath and the solution was filtered, after cooling to room temperature, to remove any undissolved impurity. Hydrazine hydrate (99% solution) was added dropwise to the solution under cooling, with slow stirring. The solution first turned blue and further addition of hydrazine hydrate afforded the blue crystalline hydrazonium oxotrifluorovanadate(IV), $N_2H_5[VOF_3]$. Addition of hydrazine hydrate was continued until $N_2H_5[VOF_3]$ ceased to appear with the mother liquor becoming very faint in colour. The compound

was separated by filtration, dried by placing between the folds of filter papers and finally in vacuo over diphosphorous pentoxide. The yield of $N_2H_5[VOF_3]$ was 1.6g (92%).

Preparation of Alkali-metal and Ammonium Oxotrifluorovanadate(IV), A$[VOF_3]$(A = Na, K or NH_4). Since the methods of preparation of A$[VOF_3]$ compounds are similar only a representative method is described.

To a saturated solution of freshly prepared hydrazonium oxotrifluorovanadate(IV), $N_2H_5[VOF_3]$, a very concentrated solution of alkali- metal fluoride, AF, maintaining the molar ratio of between $N_2H_5[VOF_3]$ and AF at 1:3, was added directly with slow stirring. A blue crystalline product was obtained almost immediately, and isolated in a manner analogous to that described above. Specific gram amounts of reactants used and the yields of various A$[VOF_3]$ (A = Na, K or NH_4) compounds are reported in Table 1. Analytical data, chemically estimated oxidation state of vanadium, magnetic moment values, structurally important i.r. bands, and electronic spectral band positions and their assignments are summarized in Table 2.

Table 1. Amounts of Reactants Used and Yields of $A[VOF_3]$ (A = Na, K or NH_4)

Compound	Yield in g (%)	Amount of $N_2H_5[VOF_3]$ in g (m mol)	Amount of AF in g (m mol)
$NH_4[VOF_3]$	0.8 (89)	1.0 (6.4)	0.71 (19.2)
$Na[VOF_3]$	0.5 (53)	1.0 (6.4)	0.81 (19.2)
$K[VOF_3]$	0.9 (90)	1.0 (6.4)	1.12 (19.2)

Results and Discussion

Since fluoride (F^-) is not capable of reducing V^{5+}, unlike Cl^- or Br^-, it was thought that the reduction of V^{5+} in the presence of fluoride, F^-, with an additional reducing agent might help in reaching the goal. Accordingly, the reduction of vanadium pentoxide, in 40% HF, with hydrazine hydrate was performed. It was observed that V_2O_5 underwent a very facile reaction

with an excess of hydrazine hydrate in the presence of aqueous hydrofluoric acid to afford hydrazonium oxotrifluorovanadate(IV), N_2H_5 [VOF_3], directly in a very high yield. The role of hydrazine hydrate, in the present case, was not only to reduce vanadium(V), but also to provide $N_2H_5^+$ cation which facilitated precipitation of the [VOF_3]$^-$ species formed in the reaction medium.

$$2V_2O_5 + 5N_2H_4.H_2O + 12HF \longrightarrow 4N_2H_5\,[VOF_3] + N_2 + 11H_2O.$$

In order to understand the course of the reaction an additional experiment was performed. In the experiment, starting from relatively higher amounts of the reagents, and after purging the reaction vessel with argon, the evolved gas was first passed through a dry sodium hydroxide tower and then over heated ($\sim$ 450°C) magnesium. The magnesium nitride thus formed was treated with water and tested for the liberation of ammonia. This, therefore, provides evidence for the formation of dinitrogen in the reaction and lends support to the above equation.

The corresponding alkali-metal and ammonium oxotrifluorovanadate(IV), A [VOF_3] (A = Na, K or NH_4),

were prepared by simple metathesis between $N_2H_5[VOF_3]$ and AF in an aqueous medium. The yield of the sodium salt, $Na[VOF_3]$, was considerably low, in comparison to any other salt described in this Chapter, owing to the comparatively high dilution of the reaction solution maintained in order to avoid contamination of the end-product by the relatively less soluble NaF. It is evident from the above reactions that the complex species oxotrifluorovanadate(IV), $[VOF_3]^-$, once formed, is very stable. In order to study the effect of relatively larger amounts of F^- ions on the reaction product, we carried out similar hydrazine hydrate reduction of V_2O_5 in the presence of higher amounts of F^- ions, e.g., V : F ratio at 1 : 5 or 1 : 6. Here again, however, the product obtained was nothing other than hydrazonium oxotrifluorovanadate(IV), $N_2H_5[VOF_3]$, suggesting thereby that a higher quantity of F^- ions does not have any net effect on the end-product, at least within the limits specified.

Characterization and Assessment of Structure.

Hydrazonium oxotrifluorovanadate(IV), $N_2H_5[VOF_3]$, and alkali-metal and ammonium oxotrifluorovanadates(IV), $A[VOF_3]$ (A = Na, K or NH_4) are all blue crystalline compounds, and stable for prolonged periods. The compounds

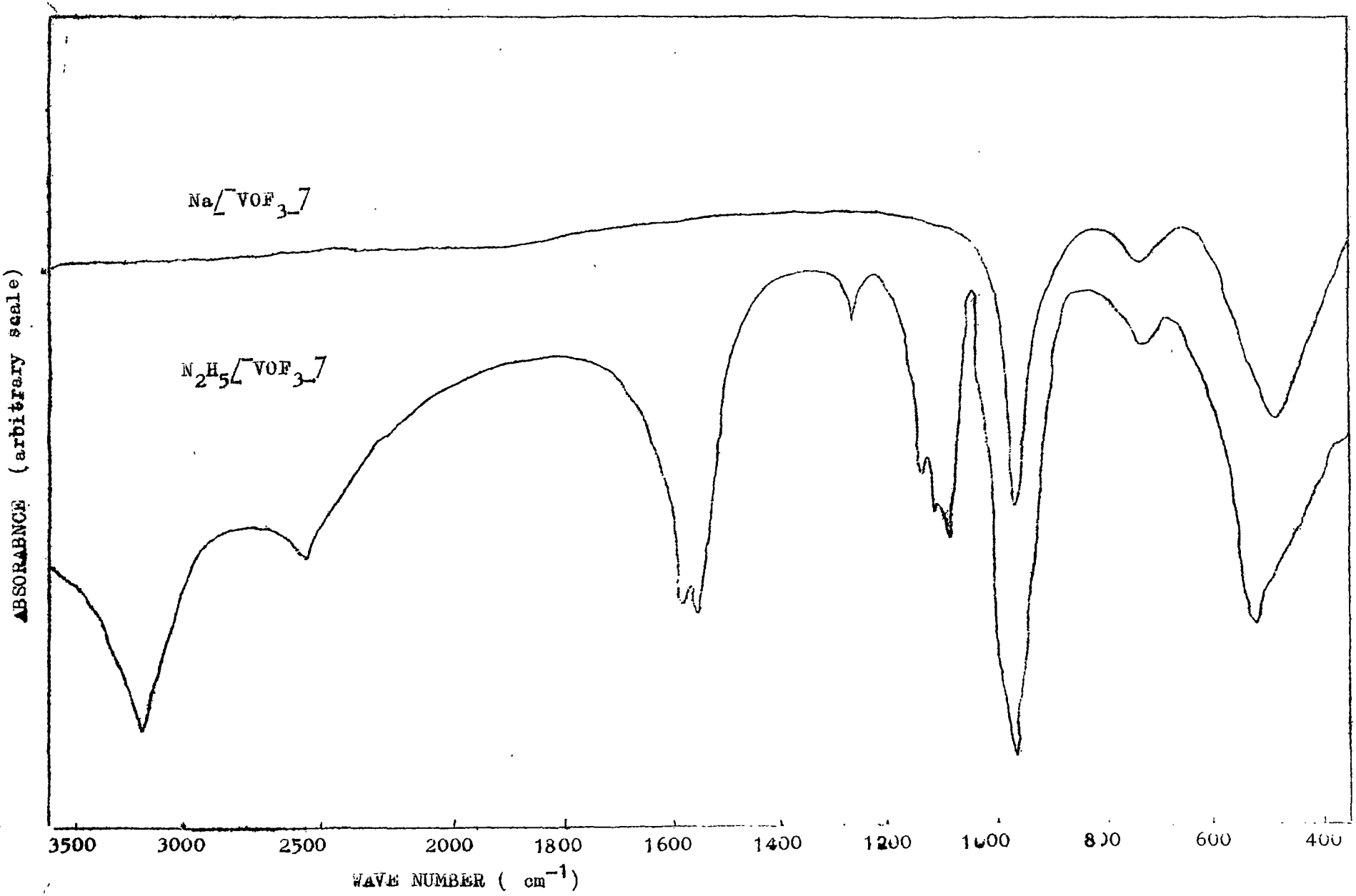
Na[VOF3]
N2H5[VOF3]
ABSORABNCE (arbitrary scale)
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
WAVE NUMBER (cm-1)

Table 2. Analytical Data, Magnetic Moments, Estimated Oxidation States of Vanadium and Structurally Significant IR and Electronic Spectral Bands of $N_2H_5[VOF_3]$ and $A[VOF_3]$ (A = Na, K or NH_4)

Compound	μ_{eff}/BM (299K)	Estimated oxidation state of V	% Found (% Calcd. A or N	V	F	IR Bands in cm^{-1}	Assignments	Electronic spectral bands in cm^{-1}	Transitions
$N_2H_5[VOF_3]$	1.51	–	17.41 (17.85)	32.63 (32.47)	36.87 (36.31)	970s	νV–O	11,950	$e \leftarrow b_2$
						730w,br	νV–O...V		
						530s,br	νV–F...V	16,000	$b_1 \leftarrow b_2$
$NH_4[VOF_3]$	1.53	3.9	9.52 (9.87)	35.68 (35.89)	40.72 (40.15)	975s	νV–O	11,990	$e \leftarrow b_2$
						735w,br	νV–O...V		
						510s,br	νV–F...V	15,825	$b_1 \leftarrow b_2$
$Na[VOF_3]$	1.53	4.1	15.88 (15.65	34.23 (34.68)	38.22 (38.79)	980s	νV–O	–	–
						730w,br	νV–O...V		
						500s,br	νV–F...V		
$K[VOF_3]$	1.51	4.1	24.34 (23.98)	31.72 (31.25)	34.87 (34.96)	970s	νV–O	11,950	$e \leftarrow b_2$
						730w,br	νV–O...V		
						505s,br	νV–F...V	16,000	$b_1 \leftarrow b_2$

can be stored in sealed polyethylene containers. The $N_2H_5[VOF_3]$ and $A[VOF_3]$ compounds are soluble in water.

The molar conductance of the compounds, measured in water, was found to lie between 130 and 135 $ohm^{-1}cm^2mol^{-1}$ suggesting an 1 : 1 electrolytic nature of each of them in conformity with the formula assigned to them. The room temperature magnetic moments of the compounds were observed to fall between 1.51 and 1.53 B.M. (1 B.M. $\simeq$ 0.927 x 10^{-23} Am^2) lending credence to the contention that the vanadium in each of the compounds has an oxidation state of +4. This was further supported by the chemically estimated oxidation states of vanadium in the alkali-metal and ammonium salts of the complex anion. The estimated oxidation states of vanadium in $A[VOF_3]$ (A = Na, K or NH_4) compounds were found to occur between 3.9 and 4.1 (Table 2). The relatively low magnetic moments indicate the existence of a weak antiferromagnetic exchange interaction in the solid state presumably through a weak V-F...V or a weak V-O....V interaction.

The infrared spectra of the series of four compounds were found to be similar to each other, except for the additional cation bands for hydrazonium and ammonium ions

in the cases of the N_2H_5 $[VOF_3]$ and NH_4 $[VOF_3]$ respectively, suggesting the structural and stoichiometric similarities of the compounds. The strong and sharp band at 970-980 cm^{-1} has been assigned to the $\nu_{V=O}$ mode arising from the presence of terminally bonded V=O group.[5] The observance of this band in the appropriate position enables us to infer that the compounds contain V=-O multiple bonds. The appearance of a weak but broad band centered around 730 cm^{-1} indicates a strong possibility of a V=O...V=O interaction in the compounds and suggest that in the solid state the compounds may have a polymeric structure through a V-O-V-O chain. A comparison of the $\nu_{V=O}$ frequencies for $[VOCl_3]^-$ (Ref. 3) and $[VOF_3]^-$ (present work) reveals no appreciable shift in the band positions suggesting thereby that the increased electronegativity of the coordinated halide ligands in going from $[VOCl_3]^-$ to $[VOF_3]^-$ does not alter the V-O bonding to any appreciable extent. The strong absorption at $\sim$ 500 cm^{-1} has been assigned to a V-F stretching mode, its position and a slightly broad nature indicate the existence of a V-F...V-F interaction in the compounds. In order to confirm the absence of any H_2O, coordinated or otherwise, a careful examination was made of the i.r. spectra of the

Na $[VOF_3]$ and K $[VOF_3]$ compounds, since in these two cases there is no interference from the cation modes, by recording their spectra in both KBr and nujol mull media. No indication with regard to the presence of water was observed. These results and those of chemical analyses render it certain that there is no water present in the compounds. The infrared spectra of N_2H_5 $[VOF_3]$ shows the bands typical for $N_2H_5^+$ ion[6], and that of NH_4 $[VOF_3]$ shows the bands characteristic for NH_4^+ ion.[7,8]

The electronic spectra of oxotrifluorovanadate(IV) complexes consist three absorption bands between 10,000 and 28,000 cm^{-1}, the region in which vanadyl complexes generally absorb. The frequencies fall at $\sim$ 11,950 cm^{-1}, at $\sim$ 16,000 cm^{-1} and $\sim$ 22,000 cm^{-1} with the third one being obscured by strong charge-transfer transitions. The first and the second absorptions are assigned to $e \leftarrow b_2$ and $b_1 \leftarrow b_2$ transition respectively in conformity with the reported spectra of oxovanadium(IV) complexes.[5] A comparison of the optical spectra of anhydrous oxotrichlorovanadates(IV)[3] with those of the oxotrifluorovanadates(IV) reveals that though the spectral pattern is generally similar, there is a

difference in the band positions. The $e \leftarrow b_2$ and $b_1 \leftarrow b_2$ transitions in the latter case have been found to shift to comparatively lower frequencies. This result lead us to believe that the complex species $[VOF_3]^-$ may have a pseudo-octahedral structure in solutions.

The solution ESR spectrum of hydrazonium oxotrifluorovanadate(IV), $N_2H_5[VOF_3]$, was found to be similar to that of various tetravalent vanadium complexes.[9] The experimentally obtained magnetic parameters of the complex $[VOF_3]^-$ are as follows:

$$g_{\parallel} = 1.937, \quad g_{\perp} = 1.978,$$

$$A_{\parallel} (^{51}V) = 530.8 \text{ MHz and}$$

$$A_{\perp} (^{51}V) = 205.1 \text{ MHz}$$

The values of spin hamiltonian parameters agree very well with those reported for $V^{4+}(d^1)$ complexes.[9] The appearance of an ESR spectrum at -150°C and the normal line widths indicate that the unpaired electron is in an orbitally non-degenerate ground state. The observed g values and ^{51}V hyperfine couplings further indicate that the ligand field is axially symmetric and the complex species may have an axially distorted octahedral structure in solutions. Based on these observations we propose that

three fluoride ions and two water molecules (coming from the solution) constitute the ligand field around VO^{2+} group. In an attempt to study the effect of an excess of F^- ions on the ESR spectrum, we recorded the spectrum in the presence of an 100 fold excess of F^- ion concentrations. However, no significant shifts in the g values and hyperfine tensors were observed. The optical spectrum of a similar solution also did not show any notable change suggesting thereby that the coordinated water molecules, in solutions, are not replaced by F^- ions. Moreover, the absence of any fluorine hyperfine coupling indicates that orbitals of the unpaired electron is not involved in the bond formation. The unpaired electron can be considered to be in the d_{xy} orbital by selecting a coordinate system with V=O being in the Z axis, and the V-F bond directions as X and Y axes. Accordingly the approximate ordering of the energy level may be written as

$d_{xy} < d_{xz} < d_{yz} < d_{x^2-y^2} < d_{z^2}$. The g values, to first order, are given by[10]

$$g_{\parallel} = g_e - \frac{2\xi_q k_1}{\Delta} \quad \ldots \quad (1)$$

and

$$g_{\perp} = g_e - \frac{8\xi_q k_2}{\delta} \quad \ldots \quad (2)$$

where g_e is the free-electron g value, k_1 and k_2 are the orbital reduction factors and ζ is the spin-orbit coupling constant of the free ion.

$$\Delta = |E_{xy} - E_{x^2-y^2}| \quad \text{and}$$

$$\delta = |E_{xy} - E_{yz}| \quad \text{or} \quad |E_{xy} - E_{xz}|$$

where E_{xy} etc. are the one-electron orbital energies.

The d-d bands observed in the electronic spectra at 16,000 cm^{-1} (ϵ = 3.6) and at 11,976 cm^{-1} (ϵ = 0.85) can be correlated to the transition (xy) $\longleftrightarrow$ (x^2-y^2), (Δ), and to (xy) $\longleftrightarrow$ (xz) or (yz), (δ), respectively. In order to get an idea regarding the extent of covalency involved in different planes, we calculated the ratio $\zeta k_1 / \zeta k_2$ by making use of the experimentally observed values for Δ and δ. The value of the ratio was found to be 0.89 indicating that the covalency involved in the xy plane is comparatively more than that in the xz plane.

Thus it is evident that under the suitable conditions oxotrifluorovanadate(IV) complexes can be synthesised from aqueous media. The complex species $[VOF_3]^-$ may have a polymeric structure, in the solid state, through weak V-F...V or V-O..V interactions.

In solutions, however, the complex species $[VOF_3]^-$ seems to have a pseudo-octahedral structure with two water molecules occupying two vacant coordination positions.

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Chapter 3

Synthesis and Assessment of Structure of Alkali-metal and Ammonium Oxodiperoxofluorovanadates(V), $A_2[VO(O_2)_2F]$ (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 fluoro compounds of vanadium (Chapters 1 and 2), the synthesis of peroxo-fluorovanadium(V) compounds was undertaken.

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

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*This work has been published:
Polyhedron, 553, 1, 1982.

oxodiperoxofluorovanadates(V), $A_2[VO(O_2)_2F]$ (A = 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 $Hg[Co(NCS)_4]$ 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): (i) Permanganometry[8]: 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

$$1ml\ (N)\ KMnO_4\ solution \equiv 0.01701\ g\ H_2O_2$$

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

(ii) Iodometry[9]: 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 CO_2-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 substraction of the contribution from vanadium(V), the contribution of active oxygen is found out.

$$1ml\ (N)\ Na_2S_2O_3\ solution \equiv 0.01701\ g\ H_2O_2$$

(iii) Ceric (Ce^{+4}) 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), $A_2[VO(O_2)_2F]$ (A = 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 ethylalcohol 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 diphosphorous pentoxide. The yields of $(NH_4)_2[VO(O_2)_2F]$, $Na_2[VO(O_2)_2F]$ and $K_2[VO(O_2)_2F]$ were 1.6 g (78%), 1.8 g(84%) and 2.1 g (84%) respectively.

The $Rb_2[VO(O_2)_2F]$ and $Cs_2[VO(O_2)_2F]$ 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 = 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

$Rb_2[VO(O_2)_2F]$ was 2.6 g (74%) and that of $Cs_2[VO(O_2)_2F]$ was 3.5 g (77%).

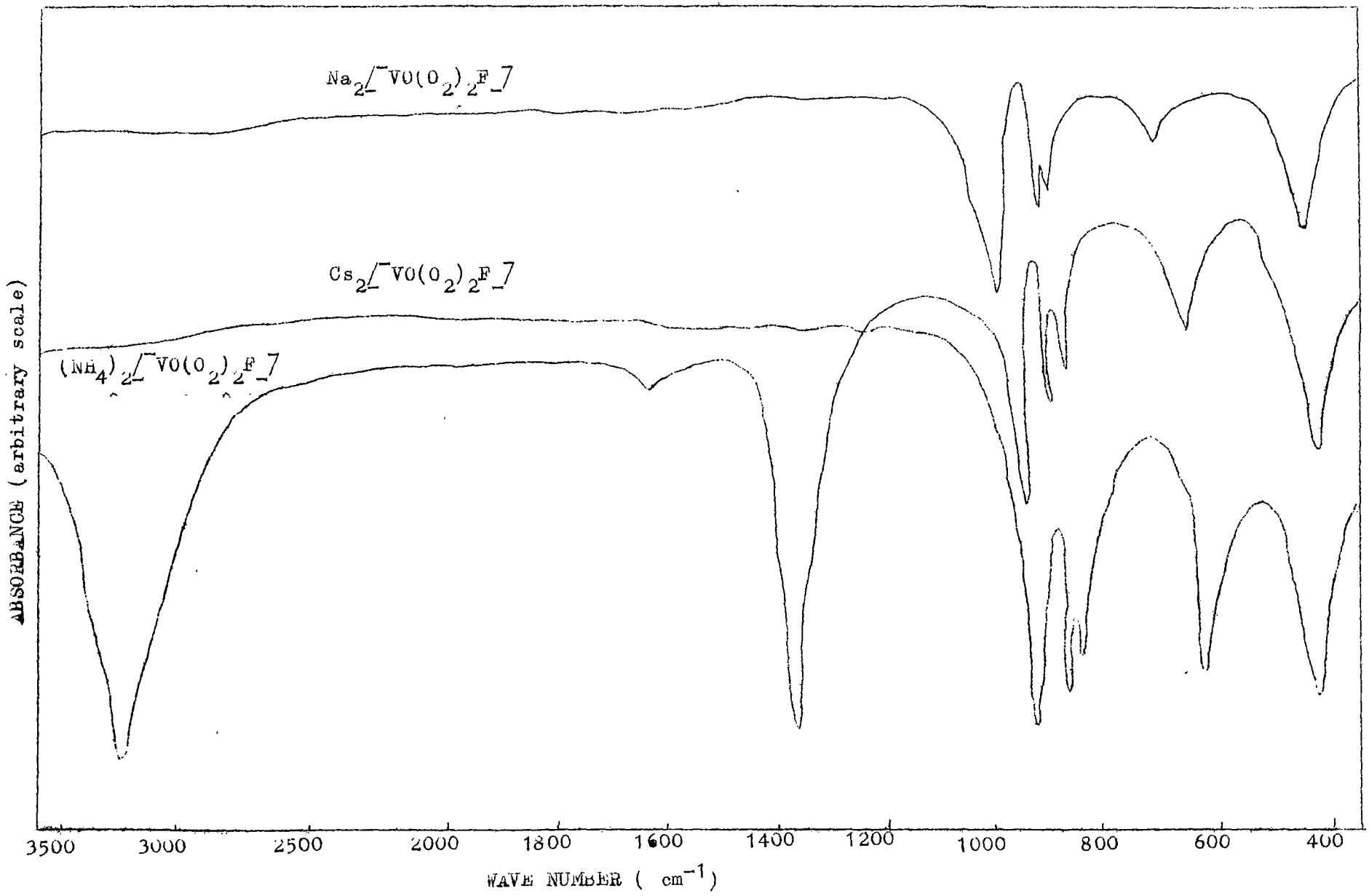
The analytical data, and the structurally significant i.r. bands of $A[VO(O_2)_2F]$ (A = Na, K, Rb, Cs or NH_4) compounds are set out in Table 1.

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_2O_5 and H_2O_2 in the presence of alkali-metal or ammonium fluoride, AF, in an alkaline medium, and thought that a heteroligand fluoroperoxo-vanadate(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_2O_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 $K_2[VO(O_2)_2F]$ 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 $A_2[VO(O_2)_2F]$ compounds.

Alkali-metal and ammonium oxodiperoxofluorovanadate(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 peroxo 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 peroxo groups per vanadium


$Na_2[VO(O_2)_2F]$
$Cs_2[VO(O_2)_2F]$
$(NH_4)_2[VO(O_2)_2F]$
ABSORBANCE (arbitrary scale)
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
WAVE NUMBER (cm^{-1})

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 triangularly bonded peroxy ligands (C_{2v}) and in keeping this there are two readily identifiable ν_{-O-O-} bands at ca 895 and at ca 870 cm^{-1} [cf. the analysis of ν_{-O-O-} in transition metal complexes].[13] Another characteristic feature of the spectra is the absorption at 935-970 cm^{-1}. This has been assigned to the ν_{V-O} mode of terminal V-O multiple bonds.[14,15] The strong absorption at 470-480 cm^{-1} in each spectrum, has been assigned as the ν_{V-F} mode owing to the presence of a 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 fluoro-peroxo-vanadium(V) complex of the type $[VO(O_2)_2F]^-$ can be synthesised from the reaction of V_2O_5 with H_2O_2 in an alkaline medium in the presence of alkali-metal or ammonium fluoride, AF. The peroxo groups are bonded to the vanadium(V) centre in a triangular bidentate manner.

The complex species $[VO(O_2)_2F]^-$ 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.

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Chapter 4

Alkali-metal and Ammonium Triperoxofluorovanadates(V), $A_2[V(O_2)_3F]$ (A = 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.[1-8] It appears from the recent literature that studies of the kinetic behaviour of peroxovanadium(V) engage the attention of most of the research groups,[1,3-8] 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), $A_2[VO(O_2)_2F]$ has been reported in chapter 3. The compounds $A_2[VO(O_2)_2F]$ 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: Inorg. Chem., 4020, 21, 1982.

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), $A_2[VO(O_2)_2F]$ (A = Na, K or 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 $[Co(NCS)_4]$ 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), $A_2[V(O_2)_3F]$ (A = Na, K or NH_4). As the methods of syntheses of the ammonium, sodium and potassium triperoxofluorovanadates(V) are similar, only a representative method is described.

Pure V_2O_5 and dry fluoride AF (A = 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 (A = Na, K or NH_4), with maintenance of the molar ratio of V_2O_5 : AOH at 1 : 10. 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 $A_2[V(O_2)_3F]$ 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 ethanol, and finally dried in vacuo over diphosphorous 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 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., $K_3[V(O_2)_4]$, has been known,[12] presumably having a dodecahedral structure analogous to that of the corresponding peroxochromium compound.[13]

In the course of our studies[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,[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 $[V(O_2)_3F]^-$ 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 favoured, or it could also be possible that the oxo oxygen of the yellow diperoxo species is converted to the third peroxo 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[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 $[V(O_2)_3F]^-$ 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 ν_{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 $[V(O_2)_3F]^{-}$. 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 V^{5+} ion in the compounds. That the

Table 1. Amounts of Reagents Used and Yields of $A_2[V(O_2)_3F]$ (A=Na,K or NH_4)

Compound	Yield in g (%)	Amount of V_2O_5 in g (mmol)	Amount of AF in g (mmol)	Amount of 6% H_2O_2 in ml(mmol)	Amount 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)	60.0 (105.8)	2.6 (65)
$K_2[V(O_2)_3F]$	2.3 (85)	1.0 (5.5)	0.64 (11)	60.0 (105.8)	3.7 (65.9)

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 $A_2[V(O_2)_3F]$ in water was unsuccessful. The values obtained were higher than that expected for a 2:2 type electrolyte. It has been generally observed[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^{-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[15] as the ν_{-O-O-} mode of coordinated peroxy groups. A single absorption in this region suggests that all three peroxo ligands in the complexes are bonded to the vanadium(V) centre in an analogous fashion. Since the

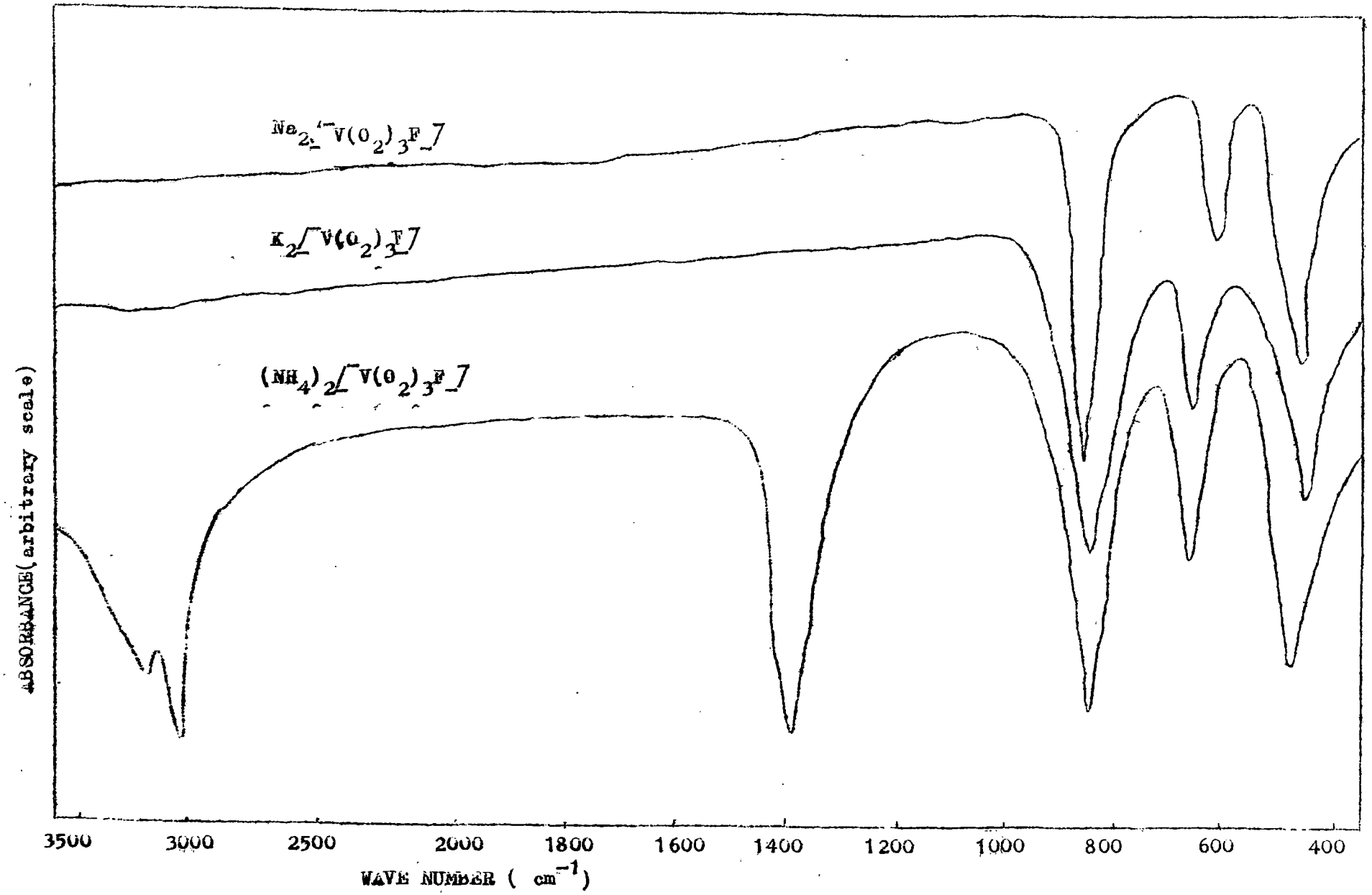
$Na_2[V(O_2)_3F]$
$K_2[V(O_2)_3F]$
$(NH_4)_2[V(O_2)_3F]$
ABSORBANCE(arbitrary scale)
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
WAVE NUMBER (cm^{-1})

Table 2. Analytical Data and Structurally Significant IR Bands of

$A_2[V(O_2)_3F]$ (A = Na, K or NH_4)

Compound	% Found (% Calcd.)				IR Bands cm^{-1}	Assignments
	A or N	V	O_A^a	F		
$(NH_4)_2[V(O_2)_3F]$	13.81 (13.87)	25.22 (25.23)	46.97 (47.54)	9.52 (9.41)	850s	ν_{-O-O-}
					475s	ν_{V-F}
					3158m	ν_3 NH_4^+
					3040s	ν_1 modes
					1400s	ν_4
$Na_2[V(O_2)_3F]$	21.56 (21.70)	24.12 (24.04)	44.87 (45.30)	8.89 (8.97)	855s	ν_{-O-O-}
					479s	ν_{V-F}
$K_2[V(O_2)_3F]$	32.11 (32.03)	20.81 (20.87)	38.93 (39.32)	7.85 (7.78)	855s	ν_{-O-O-}
					470s	ν_{V-F}

ν_{-O-O-} absorptions occur exactly in the region stipulated for the triangularly bonded peroxo groups, it may be inferred that all three peroxo ligands in the complexes are bonded in a C_{2v} 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 ν_{V-F} modes arising from the presence of fluoride ion coordinated to the vanadium(V) centre. This compares very well with the ν_{V-F} values observed in the cases of various fluoro-vanadate species.[9,16-18] The three extra vibrations at 3158m, 3040s and 1400s cm^{-1} in the spectrum of $(NH_4)_2[V(O_2)_3F]$ have been assigned to the ν_3, ν_1 and ν_4 modes of NH_4^+.

In an attempt to study effect on the basicity of peroxo ligands as a function of the number of peroxo groups coordinated to the vanadium(V) centre, 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 ν_{-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 peroxo groups in the latter case. In other words, removal of further π_{2p} density from O_2^{2-} to the vanadium appear 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+}. It is thus possible to infer from this observation that the basicity of coordinated peroxy 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 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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Chapter 5

$[VO(O_2)_2Cl]^{2-}$ —— $[V(O_2)_3Cl]^{2-}$ Pair in Peroxovanadium(V) Chemistry: Synthesis of the First Chloroperoxovanadate(V) Compounds and Evidence for Diperoxovanadate(V) —— Triperoxovanadate(V) Interconversion*

The studies of peroxovanadium chemistry has generated a considerable current interest[1-7] probably owing to the special biochemical significance[8,9] of peroxo-transition metal complexes. Whereas most of the recent reports on peroxovanadium chemistry deal with the studies in solutions,[2-7] the synthesis and structural assessment of such compounds have received only a scant attention. Moreover, only a few hetero-ligand peroxo complexes of vanadium are known in contrast to many such reported examples for the other transition metals.[9-11] Our interest in this area involving the synthesis, characterisation, structural

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

Inorg. Chem., in press (Paper No. IC 830275T)

assessment and study of chemistry of peroxovanadium compounds[12,13] (Chapters 3 and 4) has led to the synthesis of chloro-peroxo compounds of vanadium(V).

Chapter 5 of the present thesis reports the synthesis of two series of chloro-peroxovanadium(V) compounds, viz., the yellow alkali-metal and ammonium oxodiperoxochlorovanadates(V), $A_2[VO(O_2)_2Cl]$. and the blue alkali-metal and ammonium salts of triperoxochlorovanadates(V), $A_2[V(O_2)_3Cl]$ (A = Na, K or NH_4,) the first chloroperoxo compounds of vanadium. Also reported in this Chapter are a set of internally consistent data regarding the effect on the ν_{O-O} mode of O_2^{2-} ligands with the increase in the number of such ligands in going from $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$, and the facile interconversion $[VO(O_2)_2Cl]^{2-} \rightleftharpoons [V(O_2)_3Cl]^{2-}$ evidencing the ability of such compounds to undergo a basic formation reaction and an acidic dissociation reaction.

Experimental

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

Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer separately in KBr and in nujol media.

Molar conductance measurements were made using a Philips PR 9500 conductivity bridge.

Magnetic susceptibility measurements were made by Gouy method. The compound $Hg[Co(NCS)_4]$ was the calibrant.

Elemental Analyses. Vanadium was done volumetrically, after expelling the peroxo-oxygen and separating chloride, by titrating with a standard potassium permanganate solution as described in Chapter 1.

The peroxide contents of the compounds were determined by red-ox titration with a standard Ce^{4+} solution[14] (vide Chapter 3).

Chloride was estimated by Volhard's method[15] Chapter 1).

Sodium, potassium and nitrogen were determined by the methods already described in earlier Chapters.

Syntheses of Alkali-metal and Ammonium Oxodiperoxo-chlorovanadates(V), $A_2[VO(O_2)_2Cl]$ (A = Na, K or NH_4). Vanadium pentoxide, V_2O_5, and dry alkali-metal or ammonium chloride, ACl, taken in the ratio 1:2, were

intimately mixed by powdering together in an agate mortar. A concentrated solution of the corresponding alkali hydroxide, AOH, was then added to the mixed powder maintaining the molar ratio of V_2O_5 : AOH at 1 : 10, and the resulting mixture was stirred at room temperature for ca 10 min. Hydrogen peroxide (9% solution) was added to the solution slowly with constant stirring with the molar ratio of V_2O_5 : H_2O_2 rising ultimately to 1 : 14. 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 temperature for ca 20 min. An excess of ethyl alcohol was then added to the cold solution with stirring until a yellow coloured microcrystalline $A_2[VO(O_2)_2Cl]$ was obtained. The reaction container was allowed to cool at ice-bath temperature for ca 10 min. The compound was separated by centrifugation and washed several times with ethyl alcohol until it was free from alkali and finally dried in vacuo over diphosphorous pentoxide.

Syntheses of Alkali-metal and Ammonium Triperoxochlorovanadates(V), $A_2[V(O_2)_3Cl]$ (A = Na, K or NH_4). The blue $A_2[V(O_2)_3Cl]$ compounds were synthesised in a manner analogous to that described above. The only

difference was that the molar ratio of V_2O_5:ACl:AOH:H_2O_2 was maintained at 1:2:15:14. The reaction was monitored by infrared spectroscopy. The disappearance of the sharp band at ca 950 cm^{-1} owing to $\nu_{V=O}$ in the compound isolated from the reaction medium indicated completion of the reaction.

The specific gram amounts of the reagents used and the yields of the various salts of the anion $[VO(O_2)_2Cl]^{2-}$ and $[V(O_2)_3Cl]^{2-}$ are reported in Table 1. The analytical data and the IR band positions are summarized in Table 2.

Conversion of the Oxodiperoxochlorovanadate(V), $[VO(O_2)_2Cl]^{2-}$, to Triperoxochlorovanadate(V), $[V(O_2)_3Cl]^{2-}$ and Vice-versa.

The interconversion reactions were studied with the $Na_2[VO(O_2)_2Cl]$ and $Na_2[V(O_2)_3Cl]$ compounds.

Conversion of $Na_2[VO(O_2)_2Cl]$ to $Na_2[V(O_2)_3Cl]$. The sodium oxodiperoxochlorovanadate(V) (0.5g, 2.4 m mol) was dissolved in a concentrated solution of sodium hydroxide (2.2 g, 5.5 m mol) followed by an immediate addition of 9% hydrogen peroxide (30.0 ml, 79.4 m mol) and a blue solution was obtained. The solution was cooled at ice-bath temperature for ca 15 min and then an excess of ethyl alcohol was added to precipitate the

Table I. Amounts of Reagents Used and Yields of $A_2[VO(O_2)_2Cl]$ and $A_2[V(O_2)_3Cl]$ (A = Na, K or NH_4)

Compound	Yield in g(%)	Amount of V_2O_5 in g (mmol)	Amount of AOH in g (mmol)	Amount of AOH in g (mmol)	Amount of 9% H_2O_2 in ml (mmol)
$(NH_4)_2[VO(O_2)_2Cl]$	1.7 (77)	1.0 (5.5)	0.59 (11)	7.7ml (55) (25% solution)	30.0 (79.4)
$Na_2[VO(O_2)_2Cl]$	1.9 (83)	1.0 (5.5)	0.65 (11)	2.2 (55)	30.0 (79.4)
$K_2[VO(O_2)_2Cl]$	2.1 (77)	1.0 (5.5)	0.82 (11)	3.1 (55)	30.0 (79.4)
$(NH_4)_2[V(O_2)_3Cl]$	1.8 (85)	1.0 (5.5)	0.59 (11)	11.6ml (25% solution) (83)	30.0 (79.4)
$Na_2[V(O_2)_3Cl)]$	2.0 (80)	1.0 (5.5)	0.65 (11)	3.3 (83)	30.0 (79.4)
$K_2[V(O_2)_3Cl]$	2.2 (77)	1.0 (5.5)	0.82 (11)	4.7 (83)	30.0 (79.4)

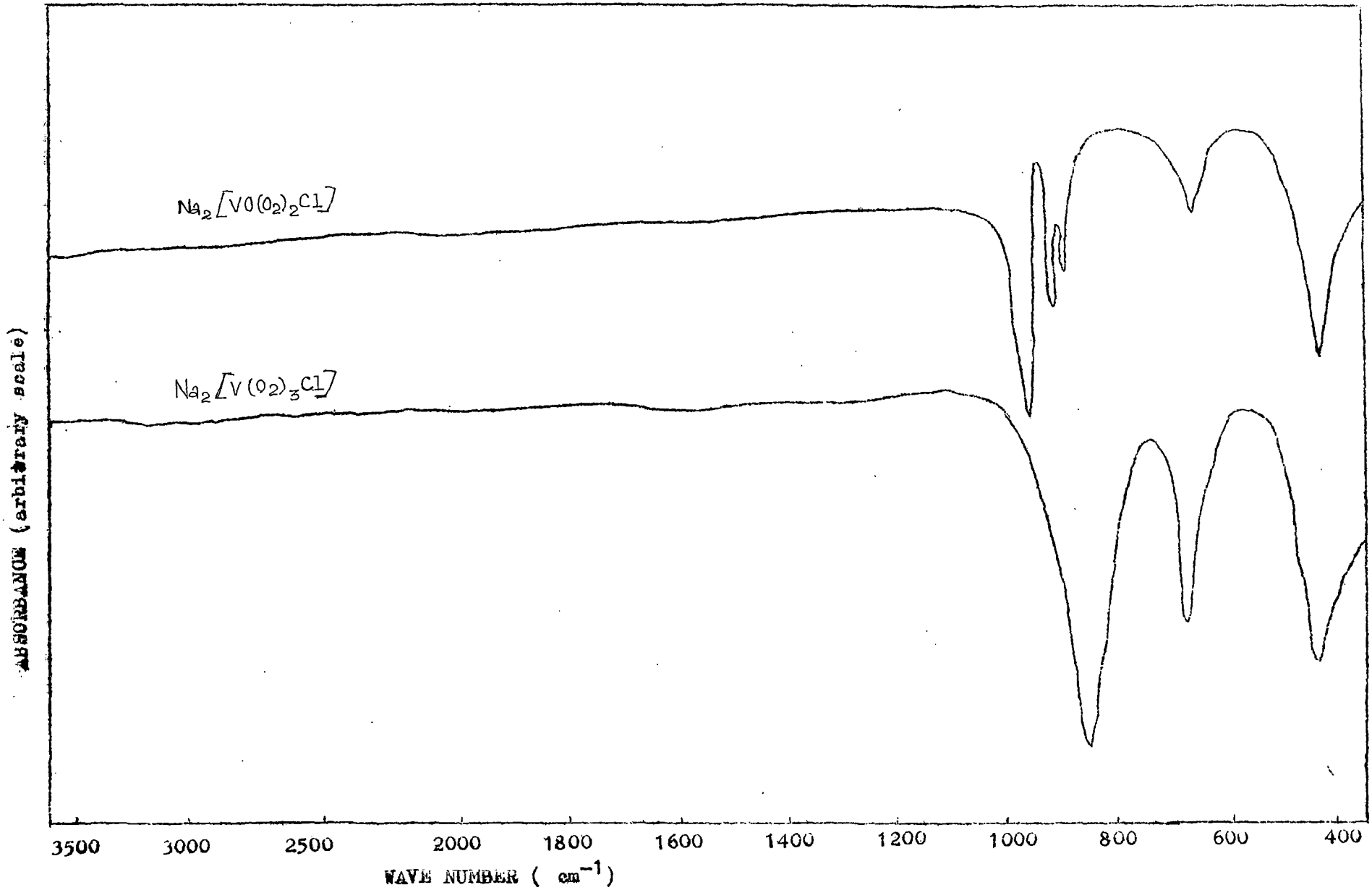
$Na_2[VO(O_2)_2Cl]$
$Na_2[V(O_2)_3Cl]$
ABSORBANCE (arbitrary scale)
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
WAVE NUMBER (cm^{-1})

Table 2. Analytical Data and Structurally Significant IR Bands of $A_2[VO(O_2)_2Cl]$ and $A_2[V(O_2)_3Cl]$ (A = Na, K or NH_4)

Compound	% Found (% Calcd.)				IR Bands (cm^{-1})	Assignments
	A or N	V	O_A^a	Cl		
$(NH_4)_2[VO(O_2)_2Cl]$	13.21 (13.84)	24.82 (25.16)	32.13 (31.61)	17.92 (17.51)	970s 870s 885s 610s 415s 3160m 3045s 1400s	ν_{V-O} ν_{-O-O-} ν_{V-O_2} ν_{V-Cl} ν_3 $\nu_1\ NH_4^+$ ν_4 modes
$Na_2[VO(O_2)_2Cl]$	22.21 (21.65)	24.34 (23.99)	31.33 (30.14)	16.28 (16.69)	955s 875s 885s 610s 410s	ν_{V-O} ν_{-O-O-} ν_{V-O_2} ν_{V-Cl}
$K_2[VO(O_2)_2Cl]$	31.57 (31.97)	20.21 (20.83)	26.88 (26.17)	14.78 (14.79)	970s 875s 890s 615s 415s	ν_{V-O} ν_{-O-O-} ν_{V-O_2} ν_{V-Cl}
$(NH_4)_2[V(O_2)_3Cl]$	12.43 (12.82)	22.79 (23.52)	44.66 (43.94)	16.72 (16.23)	855s 620s 410s 3155m 1400s	ν_{-O-O-} ν_{V-O_2} ν_{V-Cl} $\nu_3\ NH_4^+$ ν_4 modes
$Na_2[V(O_2)_3Cl]$	20.92 (20.13)	22.85 (22.31)	42.93 (42.04)	15.22 (15.52)	860s 615s 420s	ν_{-O-O-} ν_{V-O_2} ν_{V-Cl}
$K_2[V(O_2)_3Cl]$	30.83 (30.06)	20.31 (19.58)	36.13 (36.9)	13.25 (13.63)	855s 620s 415s	ν_{-O-O-} ν_{V-O_2} ν_{V-Cl}

[a] Peroxo Oxygen.

blue sodium triperoxochlorovanadate(V), $Na_2[V(O_2)_3Cl]$. The compound was separated by centrifugation, washed several times with ethyl alcohol and finally dried in vacuo.

Reconversion of $Na_2[V(O_2)_3Cl]$ to $Na_2[VO(O_2)_2Cl]$. A blue solution was obtained by dissolving an amount of 0.3g (1.3 m mol) of sodium triperoxychlorovanadate(V) in 30 ml (79.4 m mol) of 9% hydrogen peroxide containing 3.3g (83 m mol) of sodium hydroxide. Dilute hydrochloric acid (1N) was added dropwise until the solution became permanent yellow. The solution was cooled at ice-bath temperature for ca 20 min followed by the addition of an excess of ethyl alcohol to produce the yellow sodium oxodiperoxochlorovanadate(V), $Na_2[VO(O_2)_2Cl]$. The compound was isolated and purified in a similar manner as described above.

The interconversion $Na_2[VO(O_2)_2Cl] \rightleftarrows Na_2[V(O_2)_3Cl]$ was also studied in the following manner. The yellow solution was first prepared by the reaction of V_2O_5 with NaCl, NaOH and 9% H_2O_2 maintaining the molar ratio 1:2:10:14. Addition of an excess of ethyl alcohol to a part of the solution afforded the yellow sodium oxodiperoxochlorovanadate(V), $Na_2[VO(O_2)_2Cl]$.

To the remaining solution was added more sodium hydroxide in the form of its concentrated solution (total molar ratio of V_2O_5 : ACl : AOH : H_2O_2 as 1 : 2 : 15 : 14) and a blue solution was obtained. The blue solution was divided into two parts and an excess of alcohol was added to one part of it to produce the sodium triperoxochlorovanadate(V), $Na_2[V(O_2)_3Cl]$. Dropwise addition of dilute hydrochloric acid (1N) to the other part of the solution until it turned permanent yellow followed by the addition of ethyl alcohol gave the yellow sodium oxodiperoxochloro-vanadate(V), $Na_2[VO(O_2)_2Cl]$. Both the basic formation (peroxide, O_2^{2-} uptake) and the acidic dissociation , (deperoxygenation) reactions were performed at ice-bath temperatures.

Results and Discussion

Synthesis. It has been emphasised in the literature[11] very recently that only a few heteroligand peroxovanadium compounds have been known although there have been many such examples for other transition metals. It is possible that vanadium presents a different story owing to the uncertain nature of peroxovanadium species

in solutions of varying pH.[5,16,17] An elementary consideration in the course of studies described in Chapters 3 and 4 mainly involving the synthesis and structural assessment of peroxovanadium compounds suggested that the hitherto unknown chloroperoxo-vanadium compounds could be synthesised under the suitable conditions. Moreover, we were interested to ascertain the minimum number of peroxo groups responsible for the formation of blue peroxovanadates about which no mention was made in any of the studies made in solutions.[5,16,17]

Because of the very facile oxidation of chloride to chlorine by hydrogen peroxide in the presence of an acidic medium, it was thought that an alkaline medium should be conducive to the synthesis of chloroperoxovanadium compounds. In accord with the sythetic strategy, the reactions of V_2O_5 with ACl, AOH and 9% H_2O_2 in the molar ratios of V_2O_5:ACl:AOH:H_2O_2 at 1:2:10:14, and at 1:2:15:14 gave rise to the formation of the yellow $[VO(O_2)_2Cl]^{2-}$ and the blue $[V(O_2)_3Cl]^{2-}$ species respectively. The complex ions were isolated in the solid state as their alkali-metal and ammonium salts by the addition of ethyl alcohol. The role of alcohol was to facilitate

precipitation of the compounds. In the course of this work it was observed that the blue colour of the vanadium - hydrogen peroxide system, in the presence of Cl^- ions, was obtained with a relatively lower concentration of the alkaline medium at a comparatively higher temperature. However, higher temperature was not considered favourable for the synthesis of such compounds over an enhanced concentration of alkaline medium. The fact that very high concentration of the alkaline medium leads to the formation of the triperoxy species, $[V(O_2)_3Cl]^{2-}$, while the relatively lower concentration of the alkaline medium produces the $[VO(O_2)_2Cl]^{2-}$, suggest that a very high alkaline medium probably helps replacement of the last oxygen from the $[VO(O_2)_2Cl]^{2-}$ by a O_2^{2-} group thereby favouring the formation of $[V(O_2)_3Cl]^{2-}$, or that the oxo oxygen of the $[VO(O_2)_2Cl]^{2-}$ species is converted to the third peroxo ligand by abstracting an oxygen of hydrogen peroxide. It is difficult to say, in the absence of any direct evidence, which one of the two mechanisms is more probable. However, the fact that oxygen exchange on vanadium(V) is very slow,[6] and the strength of the V-O multiple bond is high, as evident from the IR spectroscopic studies of oxovanadium(V) complexes;[12,18] it appears that the latter mechanism may

be more likely. It is, therefore, evident that under the appropriate conditions, the hetero-peroxovanadium(V) compounds of the types $A_2[VO(O_2)_2Cl]$ and $A_2[V(O_2)_3Cl]$ can be synthesised, and that a minimum number of three peroxo groups are required for the formation of blue peroxovanadium compounds. It is expected that a similar synthetic strategy can be applied for the synthesis of other hetero-peroxovanadium(V) compounds.

Characterization and Structural Assessment. The alkali-metal and ammonium oxodiperoxochlorovanadates(V), $A_2[VO(O_2)_2Cl]$, are yellow microcrystalline compounds, and the similar salts of triperoxochlorovanadates(V), $A_2[V(O_2)_3Cl]$, are blue. The salts of the anion $[VO(O_2)_2Cl]^{2-}$ are generally more stable than those of the anion $[V(O_2)_3Cl]^{2-}$. A comparison of the properties of chloroperoxovanadates(V) with those of the corresponding fluoroperoxovanadates(V)[12,13] (Chapters 3 and 4) reveals that the most notable difference that results from changing the hetero ligand from F^- to Cl^- is the fall in stability, with the difference being more pronounced in the cases of hetero-triperoxovanadate(V) compounds. While the alkali-metal and ammonium salts of fluorotriperoxovanadate(V) are stable for prolonged

periods[13] (Chapter 4), those of the chloroperoxovanadate(V) are unstable. The $A_2[V(O_2)_3Cl]$ (A = NH_4 or K) decomposed to yellow coloured microcrystalline products. The decomposition products have not yet been clearly identified, however, they have been found to contain peroxo groups, as evidenced by the results of chemical determination and IR spectroscopy, but definitely not to the extent of three peroxo ligands per vanadium. The stability of the compounds was ascertained by the periodic estimation of their peroxide contents and recording their IR spectra. The determination of peroxide content of such compounds is considered to be crucial in order to decide the number of such groups coordinated to the metal centre. The peroxide estimation was accomplished by redox titration with a standard cerium(IV) solution,[14] the results of which conclusively suggested the presence of two peroxo ligands per V^{5+} ion in the yellow compounds and three peroxo groups per V^{5+} ion in the blue compounds. The diamagnetic nature of the compounds, as evidenced by their mgnetic susceptibility measurements, ensures that the vanadium occurs in its +5 oxidation state in each of the newly synthesized compounds.

The IR spectra of the three salts of the yellow $[VO(O_2)_2 Cl]^{2-}$ ion resemble each other very closely

(Table 2), indicating thereby that the compounds are similar both structurally and stoichiometrically. The absorptions occuring in the four characteristic regions viz., at 955 - 970 cm^{-1}, 870 - 890 cm^{-1}, 610 - 615 cm^{-1}, and 410 - 415 cm^{-1} are well precedented in the literature and have been assigned respectively to ν_{V-O} owing to the presence of terminally bonded V=O groups,[12,18,19] to ν_{-O-O-} mode of coordinated peroxo ligands,[12,20] to ν_{V-O_2},[20] and to ν_{V-Cl}.[21] The three extra vibrations at 3160m, 3045s and 1400s cm^{-1} in the case of the ammonium salt have been attributed to the ν_3, ν_1 and ν_4 modes of NH_4^+.

The spectra of the three salts of the $[V(O_2)_3Cl]^{2-}$ anion also resemble each other very strongly showing absorptions in the regions 855 - 860 cm^{-1}, 615-620 cm^{-1}, and 410-420 cm^{-1} respectively owing to the presence of coordinated peroxide and chloride ligands and are assigned to the ν_{-O-O-}, ν_{V-O_2} and ν_{V-Cl} modes. The three extra modes for the 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 $A_2[V(O_2)_3F]$ compounds[13] suggesting that both the triperoxochloro-vanadates(V) and triperoxofluorovanadates(V) probably have structural similarity.

The ν_{-O-O-} absorptions in the spectrum of each of the compounds occur in the region stipulated for the presence of triangularly (C_{2v}) bonded O_2^{2-} ligands[12,13,20] leading us to conclude that in each of them the peroxo group is bonded to the vanadium(V) centre in a triangular bidentate manner. A perusal of the spectra of the two series of compounds revealed that those of $A_2[V(O_2)_3Cl]$ compounds completely lack the absorption at ca 950 cm^{-1} owing to ν_{V-O}. This conforms to the formula $A_2[V(O_2)_3Cl]$. The other difference was the shift, though small, in the positions of ν_{-O-O-} modes to a relatively lower region in the cases of the blue peroxo compounds (Table 2). Whereas the ν_{-O-O-} absorptions for $A_2[VO(O_2)_2Cl]$ compounds lie in the region 870-890 cm^{-1}, those for the $A_2[V(O_2)_3Cl]$ compounds lie in the region 855 - 860 cm^{-1}. The fall in the ν_{-O-O-} frequency suggests a decrease in the -O-O- bond order of the coordinated peroxo ligands with the increase in the number of peroxo groups bound to the vanadium(V) centre.

Conversion of $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$ and the Reverse. Evidance for Facile Diperoxovanadate(V)——Triperoxovanadate(V) Interconversion. Having obtained the yellow oxodiperoxochlorovanadates(V), $A_2[VO(O_2)_2Cl]$ and

the blue triperoxochlorovanadates(V), $A_2[V(O_2)_3Cl]$, it was thought that it would be quite interesting to study the conversion of $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$ and vice-versa. The sodium salts of the anions were chosen for such studies because of their slightly higher stabilities. It was observed that under the suitalbe conditions (vide Experimental Section) the $Na_2[VO(O_2)_2Cl]$ can be easily converted to the $Na_2[V(O_2)_3Cl]$, which again can be reconverted to the $Na_2[VO(O_2)_2Cl]$. The oxodiperoxochlorovanadate(V) —— triperoxochlorovanadate(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 the compounds are formed in the presence of alkaline media and excess of hydrogen peroxide, it is the large excess of alkaline medium that favours the formation of the triperoxovanadium(V) species. The peroxide uptake and deperoxygenation reactions can be best monitored by IR spectroscopy. The complete conversion of $[VO(O_2)_2Cl]^{2-}$ species to the $[V(O_2)_3Cl]^{2-}$ is ascertained by observing the complete disappearance of the ν_{V-O} band at ca 950 cm^{-1} in a small amount of the compound isolated from the solution. The reverse reaction

i.e., the process $[V(O_2)_3]^{2-} \rightarrow [VO(O_2)_2Cl]^{2-}$ was confirmed not only by noting the colour change of the solution from blue to yellow but also by observing the appearance of the new band at about 950 cm^{-1} owing to $\nu_{V-O'}$ and the shift of ν_{-O-O-} absorption towards a relatively higher frequency.

It may be concluded that under the conditions described above, the complex species responsible for the yellow and blue colours are $[VO(O_2)_2Cl]^{2-}$ and $[V(O_2)_3Cl]^{2-}$ respectively. In each of the newly synthesised compounds the peroxo ligands are bonded in a triangular bidentate manner to the V^{5+} centre. The complex species $[VO(O_2)_2Cl]^{2-}$ may be hexacoordinated monomer or it may as well be a polymer through a weak V-O-V or a weak V-Cl-V bridging. Similarly, the complex species $[V(O_2)_3Cl]^{2-}$ may be a heptacoordinated monomer, or it may have a polymeric structure through a weak V-Cl-V interaction. The $[VO(O_2)_2Cl]^{2-} \rightleftharpoons [V(O_2)_3Cl]^{2-}$ interconversion provides a good example of a process which involves a basic formation reaction and an acedic dissociation reaction of peroxovanadium(V) compounds.

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Chapter 6

Synthesis and Assessment of Structure of Alkali-metal and Ammonium Diaquofluoro-oxoperoxovanadate(IV) Complexes $[VO(O_2)F(H_2O)_2]^-$

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

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Accordingly the reaction of alkali-metal and ammonium tetrafluoro-oxovanadates (V), A $[VOF_4]$ (A = K, Rb, Cs or NH_4), with 6% hydrogen peroxide under a weak acidic conditions (pH ca 4) was performed which enabled the synthesis of a series of alkali-metal and ammonium diaquofluoro-oxoperoxovanadates(IV), A $[VO(O_2)F(H_2O)_2]$; these peroxovanadate(IV) compounds were obtained, for the first time, in the solid state.

The present Chapter describes the synthesis and structural assessment of alkali-metal and ammonium diaquofluoro-oxoperoxovanadate(IV) complexes, A $[VO(O_2)F(H_2O)]$ (A = K, Rb, Cs or NH_4).

Experimental

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

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

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

Magnetic susceptibility measurements were made by the Gouy Method, Hg $[Co(NCS)_4]$ was the calibrant.

Molar conductance measurements were made using a Philips PR9500 conductivity bridge.

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

Preparation of Alkali-metal and Ammonium Difluorides, AHF_2 (A= K, Rb, Cs or NH_4).[10] These compounds were prepared by the methods developed in this laboratory (described in Chapter 1).

Preparation of Alkali-metal and Ammonium Tetrafluoro-oxovanadates(V), A $[VOF_4]$ compounds were prepared by the methods already described in Chapter 1.

Synthesis of Alkali-metal and Ammonium Diaquo-fluoro- oxoperoxovanadate(IV) complexes, A $[VO(O_2)F(H_2O)_2]$ (A = K, Rb, Cs or NH_4). As the methods of synthesis of these complexes are similar, only a representative method is described.

Freshly prepared alkali-metal or ammonium tetrafluoro-oxovanadate(V), A $[VOF_4]$ was dissolved in 6% hydrogen peroxide, maintaining the molar ratio A $[VOF_4]$: H_2O_2 at 1 : 12 (pH ca 4), with gentle stirring. The red solution thus obtained was cooled in an ice-bath for ca 20 min. Ethyl alcohol was added,

in excess, with constant stirring and orange-red microcrystalline alkali-metal or ammonium diaquofluoroperoxovanadate(IV), A $[VO(O_2)F(H_2O)_2]$ was obtained. The compound was separated by centrifugation and washed several times with ethanol, and finally dried over diphosphorus pentoxide.

The amounts of reagents used and the yields of the compounds A $[VO(O_2)F(H_2O)_2]$ are given in Table 1.

Table 1. Amounts of Reagents Used and Yields of A $[VO(O_2)F(H_2O)_2]$ (A = K, Rb, Cs or NH_4) Compounds

Compound	Yield in g (%)	Amount of A$[VOF_4]$ in g(mmol)	Amount of 6% H_2O in ml(mmol)
$NH_4[VO(O_2)F(H_2O)_2]$	0.4 (75)	0.5 (3.1)	22.0 (38.5)
$K[VO(O_2)F(H_2O)_2]$	0.3 (57)	0.5 (2.8)	19.0 (33.5)
$Rb[VO(O_2)F(H_2O)_2]$	0.5 (68)	0.7 (3.1)	22.0 (38.5)
$Cs[VO(O_2)F(H_2O)_2]$	0.5 (69)	0.7 (2.5)	17.0 (30)

Elemental Analyses. Vanadium estimation was done volumetrically. A solution of the peroxovanadate(IV) compounds, made slightly alkaline with a dilute sodium hydroxide solution, was boiled in order to completely expel the peroxo oxygen and to convert vanadium(IV) to vanadium(V). The solution was cooled and neutralized with dilute sulphuric acid. A near-boiling solution of vanadium(V) was treated with a stream of sulphur dioxide for 10-15 min, and then with a rapid stream of carbon dioxide to expel any excess of sulphur dioxide. The vanadium(IV) solution thus obtained was then cooled to ca 80°C, and titrated with a standard potassium permanganate solution.[12]

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

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

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

Results and Discussion

In the course of the earlier studies(Chapters 3 and 4) involving the synthesis of peroxofluoro-compounds of vanadium(V), a red solution was obtained containing V^{5+}, alkali-metal or ammonium fluoride, AF, and H_2O_2 at a pH ca 4, and presumbed that the species responsible for such a colour must be different from those isolated previously (Chapters 3 and 4). Further, it was expected that the number of peroxo-groups bonded to vanadium in acidic medium[5,12] would be less than that in alkaline medium, and that H_2O_2 would probably be able to reduce CV^{5+} to V^{4+} in an acidic medium. In view of the above considerations the reaction between A $[VOF_4]$ and 6% hydrogen peroxide was carried out and a red solution was obtained. The pH of the solution measured immediately after the formation of the red colouration was found to be ca 4. The complex species responsible for the red colouration was isolated in the solid state as its alkali-metal and ammonium salts, A $[VO(O_2)F(H_2O)_2]$, by addition of alcohol which possibly facilitated the reduction of V^{5+} to V^{4+}, and precipitation of the complex. The occurrence of reaction between alkali-metal or ammonium

tetrafluoro-oxovanadate(V), A $[VOF_4]$ and H_2O_2 was ascertained by the appearance of a new band ca 890 cm^{-1}, due to the ν_{O-O} mode of a coordinated peroxide, O_2^{2-}, from a small amount of the sample isolated from the solution. It was previously reported[15] that $K_2[V_2O_3(O_2)_2F_2]$ was isolated from the reaction of V_2O_5, 4% hydrofluoric acid, and H_2O_2 at high acidity and $K_2[VO(O_2)_2F]$ was isolated at pH 4. In the present case, however, the reaction of A $[VOF_4]$ with H_2O_2 at pH 4 followed by addition of ethanol afforded compounds of the type A $[VO(O_2)F(H_2O)_2]$.

Characterization and Assessment of Structure. The alkali-metal and ammonium diaquofluoro-oxodiperoxo-vanadates(IV), A $[VO(O_2)F(H_2O)_2]$, are all orange-red, microcrystalline products. The compounds are insoluble in organic solvents. They decompose in water thus precluding their molar conductance measurements. In fact, owing to their instability, most of the peroxovanadium compounds do not permit molar conductance measurements.[8,9,16] The compounds A$[VO(O_2)F(H_2O)_2]$ can, however, be stored in sealed containers and their stability can be ascertained by periodic estimation of the peroxide content. The estimation of peroxide is crucial in order to determine the number of O_2^{2-} ligands bonded to the

metal centre. The peroxide content was estimated by cerimetry (Ce^{4+}), and also by iodometry, the results of which conclusively suggest the presence of one O_2^{2-} group coordinated to vanadium(IV). The direct titration with a standard $KMnO_4$ solutions showed the involvement of three electron equivalents, two of which originated from O_2^{2-} and the third was due to the process $V^{4+} \longrightarrow V^{5+} + e$. The room temperature magnetic susceptibility measurements gave the magnetic moment values of the compound (295K), lying between 1.70 and 1.75 B.M. (1 B.M. $\simeq$ 9.27×10^{-24} JT^{-1}) are consistent with the presence of vanadium(IV) and are in excellent agreement with those reported in the literature for V^{4+} systems.[17]

The optical spectra of potassium and ammonium diaquofluoro-oxoperoxovanadates(IV), $A[VO(O_2)F(H_2O)_2]$ ($A = K$ or NH_4), recorded immediately after preparing solutions in cold dilute H_2O_2, showed three absorptions at *ca.* 11,700, *ca.* 17,699, and $> 21,400$ cm^{-1}, with the last being obscured by strong charge-transfer transitions. The first two Bands have been assigned to $e \leftarrow b_2$ and $b_1 \leftarrow b_2$ transitions respectively and agree very well with the reported spectra of oxovanadium(IV) complexes,[18] giving strong evidence for the presence of

vanadium(IV) in the orange-red peroxovanadium compounds. These observations also support the very recent report[6], concerning the existence of peroxovanadium(IV) in solutions.

The infrared spectra (Table 2) of the series of four salts are similar, showing absorptions at ca 3160m,br, ca. 1,630 w, br, ca. 960s, ca. 890s, ca. 615s, and ca. 475s cm^{-1}. The band at ca 960 cm^{-1} has been assigned to the $\nu_{V=O}$ mode of the terminally bonded V = O group,[18] while those at ca890 and ca 615 cm^{-1} have been assigned to ν_{-O-O-} and $\nu_{V-O}2$ respectively of the coordinated peroxide.[8,9,19,20] The absorptions at ca 3,160 m,br and ca. 1,630w, br cm^{-1} have been attributed to ν_{O-H} and δ_{H-O-H} modes of coordinated water. The lowering of the ν_{O-H} frequencies and broadening of δ_{H-O-H} bands relative to those of free water suggest the possibility of intramolecular hydrogen bonding.[21,22] The band at ca 475 cm^{-1} is attributed to a V-F stretching mode; its position suggests the presence of bridging rather than terminal F. Since the ν_{-O-O-} and the complemenatry ν_{V-O_2} fall in the regions expected for the triangularly bonded O_2^{2-} (C_{2v} symmetry) ligands,[8,9,19,20] it is inferred that the peroxide group is bonded to the V^{4+}

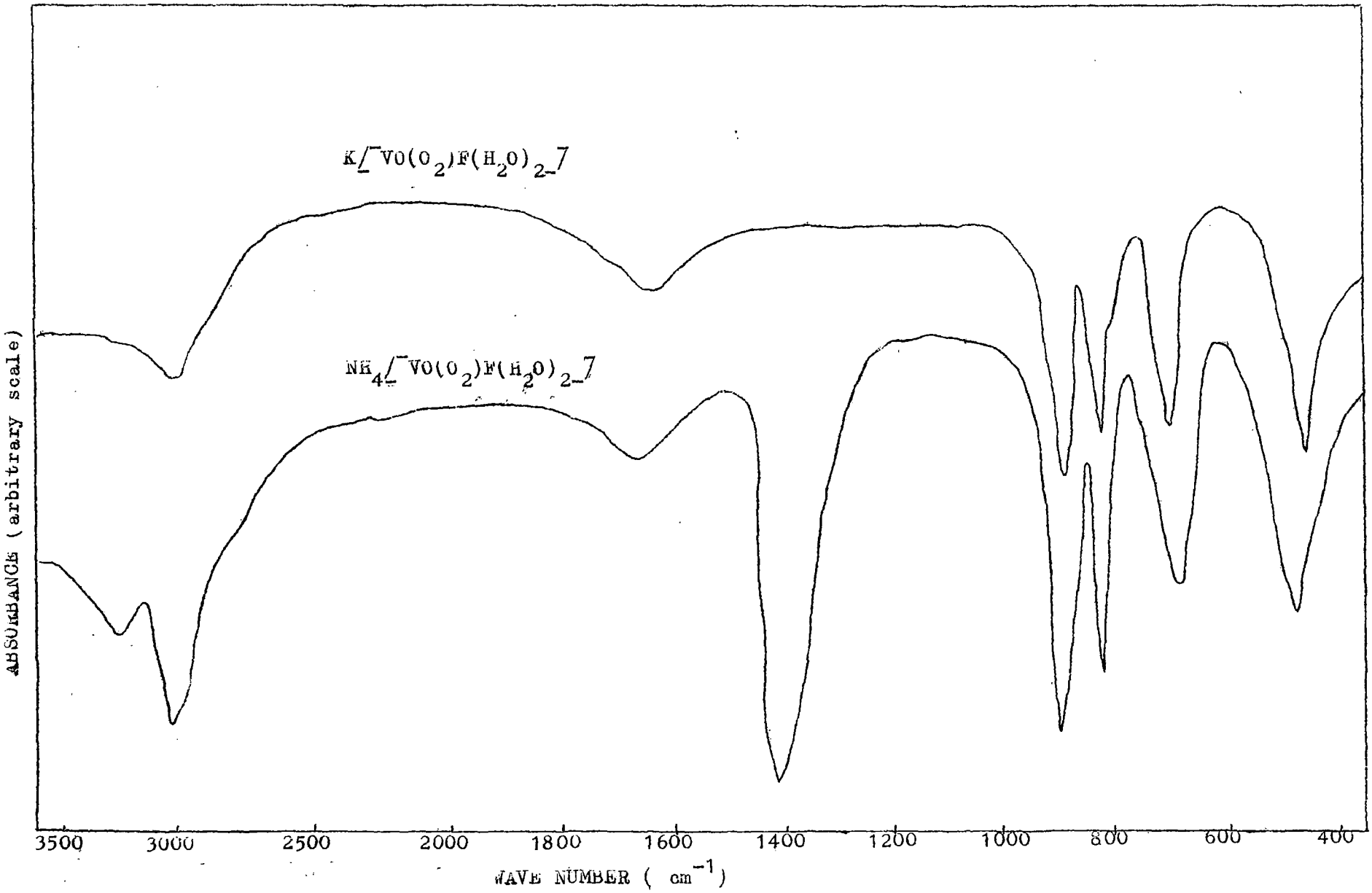
K[VO(O2)F(H2O)2]
NH4[VO(O2)F(H2O)2]
ABSORBANCE (arbitrary scale)
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
WAVE NUMBER (cm-1)

Table 2. Analytical Data, Magnetic Moments, Structurally Significant IR and Electronic Spectral Bands of $A[VO(O_2)F(H_2O)_2]$ (A = K, Rb, Cs or NH_4).

Compound	μ_{eff}/BM (295K)	% Found (% Calcd.) A or N	V	O_A[a]	F	IR Bands (cm^{-1})	Assignments (cm^{-1})	Electronic Absorption (cm^{-1})	Transition
$NH_4[VO(O_2)F(H_2O)_2]$	1.73	8.3 (8.15)	30.2 (29.6)	19.3 (18.6)	10.8 (11.05)	955s	νV-O	11,628	e ← b_1
						890s	ν-O-O-		
						610s	νV-O_2		
						475s	νV-F..V	17,699	b_1 ← b_2
						3150m,br	νO-H		
						1625w,br	δH-O-H		
						3040s	ν_1N-H..		
						1440s	ν_4N-H ..		
$K[VO(O_2)F(H_2O)_2]$	1.75	20.8 (20.25)	25.9 (26.4)	17.1 (16.55)	10.4 (9.84)	950s	νV-O	11,905	e ← b_1
						880s	ν-O-O-		
						620s	νV-O_2		
						470s	νV-F...V	17,699	b_1 ← b_2
						3165m,br	νO-H		
						1620w,br	δH-O-H		
$Rb[VO(O_2)F(H_2O)_2]$	1.70		21.7 (21.25)	13.9 (13.35)	7.6 (7.95)	970s	νV-O		
						880s	ν-O-O-		
						610s	νV-O_2		
						475s	νV-F...V		
						3160m,br	νO-H		
						1635w,br	δH-O-H		
$Cs[VO(O_2)F(H_2O)_2]$	1.73		18.3 (17.75)	11.8 (11.15)	6.8 (6.6)	965s	νV-O		
						895s	ν-O-O-		
						610s	νV-O_2		
						480s	νV-F...V		
						3150m,br	νO-H		
						1620w,br	δH-O-H		

a Peroxo-oxygen

centre in a triangular bidentate manner. Two extra vibrations at 3,140 and 1,440 cm^{-1} in the case of the ammonium salt have been assigned to the ν_1 and ν_4 modes of NH_4^+. The ν_3 mode of NH_4^+ could not be identified due to its overlap with the broad ν_{O-H} mode of water.

It thus appears that the complex ion has formula $[VO(O_2)F(H_2O)_2]^-$, containing a triangularly 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 can not be ruled out completely.

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Chapter 7

Bis(acetylacetanato) flurovanadate(III), $VF(acac)_2$. Synthesis and Assessment of Structure of a Novel Neutral Compound of Vanadium(III)*

Tripositive state of vanadium is one of its unusual oxidation states, mainly owing to the instability of vanadium(III) compounds. Predominant among the known compounds of vanadium(III) are those derived from vanadium(III) trihalides.[1] Trivalent vanadium also forms some neutral mixed ligand complexes of the types VL_3X_3 and VL_2X_3 with L being a unidentate ligand and X is a halide, particularly chloride. Neutral complex of V^{3+} of the type $V(L\text{-}L')_2X$ with L-L' being a bidentate mononegative ligand does not appear to have any reported example in the literature. Moreover, reports on the synthesis of trivalent vanadium compound from V^{5+} or V^{4+} through chemical reduction is rather scanty. As a sequel of studies on synthesis and structural assessment of fluoro[2] (Chapters 1 and 2) and a mixed fluoro[3-5] compounds (Chapters 3,4 and 6) of vanadium,

* This work has been accepted for publication: Inorg. Chem., in press (Paper No. IC 8307676)

a method has been developed for the synthesis of a new neutral complex of vanadium(III), $VF(acac)_2$, achieved by a two-steps electron-transfer process starting from vanadium pentoxide.

Chapter 7 of the thesis presents an account of the synthesis, characterisation and structural assessment of bis(acetylacetonato) fluorovanadate(III), $VF(C_5H_7O_2)_2$.

Experimental

All chemicals used were of reagent grade (B.D.H., E. Merck, S.D.'s and Sarabhai M. Chemicals).

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

Magnetic susceptibility measurements were made by the Gouy method. Hg $[Co(NCS)_4]$ was the calibrant.

The mass spectra were recorded on a Varian MAT CH-5 spectrometer using a direct insertion probe to introduce the sample directly into the ion source without any prior heating. The operation conditions were electron energy 70eV (1 eV $\simeq 1.6 \times 10^{-19}$ J); source temperature of 50, 100 and 150°C; resolution 10,000 and the accelerating voltage 8kV. The mass spectrometric

observations were made with the field of ionising field of ionising current being maintained sufficiently strong to trap primary ions.

Elemental analyses. Carbon, hydrogen, nitrogen and fluoride analyses were obtained from Amdel Australian Microanalytical Service, Port Melbourne, Victoria 3207, Australia.

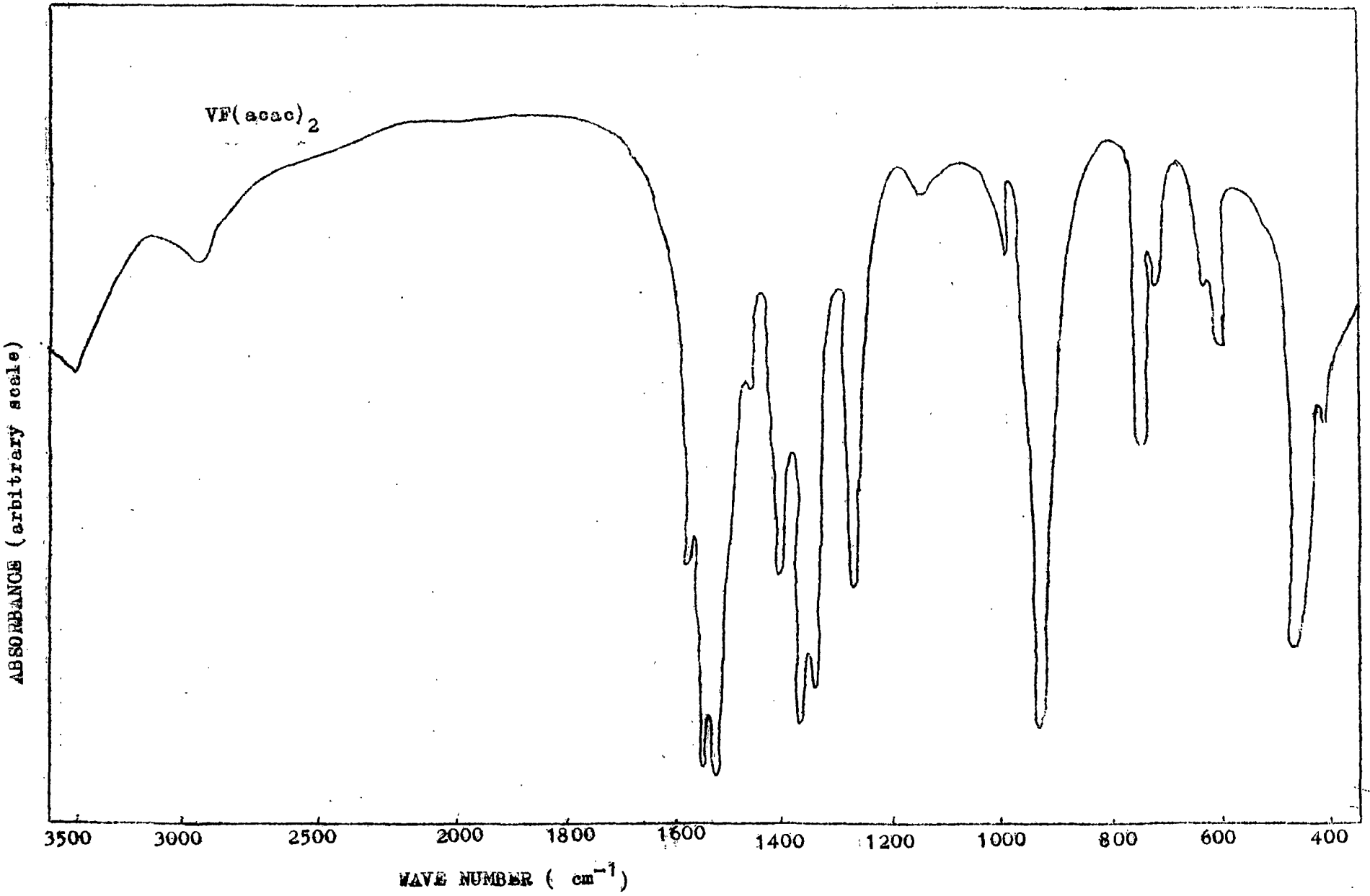
Vanadium was estimated volumetrically by titration with a standard potassium permanganate solution.[6] The compound was first decomposed and then the estimation of vanadium was made following the procedure described in Chapter 1.

Fluoride was also determined by precipitating as lead chloride fluoride, PbClF, and chloride was estimated by Volhard's method, from which the fluoride content was calculated[7] (Chapter 1).

Synthesis of Bis(acetylacetonato) fluorovanadate(III), $VF(acac)_2$. A suspension of 2.0 g (11 mmol) V_2O_5 in 10 ml water was treated with 2.2 ml (44 m mol) 40% hydrofluoric acid. The mixture was warmed on a steam-bath with stirring for 10-15 min and then cooled followed by filtration to remove any undissolved impurity. The clear solution was cooled in an ice-bath and 99% hydrazine hydrate solution was added dropwise with

occassional stirring. The solution first turned blue. The addition of hydrazine hydrate was continued until a blue crystalline compound ceased to appear with the mother liquor becoming very faint in colour. The blue compound was separated by centrifugation, dried on a filter paper, and finally in vacuo. The compound was identified as $N_2H_5VOF_3$ (vide Chapter 2) with an yield of 1.6 g (92%). [Found: N, 17.91; H, 3.14, V, 32.5, and F, 36.31%. Molar conductance (Water): 130 $\Omega^{-1}cm^2mol^{-1}$. Magnetic moment (302K):1.51 B.M. IR : 970 cm^{-1} (ν_{V-O}) and 500 cm^{-1} (ν_{V-F}). Electronic spectrum: 12,000 cm^{-1} and 16,000 cm^{-1} attributed to $e \leftarrow b_2$ and $b_1 \leftarrow b_2$ transition.[87]

The blue hydrazonium oxotrifluorovanadate(IV), $N_2H_5VOF_3$, (1.6 g, 10.2 mmol), dissolved in about 8 ml water, acetylacetone (10 g, 100 mmol) were placed in a small polyethylene conical flask, the neck of which was plugged with cotton wool, and the whole was heated on a steam-bath for ca 1h and a dark blue-green solution was obtained. On cooling, blue-green crystals of bis(acetylacetonato) fluoro-vanadate(III), $VF(acac)_2$, were formed which were removed from the flask and dried on a filter paper. The compound was recrystallised by dissolving in hot benzene followed by addition of petroleum ether


VF(acac)2
ABSORBANCE (arbitrary scale)
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
WAVE NUMBER (cm-1)

(b.p. 40 - 60°C) until the solution was cloudy. Yield of VF $(C_5H_7O_2)_2$ was 2.5 g (84.7% on the basis of V_2O_5), and m.p. 246-248°C. [Found : M (mass spectrum), 268; C, 44.32; H, 5.6; V, 18.4 and F, 6.9%. Calc. for $C_{10}H_{14}VO_4F$: M, 268; C, 44.78; H, 5.27; V, 18.99 and F, 7.1%. Magnetic moment (302K) : 2.77 B.M.]7.

Work up of the mother liquor, obtained after isolation of $VF(acac)_2$, afforded a small amount of $\alpha,\alpha,\beta,\beta$-tetraacetylethane, $(CH_3CO)_2CH-CH(CH_3CO)_2$, being the oxidation product of acetylacetone (Hacac).

Results and Discussion

Vanadium pentoxide readily reacts with 40% hydrofluoric acid and an excess of hydrazine hydrate to yield a blue crystalline compound. The compound is soluble in water, and the results of elemental analyses suggest the atom ratio N : H : V : F as 2 : 5 : 1 : 3. The inferred spectrum of the compound showed a strong band at 970 cm^{-1} indicating the presence of V-O multiple bond, and was accordingly assigned[8] to ν_{V-O}. The band at 500 cm^{-1} has been assigned as the ν_{V-F} mode arising due to the presence of fluoride coordinated[9] to the vanadium center. The infrared

spectrum also exhibited bands characteristic for $N_2H_5^+$ (Ref 10). The electronic spectrum of the compound showed two d-d transition bands at 12,000 cm^{-1} and 16,000 cm^{-1} which have been attributed to $e \leftarrow b_2$ and $b_1 \leftarrow b_2$ transition respectively.[8] Thus, on the basis of the results of chemical analyses, IR and electronic spectral studies, the formula $N_2H_5[VOF_3]$ has been assigned to the compound (for further evidence reference has to be made to Chapter 2).

The blue hydrazonium oxotrifluorovanadate(IV), $N_2H_5[VOF_3]$, reacts further with an excess of acetylacetone (Hacac) under mild conditions to give ultimately the blue-green crystalline bis (acetylacetonato) fluorovanadate(III), $VF(acac)_2$. The reaction was rather facile andgave a very high yield of the product. It is interesting to note that althrough acetylacetone (Hacac) is capable of reducing Mn^{7+} to Mn^{3+} (Ref. 11), Cr^{6+} to Cr^{3+} (Ref. 12) or Ni^{3+} to Ni^{2+} (Ref. 13) with Hacac being oxidised to $\alpha, \alpha, \beta, \beta$, - tetraacetylethane, $(CH_3CO)_2CH{-}CH(CH_3CO)_2$,[13] it alone can not reduce V^{4+} (Ref. 14). In the present case, isolation of $\alpha, \alpha, \beta, \beta$ -tetraacetylethane, after separation of $VF(acac)_2$ from the reaction solution, suggest the possibility of Hacac being acted as a

reducing agents. However, the importance of $N_2H_5^+$ can not be underestimated though we do not have any direct evidence of its oxidation.

The blue-green bis(acetylacetonato) fluorovanadate(III), $VF(C_5H_7O_2)_2$, is stable for prolonged periods, and can be stored in a sealed polyethylene capsule. The compared melts at 246 - 248°C, and is soluble in many organic solvents. The oxidimetric titration with standard potassium permanganate shows that vanadium in the compound has an oxidation state of +3, which was further confirmed by magnetic susceptibility measurements. The room temperature magnetic moment was found to be 2.77 B.M. which conforms to those reported in the literature for trivalent vanadium compounds.[15] The infrared spectrum of the compound gives a patterns typical for the presence of coordinated acetylacetonates ($acac^-$) bonded to the V^{3+} centre in a bidentate chelated manner.[11-13,16] Besides this there is a strong band at 470 cm^{-1} which has been attributed to the ν_{V-F}[9] mode arising from the presence of fluoride coordinated to the vanadium(III) centre. Somewhat broad nature of the band indicates the possibility of a weak V-F...V interaction and this leads to believe that in the solid state $VF(acac)_2$ may have a hexacoordinated structure through a weak V-F....V bridging.

In order to obtain further information, the mass spectra of the compound was recorded using the direct insertion technique. The sample was introduced directly into the ionisation chamber without any prior heating. This prevents the compound from being decomposed before electron-impact induced ionisation has taken place. The spectra were recorded at 50°, 100° and 150°C respectively, and found that the one recorded at 150°C was very well developed. The spectrum run at 150°C shows the highest m/z signal at 268 owing to the molecular ion $[VF(C_5H_7O_2)_2]^+$, suggesting thereby that in the vapour state the compound is only monomeric. The most dominant peak was observed at m/z 169 and attributed to the fragment ion $[VF(C_5H_7O_2)]^+$. The molecular ion was found to suffer a loss of CH_3 unit first, followed by the loss of $C_4H_4O_2$ to give rise to the formation of $[VF(C_5H_7O_2)]^+$. The fragment ion $[VF(C_5H_7O_2)]^+$ lost CH_3 and $C_4H_4O_2$ units respectively to ultimately give the ion $[VF]^+$. In view of the observed signals, the major fragmentation pathway of the compound $VF(C_5H_7O_2)_2$ may be represented as follows:

$$[VF(C_5H_7O_2)_2]^+ \longrightarrow [VF(C_5H_7O_2)(C_4H_4O_2)]^+ \longrightarrow$$

$$[VF(C_5H_7O_2)]^+ \longrightarrow [VF(C_4H_4O_2)]^+ \longrightarrow VF^+.$$

Table 1. Infrared Spectral Band Positions, of $VF(C_5H_7O_2)_2$, and their Assignments.

IR Bands cm^{-1}	Assignments
3070	ν(CH)
2990, 2970, 2920	$\nu(CH_3)$
1575, 1550	ν(C=C) + ν(C=O) combination.
1530	ν(C=O) + ν(C=C)
1465	δ(CH) + ν(C=C)
1410	$\delta_a(CH_3)$
1350	$\delta_s(CH_3)$
1270	$\nu(C-CH_3)$ + ν(C=C)
1100	δ(CH) + $\nu(C-CH_3)$
1015	$P_r(CH_3)$
940	ν(C=C) + ν(C=O)
780	π(CH)
685	$\nu(C-CH_3)$ + ring deformation
650	$\pi(CH_3-C<^{C}_{O})$
615	ring def. + ν(M-O)
450	ν(M-O) + $\nu(C-CH_3)$
430	ring deformation
470	ν_{V-F}

Table 2: Mass Spectrometric Data for $VF(C_5H_7O_2)_2$

Major Peaks

Assignments	m/z	Intensity (%)
$[VF(C_5H_7O_2)_2]^+$	268	95
$[VF(C_5H_7O_2)(C_4H_4O_2)]^+$	253	84
$[VF(C_5H_7O_2)(C_3H_5O)]^+$	226	32
$[VF(C_5H_7O_2)OH]^+$	186	90
$[VF(C_5H_7O_2)]^+$	169	100
$[VF(C_4H_4O_2)]^+$	154	26
$[VF(C_3H_5O)]^+$	127	22
$[VF]^+$	70	25

Metastable Transitions

(m/z)* Observed	(m/z)* Calculated	Process	Fragment lost
238.8	238.84	268 ⟶ 253	CH_3
190.7	190.58	268 ⟶ 226	CH_2CO
129.2	129.09	268 ⟶ 186	C_5H_6O
112.8	112.89	253 ⟶ 169	$C_4H_5O_2$
140.4	140.33	169 ⟶ 154	CH_3
31.9	31.82	154 ⟶ 70	$C_4H_4O_2$

The metastable peaks (Table 2) at (m/z)* 238.8, 140.4, 112.8 and at 31.9 support the above-mentioned fragmentation pattern.

Thus, it is evident from the present work that a trivalent vanadium compound, $VF(acac)_2$, can be synthesised from pentavalent vanadium under the suitable conditions, the compound may have a hexacoordinated polymeric structure, through a weak V-F....V interaction in the solid state, however, in the vapour state $VF(acac)_2$ definitely exists in its monomeric form.

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Chapter 8

Novel Synthesis and Electron-Impact Induced Mass Spectrometric Studies of Tris(acetylacetonato)-iron(III), $Fe(C_5H_7O_2)_3$ *

The chemistry of metal-acetylacetonates is a text book story, and tris(acetylacetonato) iron(III) is one of the classic examples of this type of compounds. Tris(acetylacetonato) iron(III) has been known for quite some time, but the known methods of synthesis of $Fe(acac)_3$ have some limilations in scope. The reaction between metallic iron and acetylacetone (Hacac) in th presence of oxygen[1] is extremely slow. The aqueous reaction between iron(III) chloride and acetylacetone in the presence of a large amount of sodium acetate as buffer[2,3] 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

* This work has been published:
J. Chem. Soc. Dalton Trans., 1983, 839.

metal carbonyl.

The present Chapter, indeed the last Chapter of the thesis, describes a novel synthesis of tris(acetylacetonato) iron (III), $Fe(acac)_3$, directly from iron(III) hydroxide and acetylacetone, without the use of any buffer [equation (1)], characterization and mass spectrometric studies of the compound.

$$Fe(OH)_3 + 3Hacac \longrightarrow Fe^{3+} + 3acac^- + 3H_2O \quad (1)$$

Experimental

Reagent grade (B.D.H., E. Merck, S.D.'s and Sarabhai M. Chemicals) iron(III) chloride and acetylacetone (Hacac) 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, 70eV

(1eV $\simeq 1.6 \times 10^{-19}$J); source temperatures of 50, 100 and 150°C; resolution 10,000; and accelerating voltage, 8kV. The mass spectrometric observations were made with the field of ionising current sufficiently strong to trap primary ions.

Elemental Analyses. Carbon and hydrogen were estimated by a microanalytical technique.

Chemical Determination of the Oxidation State of Iron. The chemical determination of the oxidation state or iron in the compound was done by treating a known amount of the compound with an acidified (H_2SO_4) potassium iodide solution, followed by titration of the liberated iodine with a standard sodium thiosulphate solution.

Synthesis of Tris (acetylacetonato) iron (III), $Fe(C_5H_7O_2)_3$.

Anhydrous iron(III) chloride (4.0 g, 24.7 m mol) was dissolved in 8 ml of water with gentle warming. Ammonia solution (specific gravity = 0.880, 9ml) was added in excess 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 m mol) 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 about 35 min. On cooling, large red crystals of $Fe(acac)_3$ were obtained which were dried on filter paper and recrystallised from ethanol. Yield of $Fe(acac)_3$ was 7.8 g (90%). Melting point of the compound was found to be 175°C.

Analysis

Molecular weight (M) was found to be 353, mass spectrometrically.

Found: C, 51.2%; H, 5.95%. Calcd. for $C_{15}H_{21}FeO_6$: C, 51.05% and H, 5.96%.

Magnetic moment (295K): 5.92 B.M. (1 B.M. = 0.927 x 10^{-23} A m^2). (lit.,[3] 5.90 B.M.).

Chemically determined oxidation state of Fe: + 3.

Molar conductance (H_2O) : 8 Ω^{-1} cm^2 mol^{-1}.

Results and Discussion

In view of the difficulties involved in the synthesis of metal acetylacetonates, attempts have been made to improvise newer methods for the synthesis of such

compounds. Recently tris(acetylacetonato) manganese(III), $Mn(acac)_3$ was synthesised by the reaction of MnO_4^- with acetylacetone[5] by exploiting the electron-transfer reaction between them. Subsequently, it has been shown[6] that, in such electron-transfer reactions, acetylacetone is oxidised to $\alpha, \alpha, \beta, \beta$ -tetraacetylethane $(CH_3CO)_2CH-CH(CH_3CO)_2$.

The weak acidity of acetylacetone (Hacac) in a polar medium, and the absence of any reaction of water with tris (acetylacetonato) iron(III), $Fe(acac)_3$, 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). This justifies the scope of the method. 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[2,3] in the synthesis of $Fe(acac)_3$ from $FeCl_3$.

The tris(acetylacetonato) iron(III), $Fe(C_5H_7O_2)_3$, obtained by the present method is highly crystalline and dark red in colour. The compound is stable for prolonged periods. $Fe(acac)_3$ is soluble in water and also

in many common organic solvents. The molar conductance of the compound, in water, was found to be 8 $\Omega^{-1}cm^2mol^{-1}$ supporting the non-electrolytic nature of the compound in agreement with its formula. The chemical determination of the oxidation state of iron showed that iron occurs in its +3 state in this compound. The room temperature magnetic moment of the compound was found to be 5.92 B.M. which agrees very well with the literature[3] value and is in conformity with the +3 oxidation of state of iron in the compound.

The infrared spectrum of the compound is unambiguous and exhibits the typical pattern of chelated acetylacetonates ($acac^-$) in agreement with those of various $M(acac)_3$[5,7] compounds (Table 1). The mass spectra of $Fe(acac)_3$ were obtained using a direct insertion probe to introduce the sample into the ionisation chamber without prior heating. The importance of direct insertion technique for the mass spectrometry of metal compounds has been emphasised in the literature.[5,8] The most important advantage of this technique is that it prevents decomposition of a compound before it undergoes electron-impact induced fragmentation.

The spectrum run at 150°C showed the molecule-ion signal at m/z 353 (intensity 16%) and the most dominant

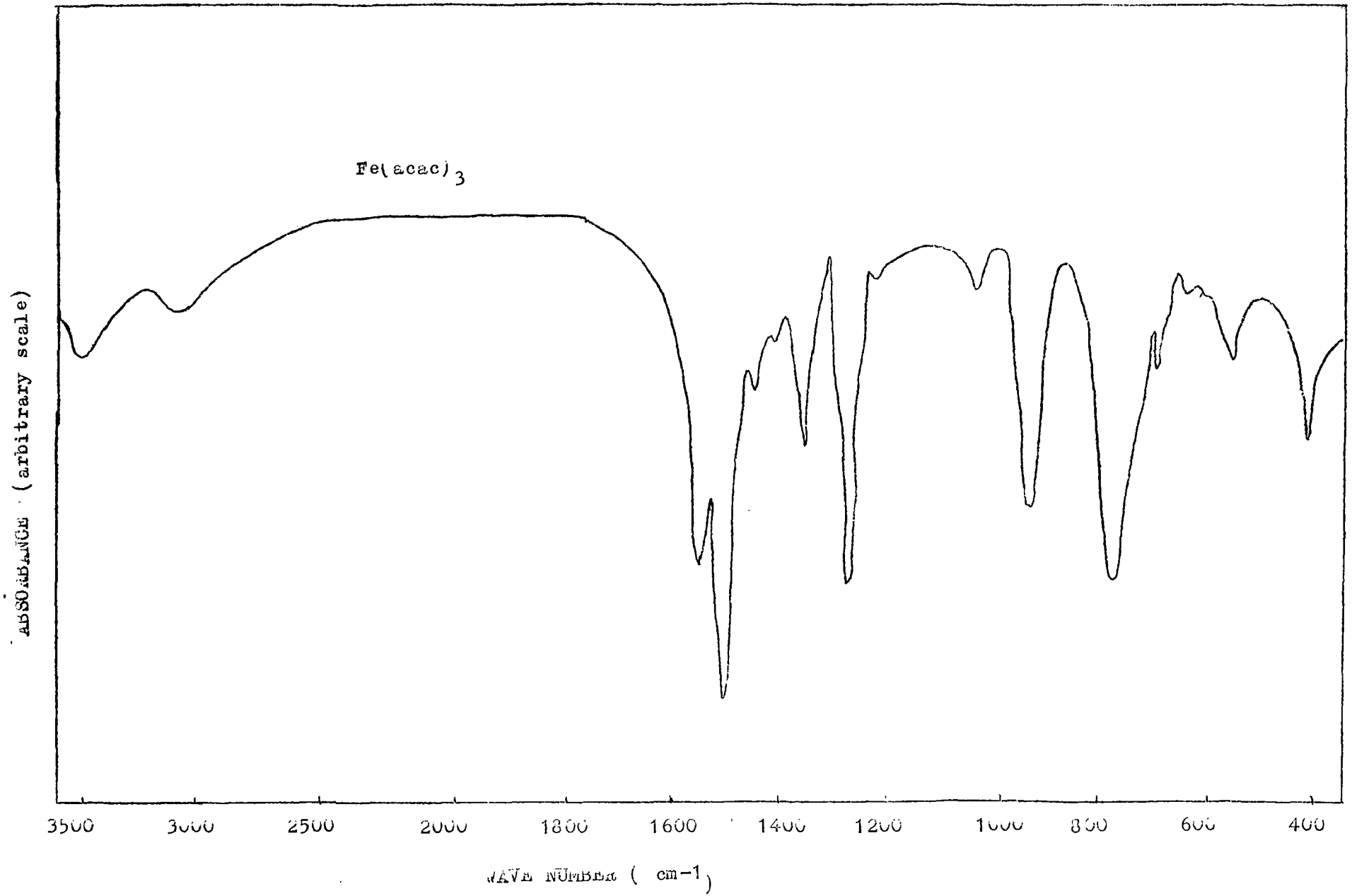

Fe(acac)3
ABSORBANCE (arbitrary scale)
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
WAVE NUMBER (cm-1)

Table 1. Infrared Spectral Bands and Their Assignments for $Fe(acac)_3$

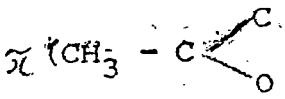
IR Bands (cm^{-1})	Assignments
3060	ν(C - H)
2995, 2960, 2925	$\nu(CH_3)$
1575	ν(C=C) + ν(C=O) combination.
1520	ν(C=O) + ν(C=C)
1450	δ(CH) + ν(C=C)
1420	$\delta_d(CH_3)$
1380, 1360	$\delta_s(CH_3)$
1270	$\nu(C{=}CH_3)$ + ν(C=C)
1190	δ(CH) + $\nu(C{-}CH_3)$
1020	$\rho_r(CH_3)$
950	ν(C=C) + ν(C=O)
800, 780, 770	π(CH)
675, 665	$\nu(C - CH_3)$ + ring deformation + ν(M - O)
655	π() +
565, 545	ring deformation + ν(M - O)
430	ν(M - O) + $\nu(C - CH_3)$
415	ring deformation

Table 2. Mass Spectral Data for $Fe(C_5H_7O_2)_3$

Major Peaks

Assignments	m/z	Intensity (%)
$[Fe(C_5H_7O_2)_3]^+$	353	17
$[Fe(C_5H_7O_2)_2]^+$	254	100
$[Fe(C_5H_7O_2)(C_4H_4O_2)]^+$	239	45
$[Fe(C_5H_7O_2)]^+$	155	75
$[Fe(C_4H_4O_2)]^+$	140	10
Fe^+	56	5
$[Fe(CH_3)(C_5H_7O_2)]^+$	170	32
$[Fe(CH_3)]^+$	71	15

Metastable Transitions

m/z*		Process	Fragment lost
Observed	Calculated		
182.7	182.76	353 ⟶ 254	$C_5H_7O_2$
224.9	224.89	254 ⟶ 239	CH_3
100.8	100.52	239 ⟶ 155	$C_4H_4O_2$
126.5	126.45	155 ⟶ 140	CH_3
113.6	113.78	254 ⟶ 170	$C_4H_4O_2$
32.5	32.52	155 ⟶ 71	$C_4H_4O_2$

peak at m/z 254 assigned to $[Fe(C_5H_7O_2)_2]^+$. Unlike the molecular ion $[Fe(C_5H_7O_2)_3]^+$, the fragment ion $[Fe(C_5H_7O_2)_2]^+$ loses a CH_3 unit followed by the loss of $C_4H_4O_2$ to produce the $[Fe(C_5H_7O_2)]^+$ ion. The $[Fe(C_5H_7O_2)]^+$ fragment then loses CH_3 and $C_4H_4O_2$ in steps to ultimately produce the bare metal ion Fe^+. The spectral pattern parallels those previously reported[9,10] with the major fragmention pathway being

$$[Fe(C_5H_7O_2)_3]^+ \longrightarrow [Fe(C_5H_7O_2)_2]^+ \longrightarrow$$
$$[Fe(C_5H_7O_2)(C_4H_4O_2)]^+ \longrightarrow [Fe(C_5H_7O_2)]^+ \longrightarrow$$
$$[Fe(C_4H_4O_2)]^+ \longrightarrow Fe^+.$$

In order to obtain support for the above fragmentation pattern, metastable transitions were studies. 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 $[Fe(CH_3)(C_5H_7O_2)]^+$ and $[Fe(CH_3)]^+$ respectively, providing evidence for each methyl migration from carbon to metal presumably favoured by the formation of a new bond between the iron atom and CH_3.

It is evident from the present studies that tris(acetylacetonato) iron(III), $Fe(acac)_3$, can be synthesised directly by the reaction of iron(III) hydroxide

with acetylacetone in the absence of any buffer. The mass spectrum of $Fe(acac)_3$ provides evidence for rearrangement to give Fe —— CH_3 species.

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APPENDIX

List of Publications

1 Synthesis of Alkali Oxytetrafluorovanadates(V)
M.K. Chaudhuri, H.S. Dasgupta, S.K. Ghosh and
D.T. Khathing
Synth. React. Inorg. Met.-Org. Chem., 63, 12, 1982.

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

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
Inorg. Chem., 4020, 21, 1982.

5 Novel Synthesis of Tris(acetylacetonato)iron(III)
M.K. Chaudhuri and S.K. Ghosh
J. Chem. Soc. Dalton Trans., 1983, 893.

6 $[VO(O_2)_2Cl]^{2-}$ — $[V(O_2)_3Cl]^{2-}$ Pair in Peroxo-
vanadium Chemistry: Synthesis of the First Chloro-
peroxyvanadate(V) Compounds and evidence for
Diperoxyvanadate(V) ---Triperoxyvanadate(V) Interconversion
M.K. Chaudhuri and S.K. Ghosh
Inorg. Chem., In press, 1984.

7 Bis(acetylacetonato)fluorovanadate(III), $VF(C_5H_7O_2)_2$
Synthesis of a Novel Neutral Compound of Vanadium(III)
from Vanadium(V)
M.K. Chaudhuri and S.K. Ghosh
Inorg. Chem., In press, 1984.

8 Synthesis of Alkali Diaquofluoro-oxoperoxovanadate(IV)
Complexes $[VO(O_2)F(H_2O)_2]^-$
M. K. Chaudhuri and S. K. Ghosh
J. Chem. Soc. Dalton Trans., In press, 1984.

dates(V) ion $[VOF_4]^-$ 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^o.[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^IVOF_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_2O_5, anhydrous HF and CsF at -30^o. We now describe a novel and simple general method for the synthesis and isolation of A^IVOF_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 $[VOF_4]^-$ 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_2O_5, alkali bifluorides A^IHF_2 and 40% HF leading to the formation of A^IVOF_4 in solution.

$$V_2O_5 + 2\ A^IHF_2 + 4\ HF \longrightarrow 2\ A^IVOF_4 + 3\ H_2O$$

The success in isolation of alkali oxytetrafluorovanadates(V) from the reaction media depends upon the

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$$V_2O_5 + 2\ A^IHF_2 + 4\ HF \longrightarrow 2\ A^IVOF_4 + 3\ H_2O$$

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 $A^{I}VOF_4$ 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 $A^{I}VOF_4$ 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 $A^{I}VOF_4$.

The molar conductance of cesium oxytetrafluorovanadates(V) gave a value of 132 $ohm^{-1}cm^{2}mol^{-1}$ at 27° in purified acetonitrile suggesting an uni-uni valent electrolytic nature of the compound in accord with the formula $CsVOF_4$. This was further supported by the diamagnetic nature of the compounds evidenced from magnetic susceptibility measurements.

The i.r. spectra of alkali oxytetrafluorovanadates(V), $A^{I}VOF_4$, 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 I

I.r. Bands of $A^{I}VOF_4$ Compounds

Compounds	NH_4VOF_4	$KVOF_4$	$RbVOF_4$	$CsVOF_4$
I.r. bands cm^{-1}	262m	261m	262m	260m
	308m	307m	311m	310m
	332s	334s	330s	334s
	480m	482m	483m	481m
	595s	594s	595s	594s
	625s	625s	623s	624s
	710w	712w	712w	712w
	970w	972w	972w	973w
	990vs	980vs	995vs	1015vs
	1015			1025

the occurence of $O_{(p\pi)} \longrightarrow {}_{(d\pi)}V$ bonding. I.r. spectra of the various $A^{I}VOF_4$ compounds are identical and correlate very well with those previously reported for $CsVOF_4$[4] and are also in agreement with the reported crystal structure of $CsVOF_4$[7], which shows $[VOF_4]^-$ to be essentially C_{4v} with weak F-bridging making $[VOF_4]^-$ pseudooctahedral.

^{19}F N.m.r. spectrum of a 1.42(M) solution of the newly synthesised $CsVOF_4$ in 48% HF measured at -85°C shows a broad doublet occuring at 258.4 ppm down field relative to HF with a value of $W_{\frac{1}{2}}$ = 1003 Hz. These agree with the values previously reported[4] for $CsVOF_4$ conforming to the suggestion that a rapid fluorine rearrangement between C_{4v} and C_{2v} stereochemistry of $[VOF_4]^-$ 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, A^IHF_2, were prepared by the method developed in this laboratory[8]. 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 $Co[Hg(SCN)_4]$ as calibrant. ^{19}F N.m.r. Spectra were recorded on a Bruker HX-60/5 instrument.

Preparation of Alkali Oxytetrafluorovanadates(V), A^IVOF_4, (A^I = NH_4, K, Rb or Cs)

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

Stoichiometric quantities of V_2O_5, 40% HF and A^IHF_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 A^IVOF_4 was obtained. Details of the gram amounts of reagents used, yields of various A^IVOF_4 compounds and analytical data are given in the Table II and i.r. have been set out in the Table I.

TABLE II

Amounts of Reagents Used, Yields and Analytical Data of $A^{I}VOF_4$ Compounds

Compound	Amounts of reagents Used		Yield of $A^{I}VOF_4$ gm(%)	Found% (Calcd.%)		
	Reagent	Amount		V	F	A^{I} or N
NH_4VOF_4	V_2O_5	2.00g (11mmol)	1.83 (52)	31.80 (31.64)	47.28 (47.21)	8.21 (8.70)
	40%HF	2.2ml (44mmol)				
	NH_4HF_2	1.26g (22mmol)				
$KVOF_4$	V_2O_5	2.00g (11mmol)	2.44 (61)	28.08 (27.98)	42.05 (41.75)	21.54 (21.48)
	40%HF	2.2ml (44mmol)				
	KHF_2	1.72g (22mmol)				
$RbVOF_4$	V_2O_5	2.00g (11mmol)	2.52 (50)	22.02 (22.30)	33.61 (33.26)	37.88 (37.42)
	40%HF	2.2ml (44mmol)				
	$RbHF_2$	2.74g (22mmol)				
$CsVOF_4$	V_2O_5	1.00g (5.5mmol)	1.76 (58)	18.83 (18.47)	27.61 (27.55)	48.65 (48.18)
	40%HF	1.1ml (22mmol)				
	$CsHF_2$	1.9g (11mmol)				

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SYNTHESIS OF ALKALI OXYDIPEROXYFLUOROVANADATES(V)

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Abstract — The reaction of vanadium pentoxide with hydrogen peroxide in an alkaline medium in the presence of alkali fluorides AF (A = NH_4, Na, K, Rb or Cs) gives alkali oxydiperoxyfluorovanadates(V), $A_2[VO(O_2)_2F]$ 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 peroxyvanadium(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 $Hg[Co(NCS)_4]$ as the calibrant.

Synthesis of alkali oxydiperoxyfluorovanadates(V)

$A_2[VO(O_2)_2F]$ (A = NH_4, 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 microscrystalline 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 $(NH_4)_2[VO(O_2)_2F]$, $Na_2[VO(O_2)_2F]$ and $K_2[VO(O_2)_2F]$ were 1.6g (78%), 1.8g (84%) and 2.1g (84%) respectively.

The $Rb_2[VO(O_2)_2F]$ and $Cs_2[VO(O_2)_2F]$ compounds were prepared in a manner similar to that described above, however, the solution of V_2O_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 $Rb_2[VO(O_2)_2F]$ was 2.6g (74%) and that of $Cs_2[VO(O_2)_2F]$ was 3.5g (77%).

Table 1. Analytical data and structurally significant i.r. bands of $A_2[VO(O_2)_2F]$ (A = NH_4,Na,K,Rb or Cs)

Compound	Analysis[a] (%)				ν/cm^{-1}	Assignments
	A	V	O_A^b	F		
$(NH_4)_2[VO(O_2)_2F]$	14.9[c] (15.06)	27.7 (27.40)	34.2 (34.41)	10.1 (10.22)	970s 870s 885s 472s	ν V-O ν O-O- V-F
$Na_2[VO(O_2)_2F]$	23.6 (23.47)	26.2 (26.01)	32.3 (32.66)	9.5 (9.70)	935s 880s 895s 474s	ν V-O ν O-O- V-F
$K_2[VO(O_2)_2F]$	34.5 (34.29)	22.6 (22.33)	27.5 (28.04)	8.2 (8.33)	965s 870s 890s 470s	ν V-O ν O-O- V-F
$Rb_2[VO(O_2)_2F]$	53.5 (53.28)	16.1 (15.88)	19.7 (19.94)	5.7 (5.92)	970s 885s 895s 472s	ν V-O ν O-O- ν V-F
$Cs_2[VO(O_2)_2F]$	63.7 (63.94)	12.4 (12.25)	15.1 (15.39)	4.6 (4.57)	945s 870s 885s 476s	ν V-O ν O-O- V-F

[a]Calculated values in parentheses, [b]Peroxy oxygen, [c] Analysis for N.

RESULTS AND DISCUSSION

It has long been recognised that vanadium forms yellow diperoxyvanadate(V) in alkaline medium[10] and is converted to red monoperoxy species in acidic solution.[5] The reaction of V_2O_5 with alkali fluoride, AF and hydrogen peroxide in an alkaline medium gave alkali oxydiperoxyfluorovanadates(V), $A_2[VO(O_2)_2F]$ in very high yields. A report on the synthesis of $K_2[VO(O_2)_2F]$ 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 $A_2[VO(O_2)_2F]$ compounds are all yellow coloured microcrystalline products. They are soluble in water with slow decomposition. Estimation of peroxide content[12] showed the presence of two peroxy groups in each of the compounds. This result and the diamagnetic nature of the compounds suggest that the complex ion contains two peroxy groups per vanadium atom and that the vanadium has an oxidation state of +5.

The occurrence of sharp vibrations around 880cm^{-1} (Table 1) in the IR spectra of the compounds imply the presence of triangularly bonded peroxy ligands, and in keeping with this there are two readily identifiable ν(-O-O-) bands at ca 895 and at ca 870 cm^{-1} [cf. the analysis of ν(-O-O-) in transition metal complexes].[13] Another characteristic feature of the spectra is the absorption at 935-970 cm^{-1}, which has been assigned as the ν(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 ν(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]

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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)

compd	% found (% calcd)				IR, cm^{-1}	assignts
	A or N	V	O_A[a]	F		
$(NH_4)_2[V(O_2)_3F]$	13.81 (13.87)	25.22 (25.23)	46.97 (47.54)	9.52 (9.41)	850 (s)	ν_{O-O-}
					475 (s)	ν_{V-F}
					3158 (m)	ν_3
					3040 (s)	ν_1
					1400 (s)	ν_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)	ν_{O-O-}
					470 (s)	ν_{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)	ν_{O-O-}
					470 (s)	ν_{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 ν_{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 ν_{-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 ν_{-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 ν_{V-F} modes arising from the presence of fluoride ion coordinated to the vanadium(V) center. This compares very well with the ν_{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 ν_3, ν_1, and ν_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 ν_{-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 π_{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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Synthesis of Alkali Diaquafluoro-oxoperoxovanadate(IV) Complexes $[VO(O_2)F(H_2O)_2]^-$

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Orange-red alkali metal diaquafluoro-oxoperoxovanadates(IV), $A[VO(O_2)F(H_2O)_2]$ (A = NH_4, K, Rb, or Cs) have been synthesised by the reaction of $A[VOF_4]$ with H_2O_2 in the molar ratio 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.r. and electronic spectroscopic studies and magnetic susceptibility measurements. I.r. spectra suggest that the peroxo-ligand is bonded to the V^{4+} centre in a triangular bidentate fashion.

Studies on various aspects of peroxovanadium chemistry has gained considerable current interest [1-5] probably because of the biochemical significance of peroxovanadium compounds.[2] While most of the recent papers on the topic deal with the solution chemistry of peroxovanadium complexes, synthesis and structural assessment of peroxo- and hetero-ligand peroxo-compounds of vanadium have received much less attention. In a continuation of our studies on the synthesis and structural assessment of hetero-ligand peroxo-compounds of vanadium(V) [6-9] we thought it would be worth while to synthesise hetero-ligand peroxovanadate(IV) compounds. Accordingly, we have now performed the reaction of alkali tetrafluoro-oxovanadates(V), $A[VOF_4]$ (A = NH_4, K, Rb, 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), $A[VO(O_2)F(H_2O)_2]$; these peroxovanadate(IV) compounds were obtained, for the first time, in the solid state.

Experimental

The chemicals used were all reagent grade products. Alkali metal difluorides, AHF_2,[10] required for the preparation of the alkali metal tetrafluoro-oxovanadates(V), $A[VOF_4]$,[11] were synthesised by the methods developed in this laboratory. I.r. spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. Electronic spectral measurements were made on a (Beckman) model UV-26 spectrophotometer. Magnetic susceptibility measurements were made by the Guoy 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*, $A[VO(O_2)F(H_2O)_2]$ (A = NH_4, K, Rb, *or* Cs).—As the methods of synthesis of these complexes are similar, only a representative method is described.

Freshly prepared $A[VOF_4]$ was dissolved in 6% hydrogen peroxide, maintaining the molar ratio $A[VOF_4]$: H_2O_2 at 1 : 12 (pH *ca.* 4), with gentle stirring. The red solution thus obtained was cooled in an ice-bath for *ca.* 20 min. Alcohol was added, in excess, with constant stirring and orange-red microcrystalline $A[VO(O_2)F(H_2O)_2]$ was obtained. The compound was separated by centrifugation and washed several times with ethanol and finally dried *in vacuo* over diphosphorus pentaoxide.

The amounts of reagents and the yields of the compounds $A[VO(O_2)F(H_2O)_2]$ are given in Table 1.

Table 1. Amounts of reagents used and yields of alkali metal diaquafluoro-oxoperoxovanadates(IV)

Compound	Yield/g (%)	Amount of $A[VOF_4]$/g (mmol)	Amount of 6% H_2O_2/cm³ (mmol)
$[NH_4][VO(O_2)F(H_2O)_2]$	0.9 (75)	0.5 (3.1)	22.0 (38.5)
$K[VO(O_2)F(H_2O)_2]$	0.3 (57)	0.5 (2.8)	19.0 (33.5)
$Rb[VO(O_2)F(H_2O)_2]$	0.5 (68)	0.7 (3.1)	22.0 (38.5)
$Cs[VO(O_2)F(H_2O)_2]$	0.5 (69)	0.7 (2.5)	17.0 (30)

Elemental Analysis.—Vanadium estimation was done volumetrically. A solution of the peroxovanadate(IV) compounds, made slightly alkaline with a dilute sodium hydroxide solution, was boiled in order to completely expel the peroxo-oxygen and to convert vanadium(IV) to vanadium(V). The solution was cooled and 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(IV) solution thus obtained was then cooled to *ca.* 80 °C, and titrated with a standard potassium permanganate solution.[12] The peroxide content in each of the compounds was determined by iodometry,[13] and also by titration with a standard Ce^{4+} solution.[14] Fluoride, potassium, and nitrogen were estimated by the methods described in our earlier paper.[9]

The analytical data, i.r. 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 peroxofluoro-compounds of vanadium(V),[6-9] we obtained a red solution containing V^{5+}, AF, and H_2O_2 at a pH *ca.* 4, and presumed that the species responsible for such a colour must be different from those previously isolated by us.[6,9] Further, it was expected that the number of peroxo-groups bonded to vanadium in acidic medium [5,12] would be less than that in alkaline medium, and that H_2O_2 would probably be able to reduce V^{5+} to V^{4+} in acidic medium. In view of the above considerations the reaction between $A[VOF_4]$ and 6% H_2O_2 was carried out and a red solution was obtained. The pH of the solution was found to be *ca.* 4. The peroxovanadium complex species was isolated in the solid state as its alkali metal salts, $A[VO(O_2)F(H_2O)_2]$, by addition of alcohol which

Table 2. Analytical data, magnetic moments, structurally significant i.r. and electronic spectral bands of $A[VO(O_2)F(H_2O)_2]$ (A = NH_4, K, Rb, or Cs)

Compound	$\mu_{eff.}$ [a]/B.M.	Analysis [b] (%) A	V	O [c]	F	I.r. [a] (cm^{-1})	Assignment	Electronic absorption (cm^{-1})	Transition
$[NH_4][VO(O_2)F(H_2O)_2]$	1.73	8.3 [d] (8.15) [d]	30.2 (29.6)	19.3 (18.6)	10.8 (11.05)	955s	ν(V=O)	11 628	$e \longleftarrow b_2$
						890s	ν(O–O)		
						610s	$\nu(V-O_2)$		
						475s	ν(V–F ··· V)	17 699	$b_1 \longleftarrow b_2$
						3 150m,br	ν(O–H)		
						1 625w,br	δ(H–O–H)		
						3 040s	ν(N–H) ν_1		
						1 440s	ν(N–H) ν_4		
$K[VO(O_2)F(H_2O)_2]$	1.75	20.8 (20.25)	25.9 (26.4)	17.1 (16.55)	10.4 (9.85)	950s	ν(V=O)	11 905	$e \longleftarrow b_2$
						880s	ν(O–O)		
						620s	$\nu(V-O_2)$		
						470s	ν(V–F ··· V)	17 699	$b_1 \longleftarrow b_2$
						3 165m,br	ν(O–H)		
						1 620w,br	δ(H–O–H)		
$Rb[VO(O_2)F(H_2O)_2]$	1.70		21.7 (21.25)	13.9 (13.35)	7.6 (7.95)	970s	ν(V=O)		
						880s	ν(O–O)		
						610s	$\nu(V-O_2)$		
						475s	ν(V–F ··· V)		
						3 160m,br	ν(O–H)		
						1 635w,br	δ(H–O–H)		
$Cs[VO(O_2)F(H_2O)_2]$	1.73		18.3 (17.75)	11.8 (11.15)	6.8 (6.6)	965s	ν(V=O)		
						895s	ν(O–O)		
						610s	$\nu(V-O_2)$		
						480s	ν(V–F ··· V)		
						3 150m,br	ν(O–H)		
						1 620w,br	δ(H–O–H)		

[a] Measured at 295 K. [b] Calculated values are in parentheses. [c] Peroxo-oxygen. [d] Analysis for N.

possibly facilitated the reduction of V^{5+} to V^{4+} and precipitation of the complex. The occurrence of reaction between $A[VOF_4]$ and H_2O_2 was ascertained by the appearance of a new band at *ca.* 890 cm^{-1}, due to the ν(O–O) mode of a co-ordinated O_2^{2-}, from a small amount of the sample isolated from the solution. It was previously reported [15] that $K_2[V_2O_3(O_2)_2F_2]$ was isolated from the reaction of V_2O_5, 40% HF, and H_2O_2 at high acidity and $K_2[VO(O_2)_2F]$ was isolated at pH 4. In the present case, however, the reaction of $A[VOF_4]$ with H_2O_2 at pH 4 followed by addition of alcohol afforded compounds of the type $A[VO(O_2)F(H_2O)_2]$.

Characterisation and Assessment of Structure.—The compounds $A[VO(O_2)F(H_2O)_2]$ 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.[8,9,16] The compounds $A[VO(O_2)F(H_2O)_2]$ can, however, be stored in sealed containers and their stability can be ascertained by periodic estimation of the peroxide content. The estimation of peroxide is crucial in order to determine the number of O_2^{2-} ligands bonded to the metal centre. The peroxide content was estimated by cerimetry (Ce^{4+}) and also by iodometry, the results of which conclusively suggest the presence of one O_2^{2-} group co-ordinated to vanadium(IV). The direct titration with a standard $K[MnO_4]$ solution showed the involvement of three electron equivalents, two of which originated from O_2^{2-} and the third was due to the process $V^{4+} \longrightarrow V^{5+} + e$. The magnetic moment values of the compounds (295 K), lying between 1.70 and 1.75 B.M. (1 B.M. $\simeq 9.27 \times 10^{-24}$ J T^{-1}) are consistent with the presence of vanadium(IV) and are in excellent agreement with those reported in the literature for V^{4+} systems.[17]

The optical spectra of $A[VO(O_2)F(H_2O)_2]$ (A = Na or K), recorded immediately after preparing solutions in cold dilute H_2O_2, showed three absorptions at *ca.* 11 700, *ca.* 17 699, and >21 400 cm^{-1}, with the last being obscured by strong charge-transfer transitions. The first two bands have been assigned to $e \longleftarrow b_2$ and $b_1 \longleftarrow b_2$ transitions respectively and agree very well with the reported spectra of oxovanadium(IV) complexes,[18] giving strong evidence for the presence of vanadium(IV) in the orange-red peroxovanadium compounds. Our observations also support the very recent report [6] concerning the existence of peroxovanadium(IV) in solutions.

The i.r. spectra (Table 2) of the series of four salts are similar, showing absorptions at *ca.* 3 160m, br, *ca.* 1 630w, br, *ca.* 960s, *ca.* 890s, *ca.* 615s, and *ca.* 475s cm^{-1}. The band at *ca.* 960 cm^{-1} has been assigned to the ν(V=O) mode of the terminally bonded V=O group,[18] while those at *ca.* 890 and *ca.* 615 cm^{-1} have been assigned to ν(O–O) and $\nu(V-O_2)$ respectively of the co-ordinated peroxide.[8,9,19,20] The absorptions at *ca.* 3 160m, br and *ca.* 1 630w, br cm^{-1} have been attributed to ν(O–H) and δ(H–O–H) modes of co-ordinated water. The lowering of the ν(O–H) frequencies and broadening of δ(H–O–H) bands relative to those of free water suggest the possibility of intramolecular hydrogen bonding.[21,22] The band at *ca.* 475 cm^{-1} is attributed to a V–F stretching mode; its position suggests the presence of bridging rather than terminal F. Since the ν(O–O) and the complementary $\nu(V-O_2)$ fall in the regions expected for the triangularly bonded O_2^{2-} ligands,[8,9,19,20] we infer that the peroxide group is bonded to the V^{5+} centre in a triangular bidentate manner. Two extra vibrations at 3 140 and 1 440 cm^{-1} in the case of the ammonium salt have been attributed to the ν_1 and ν_4 modes of NH_4^+. The ν_3 mode of NH_4^+ could not be identified due to its overlap with the broad ν(O–H) mode of water.

It thus appears that the complex ion has the formula $[VO(O_2)F(H_2O)_2]^-$ containing a triangularly bonded peroxide ligand. The complex species may have a polymeric structure

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through V–F–V bridging; however, the possibility of a weak V–O–V interaction can not be ruled out completely.

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Notes

Novel Synthesis of Tris(acetylacetonato)iron(III)

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The reaction of iron(III) hydroxide with acetylacetone, in the absence of any buffer, readily gives highly crystalline tris(acetylacetonato)iron(III), $[Fe(acac)_3]$, in very high yield. Its mass spectrum provides evidence for rearrangement to give $Fe-CH_3$ species.

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 [1] is extremely slow. The aqueous reaction between iron(III) chloride and acetylacetone in the presence of a large amount of sodium acetate as buffer [2,3] 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)].

$$Fe(OH)_3 + 3\ Hacac \longrightarrow Fe^{3+} + 3\ acac^- + 3H_2O \quad (1)$$

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 $\simeq 1.6 \times 10^{-19}$ 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), $[Fe(C_5H_7O_2)_3]$.—Anhydrous iron(III) chloride (4.0 g, 24.7 mmol) was dissolved in water (6 cm^3) with gentle warming. Ammonia solution (specific gravity 0.880, 9 cm^3, 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 spectrum), 353; C, 51.2. Calc. for $C_{15}H_{21}FeO_6$: *M*, 353; C, 51.05%]. Molar conductance (H_2O): 1 Ω^{-1} cm^2 mol^{-1}. Magnetic moment (295 K): 5.92 B.M. (1 B.M. = 0.927×10^{-23} A m^2) (lit.,[3] 5.90 B.M.).

Results and Discussion

Recently $[Mn(acac)_3]$ was synthesised by the reaction of $[MnO_4]^-$ 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 [2,3] in the synthesis of $[Fe(acac)_3]$ from $FeCl_3$.

The i.r. spectrum of the compound is unambiguous and exhibits the typical pattern of chelated acetylacetonates ($acac^-$) in agreement with those of various $[M(acac)_3]$ [5,6] 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 [8,9] showing the molecular ion at *m/z* 353 (intensity 16%) and the most dominant peak at *m/z* 254 assigned to $[Fe(acac)_2]^+$ with the major fragmentation pathway being $[Fe(C_5H_7O_2)_3]^+ \longrightarrow [Fe(C_5H_7O_2)_2]^+ \longrightarrow [Fe(C_5H_7O_2)(C_4H_4O_2)]^+ \longrightarrow [Fe(C_5H_7O_2)]^+ \longrightarrow [Fe(C_4H_4O_2)]^+ \longrightarrow Fe^+$. 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 $[Fe(CH_3)(C_5H_7O_2)]^+$ and $[Fe(CH_3)]^+$ 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 CH_3.

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Contribution from the Department of Chemistry, North-Eastern Hill University, Shillong 793003, India

$[VO(O_2)_2Cl]^{2-}$–$[V(O_2)_3Cl]^{2-}$ Pair in Peroxyvanadium(V) Chemistry: Synthesis of the First Chloroperoxyvanadate(V) Compounds and Evidence for Diperoxyvanadate(V)–Triperoxyvanadate(V) Interconversion

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Received March 24, 1983

Alkali-metal and ammonium salts of yellow oxydiperoxychlorovanadates(V), $A_2[VO(O_2)_2Cl]$, and blue triperoxychlorovanadates(V), $A_2[V(O_2)_3Cl]$ (A = Na, K, or NH_4) have been synthesized, for the first time, by reacting V_2O_5 with alkali chloride, ACl, and hydrogen peroxide in varying concentrations of alkaline media. The three salts of the anion $[VO(O_2)_2Cl]^{2-}$ are comparatively more stable than those of the complex anion $[V(O_2)_3Cl]^{2-}$. Characterization of the compounds has been made from the results of elemental analyses, magnetic susceptibility measurements, and IR spectroscopic studies. The IR spectra suggest that the peroxy groups are bonded to vanadium(V) in a triangular bidentate manner and that the O–O bond order of peroxy ligands decreases with the increase in the number of peroxy ligands coordinated to the metal center. The conversion of $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$ and the reverse provide good evidence for the facile diperoxyvanadate(V)–triperoxyvanadate(V) interconversion.

Studies of peroxyvanadium chemistry have generated considerable current interest[1-7] probably owing to the special biochemical significance[8,9] of peroxy–transition-metal complexes. Whereas most of the recent reports on peroxyvanadium chemistry deal with the studies in solutions,[2-7] the synthesis and structural assessment of such compounds have received only scant attention. Moreover, only a few heteroligand peroxy complexes of vanadium are known, in contrast to many such reported examples for the other transition metals.[9-11] Our interest in this area involving the synthesis, characterization, structural assessment, and study of the chemistry of peroxyvanadium compounds[12,13] has led to the synthesis of chloroperoxy compounds of vanadium(V). In this paper we wish to report the synthesis of two series of chloroperoxyvanadium(V) compounds, viz., the yellow alkali-metal and ammonium oxydiperoxychlorovanadates(V), $A_2[VO(O_2)_2Cl]$, and the blue alkali-metal and ammonium salts of triperoxychlorovanadate(V), $A_2[V(O_2)_3Cl]$ (A = Na, K, or NH_4), the first chloroperoxy compounds of vanadium. Also reported in this paper are a set of internally consistent data regarding the effect on the ν_{O-O} mode of O_2^{2-} ligands with the increase in the number of such ligands in going from $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$ and the facile interconversion $[VO(O_2)_2Cl]^{2-} \rightleftharpoons [V(O_2)_3Cl]^{2-}$, evidencing the ability of such compounds to undergo a basic formation reaction and an acidic dissociation reaction.

FNT 1–7
FNT 8,9
FNT 9–11
FNT 12,13

Experimental Section

The chemicals used in the present work were all reagent grade products (B.D.H., Merck, or Sarabhai M. Chemicals). Infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer separately in KBr and in Nujol media. Molar conductance measurements were made by using a Philips PR 9500 conductivity bridge. Magnetic susceptibility measurements were made by the Gouy method. The compound $Hg[Co(NCS)_4]$ was the calibrant.

Syntheses of $A_2[VO(O_2)_2Cl]$ (A = Na, K, or NH_4). 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 V_2O_5:AOH was maintained at 1:10, and the resulting mixture was stirred at room temperature for ca. 10 min. Hydrogen peroxide (9% solution) was slowly added to the solution with constant stirring, with the molar ratio of V_2O_5:H_2O_2 rising ultimately to 1:14. 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 microcrystalline $A_2[VO(O_2)_2Cl]$ was obtained. The reaction container was allowed to cooled at ice-bath temperatures for ca. 10 min. The compound was separated by centrifugation, washed several times with ethyl alcohol until it was free from alkali, and finally dried in vacuo over phosphorus pentoxide. The yields of $(NH_4)_2[VO(O_2)_2Cl]$, $Na_2[VO(O_2)_2Cl]$, and $K_2[VO(O_2)_2Cl]$ were 77%, 83%, and 77%, respectively.

Syntheses of $A_2[V(O_2)_3Cl]$ (A = Na, K or NH_4). The blue alka-

TXT06
PAR12
SEN06 6 li-metal and ammonium triperoxychlorovanadates(V), $A_3[V(O_2)_3Cl]$,
SEN09 9 were synthesized in a manner analogous to that described above. The
3 only difference was that the molar ratio V_2O_5:ACl:AOH:H_2O_2 was
SEN12 12 maintained at 1:2:15:14. The reaction was monitored by infrared
SEN15 8 spectroscopy. The disappearance of the sharp band at ca. 950 cm^{-1}
12 owing to $\nu_{V=O}$ in the compound isolated from the reaction medium
SEN18 23 indicated completion of the reaction. The yields of $(NH_4)_2[V(O_2)_3Cl]$,
6 $Na_2[V(O_2)_3Cl]$, and $K_2[V(O_2)_3Cl]$ were 85%, 80%, and 77%, re-
14 spectively.

PAR15
SEN03 1 **Conversion of Oxydiperoxychlorovanadate(V), $[VO(O_2)_2Cl]^{2-}$, to**
SEN06 7 **Triperoxychlorovanadate(V), $[V(O_2)_3Cl]^{2-}$, and Vice Versa.** The in-
8 terconversion reactions were studied with the $Na_2[VO(O_2)_2Cl]$ and
11 $Na_2[V(O_2)_3Cl]$ compounds.

PAR18
SEN03 1 **Conversion of $Na_2[VO(O_2)_2Cl]$ to $Na_2[V(O_2)_3Cl]$.** Sodium oxydi-
SEN06 3 peroxychlorovanadate(V) (0.5 g, 2.4 mmol) was dissolved in a con-
12 centrated solution of sodium hydroxide (2.2 g, 5.5 mmol) followed
22 by immediate addition of 9% hydrogen peroxide (30.0 mL, 79.4 mmol);
SEN09 33 a blue solution was obtained. The solution was cooled at ice-bath
8 temperatures for ca. 15 min, and then an excess of ethyl alcohol was
21 added to precipitate the blue sodium triperoxychlorovanadate(V),
SEN12 28 $Na_2[V(O_2)_3Cl]$. The compound was separated by centrifugation,
6 washed several times with ethyl alcohol, and finally dried in vacuo.

PAR21
SEN03 1 **Reconversion of $Na_2[V(O_2)_3Cl]$ to $Na_2[VO(O_2)_2Cl]$.** A blue solution
SEN06 5 was obtained by dissolving 0.3 g (1.3 mmol) of sodium triperoxy-
15 chlorovanadate(V) in 30 mL (79.4 mmol) of 9% hydrogen peroxide
SEN09 25 containing 3.3 g (83 mmol) of sodium hydroxide. Dilute hydrochloric
4 acid (1 N) was added dropwise until the solution became permanently
SEN12 15 yellow. The solution was cooled at ice-bath temperatures for ca. 20
12 min followed by the addition of an excess of ethyl alcohol to produce
25 the yellow sodium oxydiperoxychlorovanadate(V), $Na_2[VO(O_2)_2Cl]$.
SEN15 1 The compound was isolated and purified in a similar manner to that
14 described above.

PAR24
SEN03 1 **Intercomersion of $Na_2[VO(O_2)_2Cl] \rightleftharpoons Na_2[V(O_2)_3Cl]$** was also
SEN06 9 studied in the following manner. The yellow solution was first prepared
8 by the reaction of V_2O_5 with NaCl, NaOH, and 9% H_2O_2 with the
SEN09 21 molar ratio maintained at 1:2:10:14. Addition of an excess of ethyl
8 alcohol to a part of the solution afforded the yellow sodium oxydi-
SEN12 19 peroxychlorovanadate(V), $Na_2[VO(O_2)_2Cl]$. To the remaining so-
5 lution was added more sodium hydroxide in the form of its concen-
16 trated solution (total molar ratio of V_2O_5:ACl:AOH:H_2O_2 as
SEN15 24 1:2:15.14), and a blue solution was obtained. The blue solution was
6 divided into two parts, and an excess of alcohol was added to one part
20 of it to produce the sodium triperoxychlorovanadate(V), $Na_2[V(O_2)_3Cl]$.
SEN18 27 Dropwise addition of dilute hydrochloric acid (1 N) to the
12 other part of the solution until it turned permanently yellow, followed
23 by the addition of ethyl alcohol, gave the yellow sodium oxydiper-
SEN21 33 oxychlorovanadate(V), $Na_3[VO(O_2)_2Cl]$. Both the basic formation
6 (peroxide, O_2^{2-} uptake) and the acidic dissociation (deperoxygenation)
14 reactions were performed at ice-bath temperatures.

PAR27
SEN03 1 **Elemental Analyses.** Vanadium analysis was done volumetrically,
SEN06 7 after expelling the peroxy oxygen and separating chloride, by titration
17 with a standard potassium permanganate solution was described in
SEN09 26 our previous paper.[13] The peroxide content of the compounds was
9 determined by redox titration with a standard Ce^{4+} solution[14] and
SEN12 19 chloride by Volhard's method.[15] Sodium, potassium, and nitrogen
SEN15 6 were determined by the methods described in our earlier paper.[13] The
3 analytical data and the IR band positions are summarized in Table
14 I.

FXT09
SEN03 1 **Results and Discussion**

PAR30
SEN03 1 **Synthesis.** It has been emphasized in the literature[11] very
SEN06 10 recently that only a few heteroligand peroxyvanadium com-
17 pounds have been known although there have been many such
SEN09 27 examples for other transition metals. It is possible that va-
6 nadium presents a different story owing to the uncertain nature
16 of peroxyvanadium species in solutions of varying pH.[5,16,17]
SEN12 1 An elementary consideration in the course of our studies[12,13]
11 mainly involving the synthesis and structural assessment of
19 peroxyvanadium compounds suggested that hitherto unknown
25 chloroperoxyvanadium compounds could be synthesized under
SEN15 31 suitable conditions. Moreover, we were interested in ascer-
7 taining the minimum number of peroxy groups responsible
15 for the formation of blue peroxyvanadates about which no
24 mention was made in any of the studies made in solutions.[5,16,17]

PAR33
SEN01 1 Because of the very facile oxidation of chloride to chlorine
12 by hydrogen peroxide in the presence of an acidic medium,
22 we thought that an alkaline medium should be conducive to

FNT 14
FNT 15
TBL I (015,14-15)
FNT 16,17

TXT99
PAR33

SEN06 32 the synthesis of chloroperoxyvanadium compounds. In accord
4 with the synthetic strategy, the reactions of V_2O_5 with ACl,
14 AOH, and 9% H_2O_2 in the molar ratios of V_2O_5:ACl:
23 AOH:H_2O_2 of 1:2:10:14 and 1:2:15:14 gave rise to the for-
33 mation of the yellow $[VO(O_2)_2Cl]^{2-}$ and blue $[V(O_2)_3Cl]^{2-}$
SEN09 40 species, respectively. The complex ions were isolated in the
9 solid state as their alkali-metal and ammonium salts by the
SEN12 19 addition of ethyl alcohol. The role of alcohol was to facilitate
SEN15 9 precipitation of the compounds. In the course of our work we
9 observed that the blue color of the vanadium–hydrogen per-
17 oxide system, in the presence of Cl^- ion, was obtained with
28 a relatively lower concentration of the alkaline medium at a
SEN18 38 comparatively higher temperature. However, the higher
5 temperature was not considered favorable for the synthesis of
14 such compounds over an enhanced concentration of alkaline
SEN21 22 medium. The fact that a very high concentration of the al-
11 kaline medium leads to the formation of the triperoxy species
21 $[V(O_2)_3Cl]^{2-}$ while the relatively lower concentration of the
29 alkaline medium produces $[VO(O_2)_2Cl]^{2-}$ suggests that a very
37 high alkaline medium probably helps replacement of the last
44 oxygen from the $[VO(O_2)_2Cl]^{2-}$ by a O_2^{2-} group, thereby
45 favoring the formation of $[V(O_2)_3Cl]^{2-}$, or that the oxo oxygen
45 of the $[VO(O_2)_2Cl]^{2-}$ species is converted to the third peroxy
SEN14 55 ligand by abstracting an oxygen of hydrogen peroxide. It is
4 difficult for us to say, in the absence of any direct evidence,
SEN27 16 which of the two mechanisms is more probable. However, the
4 fact that oxygen exchange on vanadium(V) is very slow[6] and
14 the strength of the V–O multiple bond is high, as evident from
26 the IR spectroscopic studies of oxovanadium(V) complexes,[12,13]
SEN30 33 indicates that the latter mechanism may be more likely. It
3 is, therefore, evident that under the appropriate conditions,
11 the heteroperoxyvanadium(V) compounds of the types A_2-
17 $[VO(O_2)_2Cl]$ and $A_2[V(O_2)_3Cl]$ can be synthesized and that
25 a minimum number of three peroxy groups are required for
SEN33 35 the formation of blue peroxyvanadium compounds. We expect
4 that a similar synthetic strategy can be applied for the synthesis
13 of other heteroperoxyvanadium(V) compounds.

PAR36

SEN03 1 **Characterization and Structural Assessment.** The alkali-
SEN06 3 metal and ammonium oxydiperoxychlorovanadates(V), A_2-
7 $[VO(O_2)_2Cl]$, are yellow microcrystalline compounds, and the
14 similar salts of triperoxychlorovanadates(V), $A_2[V(O_2)_3Cl]$,
SEN09 19 are blue. The salts of the anion $[VO(O_2)_2Cl]^{2-}$ are generally
SEN12 16 more stable than those of the anion $[V(O_2)_3Cl]^{2-}$. A com-
3 parison of the properties of chloroperoxyvanadates(V) with
10 those of the corresponding fluoroperoxyvanadates(V)[12,13] re-
15 veals that the most notable difference that result from changing
25 the hetero ligand from F^- to Cl^- is the fall in stability, with
38 the difference being more pronounced in the cases of hetero-
SEN15 47 triperoxyvanadate(V) compounds. While the alkali-metal and
6 ammonium salts of fluorotriperoxyvanadate(V) are stable for
13 prolonged periods,[12] those of the chloroperoxyvanadate(V) are
SEN18 20 unstable. $A_2[V(O_2)_3Cl]$ ($A = NH_4$ or K) decomposed to a
SEN21 11 yellow microcrystalline product. The decomposition products
5 have not yet been clearly identified; however, they have been
15 found to contain peroxy groups, as evidenced by the results
25 of chemical determination and IR spectroscopy, but definitely
SEN24 33 not to the extent of three peroxy ligands per vanadium. The
3 stability of the compounds was ascertained by periodically
11 estimating their peroxide content and recording their IR
SEN27 19 spectra. The determination of peroxide content of such com-
9 pounds is considered to be crucial in order to decide the
SEN30 20 number of such groups coordinated to the metal center. The
3 peroxide estimation was accomplished by redox titration with
11 a standard cerium(IV) solution,[14] the results of which con-
19 clusively suggested the presence of two peroxy ligands per V^{5+}
29 ion in the yellow compounds and three peroxy groups per V^{5+}
SEN32 40 ion in the blue compounds. The diamagnetic nature of the
7 compounds, as evidenced by their magnetic susceptibility
14 measurements, ensures that the vanadium occurs in its +5
23 oxidation state in each of the newly synthesized compounds.

PAR39

SEN03 1 The IR spectra of the three salts of the yellow $[VO-(O_2)_2Cl]^{2-}$ ion resemble each other very closely (Table I),
12 indicating thereby that the compounds are similar both
21 structurally and stoichiometrically. The absorptions occurring
SEN06 29 in the four characteristic regions, viz. at 955–970, 870–890,
5

FNT 18

TXT09
PAR39

610–615, and 410–415 cm^{-1}, are well precedented in the literature and have been assigned respectively to $\nu_{V=O}$ of the terminally bonded V=O group,[12,18,19] to the ν_{O-O} mode of coordinated peroxy ligands,[17,20] to ν_{V-O_2},[20] and to ν_{V-Cl}.[21] The three extra vibrations at 3160 (m), 3045 (s), and 1400 (s) cm^{-1} in the case of the ammonium salt have been attributed to the ν_3, ν_1, and ν_4 modes of NH_4^+. The spectral pattern is in order and conforms well with the formula $A_2[VO(O_2)_2Cl]$

FNT 19
FNT 20, FNT 21

PAR42

The spectra of the three salts of the $[V(O_2)_3Cl]^{2-}$ anion also resemble each other very strongly, showing absorptions in the regions 855–860, 615–620, and 410–420 cm^{-1}, respectively, owing to the presence of coordinated peroxide and chloride ligands, and the peaks are assigned to the ν_{O-O}, ν_{V-O_2}, and ν_{V-Cl} modes. The three extra modes for the 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 $A_2[V(O_2)_2F]$ compounds,[17] suggesting that both the triperoxychlorovanadates(V) and triperoxyfluorovanadates(V) probably have structural similarity.

PAR45

The ν_{O-O} absorptions in the spectrum of each of the compounds occur in the region stipulated for the presence of triangularly bonded O_2^{2-} ligands,[12,13,20] leading us to conclude that in each of them the peroxy group is bonded to the vanadium(V) center in a triangular bidentate manner. A perusal of the spectra of the two series of compounds revealed that those of $A_2[V(O_2)_3Cl]$ compounds completely lack the absorption at ca. 950 cm^{-1} of $\nu_{V=O}$. This conforms to the formula $A_2[V(O_2)_3Cl]$. The other difference was the shift, though small, in the positions of ν_{O-O} modes to a relatively lower region in the cases of the blue peroxy compounds (Table I). Whereas the ν_{O-O} absorptions for $A_2[VO(O_2)_2Cl]$ compounds lie in the region 870–890 cm^{-1}, those for the $A_2[V(O_2)_3Cl]$ compounds lie in the region 855–860 cm^{-1}. The fall in the ν_{O-O} frequency suggests a decrease in the O–O bond order of the coordinated peroxy ligands with the increase in the number of peroxy groups bound to the vanadium(V) center.

PAR48

Conversion of $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$ and the Reverse. Evidence for Facile Diperoxyvanadate(V)–Triperoxyvanadate(V) Interconversion. Having obtained the yellow oxydiperoxychlorovanadates(V), $A_2[VO(O_2)_2Cl]$, and the blue triperoxychlorovanadates(V), $A_2[V(O_2)_3Cl]$, we thought it would be interesting to study the conversion of $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$ 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) $Na_2[VO(O_2)_2Cl]$ can be easily converted to $Na_2[V(O_2)_3Cl]$, which again can be reconverted to $Na_2[VO(O_2)_2Cl]$. The oxydiperoxychlorovanadate(V)–triperoxychlorovanadate(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 alkaline medium and an excess of hydrogen peroxide, it is the large excess of alkaline medium that favors the formation of the triperoxyvanadium(V) species. The peroxide uptake and the deperoxygenation reactions can be best monitored by IR spectroscopy. The complete conversion of the $[VO(O_2)_2Cl]^{2-}$ species to $[V(O_2)_3Cl]^{2-}$ is ascertained by observing the complete disappearance of the $\nu_{V=O}$ band at ca. 950 cm^{-1} in a small amount of the compound isolated from the solution. The reverse reaction, i.e., the process $[V(O_2)_3Cl]^{2-} \rightarrow [VO(O_2)_2Cl]^{2-}$, was confirmed not only by observing the color change of the solution from blue to yellow but also by noting the appearance of the new band at about 950 cm^{-1} owing to $\nu_{V=O}$ and the shift of the ν_{O-O} absorption toward a relatively higher frequency.

PAR51

It may be concluded that under the conditions described above, the complex species responsible for yellow and blue colors are $[VO(O_2)_2Cl]^{2-}$ and $[V(O_2)_3Cl]^{2-}$, respectively. In each of the compounds the peroxy ligands are bonded in a triangular bidentate manner to the V^{5+} center. The complex species $[VO(O_2)_2Cl]^{2-}$ may be a hexacoordinated monomer or it may as well be a polymer through a weak V–O–V or a

TXT09
PAR51
SEN12 75 weak V–Cl·V bridging. Similarly the complex species $[V(O_2)_3Cl]^{2-}$ may be a heptacoordinated monomer or it may have
6 a polymeric structure through a weak V–Cl–V interaction.
SEN15 1 The $[VO(O_2)_2Cl]^{2-} \rightleftharpoons [V(O_2)_3Cl]^{2-}$ interconversion provides
9 a good example of a process that involves a basic formation
19 reaction and an acidic dissociation reaction of peroxy-
26 vanadium(V) compounds
TXT12
PAR54
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Running Heads

Chloroperoxovanadate(V) Compounds

Chaudhuri and Ghosh

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Table I. Analytical Data and Structurally Significant IR Bands of $A_2[VO(O_2)_2Cl]$ and $A_2[V(O_2)_2Cl]$ (A = Na, K, or NH_4)

compd	% found (% calcd)				IR, cm^{-1}	assignt
	A or N	V	O_A[a]	Cl		
$(NH_4)_2[VO(O_2)_2Cl]$	13.21 (13.84)	24.82 (25.16)	32.13 (31.61)	17.92 (17.51)	970 (s)	ν_{V-O}
					870 (s)	ν_{O-O}
					885 (s)	
					610 (s)	ν_{V-O_2}
					415 (s)	ν_{V-Cl}
					3160 (m)	ν_3
					3045 (s)	ν_1
					1400 (s)	ν_4
$Na_2[VO(O_2)_2Cl]$	22.21 (21.65)	24.34 (23.99)	31.33 (30.14)	16.28 (16.69)	955 (s)	ν_{V-O}
					875 (s)	ν_{O-O}
					885 (s)	
					610 (s)	ν_{V-O_2}
					410 (s)	ν_{V-Cl}
$K_2[VO(O_2)_2Cl]$	31.57 (31.97)	20.21 (20.83)	26.88 (26.17)	14.78 (14.49)	970 (s)	ν_{V-O}
					875 (s)	ν_{O-O}
					890 (s)	
					615 (s)	ν_{V-O_2}
					415 (s)	ν_{V-Cl}
$(NH_4)_2[V(O_2)_2Cl]$	12.43 (12.82)	22.79 (23.32)	44.66 (43.94)	16.72 (16.23)	855 (s)	ν_{O-O}
					620 (s)	ν_{V-O_2}
					410 (s)	ν_{V-Cl}
					3155 (m)	ν_3
					3040 (s)	ν_1
					1400 (s)	ν_4
$Na_2[V(O_2)_2Cl]$	20.92 (20.13)	22.85 (22.31)	42.93 (42.04)	15.22 (15.52)	860 (s)	ν_{O-O}
					615 (s)	ν_{V-O_2}
					420 (s)	ν_{V-Cl}
$K_2[V(O_2)_2Cl]$	30.83 (30.06)	20.31 (19.58)	36.13 (36.90)	13.25 (13.63)	855 (s)	ν_{O-O}
					620 (s)	ν_{V-O_2}
					415 (s)	ν_{V-Cl}

[a] Peroxy oxygen.

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SYNTHESIS OF ALKALI OXYTETRAFLUOROVANADATES(V)

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ABSTRACT

I.R. and ^{19}F N.m.r. spectroscopy, molar conductance, magnetic moments and chemical analyses show that alkali oxytetrafluorovanadates(V), $A^I[VOF_4]$, are the principal products of the reactions of V_2O_5 with 40% HF and alkali bifluorides A^IHF_2 in presence of a small amount of alcohol at steam bath temperature. While the i.r. spectra suggest square pyramidal C_{4v} structures for solid $A^I[VOF_4]$, the ^{19}F N.m.r. spectrum shows stereochemical non-rigidity owing to rapid fluorine rearrangement between C_{4v} and the trigonal bipyramidal C_{2v} stereochemistry of $[VOF_4]^-$ in solution.

INTRODUCTION

Although there is ^{19}F N.m.r. spectroscopic evidence for the existence of the oxytetrafluorovana-