STUDIES ON PEROXO AND HETERO-LIGAND-PEROXO COMPLEXES OF VANADIUM(V) AND FLUORO AND MIXED-LIGAND-FLUORO COMPLEXES OF IRON(III)

ABSTRACT

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

To

THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG
INDIA

DECEMBER, 1987

Studies On
Peroxo and Hetero-Ligand-Peroxo Complexes of Vanadium(V)
And
Fluoro and Mixed-Ligand-Fluoro Complexes of Iron(III)

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The present thesis deals with the results of studies involving syntheses, assessment of structure, and reactivity of some peroxo and heteroligand-peroxo complexes of vanadium(V), as well as synthesis and physico-chemical studies of fluoro and mixed-ligand-fluoro complexes of iron(III). Further, the optimum conditions for oxidation of SCN^- to SO_4^{2-} by hydrogen peroxide are also described in the thesis, as these became necessary in the context of some other work related to the present research. The contents of the thesis has been distributed over six chapters,

Chapter 1 presents a brief introduction pertaining to the work embodied in the thesis. The importance of and the interest in peroxo-metal chemistry in general, and peroxo and hetero-ligand peroxovanadium(V) compounds in particular are highlighted. Also emphasised in this chapter are the lack of information concerning the reactions of highly peroxygenated-metal species with inorganic substrates and the relevance of such studies in the context of contemporary interest involving metal-dioxygen chemistry.

Apart from the importance of studies on peroxovanadium chemistry, attention has also been drawn to the current interest on the study of fluoro-metal compounds together with the difficulties in getting an access to them. As a case in point the problems encountered in the reported synthesis of hexafluoroferrates(III) and also the absence of any reported existance of mixed-ligand-fluoroferrates(III) are stressed herein. Further, the synthetic utility of the reaction of SCN^- oxidation to SO_4^{2-} by hydrogen peroxide is mentioned in Chapter 1. This Chapter also projects the scope of work on the chosen aspects of vanadium and iron chemistry.

Chapter 2 describes the details of the methods of elemental analyses, and instruments/equipment used for characterisation and structural assessment of the newly synthesised compounds.

Chapter 3 of the thesis presents the details of first isolation in the solid state, characterisation, and structural assessment of alkali oxodiperoxovanadate(V) complexes, $A[VO(O_2)_2]$ (A = NH_4, Na or K). This Chapter also provides an account of the results of reactions of vanadium(V) with alkali sulphate or thiocyanate and hydrogen peroxide.

Alkali oxodiperoxovanadates(V), $A[VO(O_2)_2]$ (A = NH_4, Na or K), have been synthesised from the reaction of V_2O_5 with 30% hydrogen peroxide at pH 7-8 maintained by the addition of corresponding alkali hydroxide, AOH, or aqueous ammonia, in the concentration ratio V_2O_5:H_2O_2:AOH as 1:41.8:5.3-6.6.

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Compounds were precipitated with ethanol. $A[VO(O_2)_2]$ compounds were diamagnetic, and their molar conductances in water recorded at ambient temperatures, were found to lie between 130 and 140 $\Omega^{-1}cm^2mol^{-1}$. The results of infrared and laser Raman spectroscopic studies suggest that the complex, $[VO(O_2)_2]^-$ species, contains a terminally bonded V=O group, and that the peroxide (O_2^{2-}) ligands are bonded to the vanadium(V) centre in a triangular bidentate (C_{2v}) manner. The complex ion, $[VO(O_2)_2]^-$ may be a pentaco-ordinated monomer, however, a hexaco-ordinated structure through a weak -V=O....V=O....V=O.... interaction cannot be discounted. As an example of its reactivity, the potassium salt of the complex ion $K[VO(O_2)_2]$, has been shown to undergo facile reaction with KF, and 2,2-bipyridine(bipy) to produce $K_2[VO(O_2)_2F]$, and $K[VO(O_2)_2bipy]$, respectively.

In order to explore the reactions of vanadium(V) with alkali sulphate or thiocyanate in the presence of hydrogen peroxide, V_2O_5 was allowed to react with alkali sulphate or alkali thiocyanate in the molar ratio of $V_2O_5:A_2SO_4$ or ASCN as 1:2 and an excess of hydrogen peroxide ($V_2O_5:H_2O_2::1:32$) at pH 7-8, maintained by the addition of corresponding alkali hydroxide or aqueous ammonia. From the resulting yellow solution, yellow oxodiperoxovanadate(V) complexes containing sulphate were precipitated out by the addition of ethanol. The compounds were characterised by elemental analyses, molar conductance measurements, and IR and laser Raman spectroscopic studies. These results showed that the compounds synthesised were oxodiperoxovanadate(V) complexes containing ionic sulphate (T_d) and could be best formulated as $A[VO(O_2)_2].A_2SO_4$ (A = NH_4, Na or K). The peroxide has been shown to be bonded to the metal centre in a chelated fashion.

Chapter 4 of the thesis describes the first synthesis and structural assessment of hitherto unreported peroxovanadate(V) compounds containing an amino acid, namely glycine(GlyH), as the heteroligand.

The synthesis of alkaliglycineoxodiperoxovanadate(V)-monohydrates, $A[VO(O_2)_2GlyH].H_2O$ (A = NH_4 or K), has been achieved by reacting vanadium pentoxide, V_2O_5, with a hydrogen peroxide solution of glycine at pH 3-4 maintained by the addition of aqueous ammonia or KOH. The molar ratio of V_2O_5:GlyH:H_2O_2 was maintained as 1:2:32. The reaction was carried out an an ice-bath temperature and the precipitation of the compounds were brought about by the addition of ethanol. The yellow glycine-oxodiperoxovanadate(V)monohydrate, $A[VO(O_2)_2GlyH].H_2O$, complexes are hygroscopic in nature. The IR spectra of the compounds exhibit bands characteristic of ν (V=O), ν (O-O), and ν ($V-O_2$) in addition to the absorptions originating from the presence of co-ordinated glycine(GlyH). The amino acid (GlyH) occurs in the compounds in its zwitterionic form and co-ordinates with the metal centre through its carboxylic oxygen atom. The spectra also provide strong evidence for the presence of a triangularly bonded (C_{2v}) peroxide (O_2^{2-}) in each of the complexes. The compounds are diamagnetic in nature in conformity with the presence of vanadium(V)

Reported in Chapter 5 are the first synthesis, isolation in the solid state, and structural assessment of blue alkali-metal triperoxovanadates(V), $A[V(O_2)_3]$ (A = Na or K). Also reported in this Chapter are the results of studies of reactivity of $A[V(O_2)_3].3H_2O$ with $SO_2(g)$.

Blue alkali-metal triperoxovanadate(V) complexes, $A[V(O_2)_3]$ (A = Na or K), have been synthesised from the reactions of vanadium pentoxide with hydrogen peroxide in the presence of concentrated alkaline media, with the molar ratio of $V_2O_5:H_2O_2:$ AOH being maintained as 1:42.5:10-12, followed by precipitation with ethanol. The $A[V(O_2)_3]$ compounds are relatively more stable than the corresponding heteroligand triperoxovanadates(V), and permit molar conductance measurements. The compounds are diamagnetic. The IR and laser Raman spectra suggest that the peroxo ligands are bonded to the vanadium(V) centre in a triangular bidentate (C_{2v}) manner with the structure of the complex, $[V(O_2)_3]$ ion, being similar in the solid state as well as in a solution. The electronic spectra of $A[V(O_2)_3]$ exhibit absorptions at 560 and 192 nm. The compounds are obtained as $A[V(O_2)_3]$ if the final products are dried over P_4O_{10} for a prolonged period, however, they are otherwise obtained as trihydrates, $A[V(O_2)_3].3H_2O$ when they are dried over conc. H_2SO_4.

The reactions of $A[V(O_2)_3].3H_2O$ (A = Na or K) with $SO_2(g)$ were carried out in an aqueous medium. The deep blue $A[V(O_2)_3].3H_2O$ compounds were dissolved in a minimum volume of water and $SO_2(g)$ was bubbled through it. The $A[V(O_2)_3].3H_2O$ reacts readily with

SO_2(g) and first generates a yellow colour which ultimately turns into a permanent green-blue solution. Our endeavour to isolate products at each stage of colour change was successful.

The yellow microcrystalline product, potassium aquooxodiperoxovanadate(V), $K[VO(O_2)_2(H_2O)]$, was thwarted out from the yellow solution, pH of which was ca 6, when $K[V(O_2)_3].3H_2O$ reacted with SO_2(g). The product was characterised by elemental analyses, conductivity measurements, and ESR, IR, and LR spectroscopic studies. The compound was ESR silent suggesting that the metal centre did not undergo any reduction. The molar conductance recorded at ambient temperatures were found to be 130 $\Omega^{-1}cm^2mol^{-1}$. The significant features of IR spectrum of the yellow $K[VO(O_2)_2H_2O]$ compound involve the bands due to co-ordinated peroxide bonded to the vanadium(V) centre in a triangular bidentate fashion, terminally bonded V=O, and co-ordinated water. The results were further augmented by LR spectroscopic studies. Attempts to isolate the sodium salt of yellow $[VO(O_2)_2(H_2O)]^-$ species, from the reaction of corresponding $Na[V(O_2)_3].3H_2O$ with SO_2(g), were futile.

The deep blue $A[V(O_2)_3].3H_2O$ (A = Na or K) reacts with SO_2(g) to generate ultimately a permanent green-blue solution (pH ca 2) from which a blue complex was obtained. The compounds were characterised as salts of triaquobis(sulphato)oxovanadate(IV) complex, $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ (A = Na or K). The molar conductances of the complexes at ambient temperatures were found to lie between 235 and 262 $\Omega^{-1}cm^2mol^{-1}$. The room temperature magnetic moment of the compounds were found to be 1.51 - 1.53 μ_B. The ESR spectra of the compounds in aqueous solution recorded at room temperature and also at 77°K showed signals characteristic of oxovanadium(IV) species. The IR and LR spectra exhibited the characteristic absorptions of co-ordinated SO_4^{2-} ligand, co-ordinated and lattice water, and the V=O stretching. The IR and LR spectral studies further showed the occurrence of SO_4^{2-} ligand bonded to the metal centre in a unidentate (C_{3v}) manner. It is evident from the compounds isolated from the reactions of $A[V(O_2)_3].3H_2O$ with SO_2(g), that it is one of the co-ordinated peroxide groups which participates in an electron transfer reaction preferentially over vanadium(V), which is also otherwise known to undergo ready electron-transfer reaction.

Newer information concerning the reactivity of co-ordinated dioxygen may be anticipated from further studies on similar highly peroxygenated metal systems.

The reactions of $A[V(O_2)_3].3H_2O$ with SO_2(g) conducted in the presence of alkali fluoride, AF, taken in a molar ratio between V:F as 1:2 afforded a novel blue coloured ternary complex vanadate(IV), $A_4[VO(SO_4)_2F_2(H_2O)].2H_2O$ (A = Na or K). The compounds are hygroscopic in nature and soluble in water. The molar conductances of the complexes were recorded to be 510-522 $\Omega^{-1}cm^2mol^-$ The ESR spectra in aqueous solution at room temperature as well as at 77°K exhibit signals characteristic of oxovanadium(IV) species with g_{av} = 1.996. The IR and LR spectra of the compounds, $A_4[VO(SO_4)_2F_2(H_2O)].2H_2O$, resemble those of $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ closely and show absorptions of co-ordinated SO_4^{2-}, co-ordinated

H_2O, and V=O stretching. In addition, the absorption at ca 520 cm^{-1} has been attributed to ν_{M-F} of co-ordinated F^- ligands. The SO_4^{2-} ligands are co-ordinated to the vanadium(IV) centre in a unidentate (C_{3v}) manner. This reaction serves as a paradigm for the synthesis of ternary complexes of vanadyl, VO^{2+}, and may provide an easy access to such compound for further studies.

The direct synthesis of alkali-metal and ammonium hexafluoroferrates(III), A_3FeF_6 (A = NH_4, Na or K), the results of studies concerning optimum conditions for quantitative conversion of SCN^- to SO_4^{2-} through electron-transfer reaction between H_2O_2 and SCN^- along with the scope of this reaction, and a detailed account of the first reported synthesis of fluoro(sulphato)ferrate(III) complexes, $(NH_4)_2[Fe(SO_4)F_3]$ and $K_3[Fe(SO_4)F_4]$, as well as their characterisation and structural assessment form the subject matter of Chapter 6 which is indeed the concluding Chapter of the thesis.

The reaction of iron(III) hydroxide with alkali metal or ammonium fluoride and 48% hydrofluoric acid in the presence of hydrogen peroxide,followed by the addition of ethanol, directly gives alkali metal or ammonium hexafluoroferrates(III), A_3FeF_6 (A = Na, K or NH_4), in very high yields. The compounds were characterised and their identity established from the results of chemical analyses, magnetic susceptibility measurements, and IR and LR spectroscopy.

The optimum conditions for oxidations of SCN^- to SO_4^{2-} by the reaction between SCN^- and H_2O_2 have been determined. Ammonium or potassium thiocyanate and 30% H_2O_2, in the molar ratio of SCN^- to H_2O_2 at 1:8-10 was allowed to react at pH 7-8 to yield quantitatively the corresponding sulphate. While the pH > 8 reduced the yield of A_2SO_4 ($A = NH_4$ or K), the pH < 6 has not been found conducive to the quantitative conversion of SCN^- to SO_4^{2-}. Likewise, the $SCN^-:H_2O_2$ molar ratio 1:6, at a pH 7-8, did not produce SO_4^{2-} in more than 90% yield, and an excess of H_2O_2 ($SCN^-:H_2O_2$ as $1: > 10$) was found to be redundent. The knowledge obtained from the study of this reaction has been of some practical utility in the context of the synthesis of fluoro(sulphato)ferrates(III) complexes.

An investigation of the reaction of ammonium or potassium thiocyanate and 48% HF with iron(III) hydroxide in the presence of hydrogen peroxide has been carried out. Sulphate has been obtained as the oxidation product of SCN^-, without involving reduction of iron(III), and providing an access to fluoro(sulphato)ferrates(III) of the types $(NH_4)_2[Fe(SO_4)F_3]$ and $K_3[Fe(SO_4)F_4]$. Similar reactions with sulphates in lieu of thiocyanates, either in the presence or in the absence of H_2O_2, do not afford fluoro(sulphato)ferrates(III), however.IR and Laser Raman spectroscopy provide evidence for a chelated sulphate in each of the fluoro(sulphato)ferrates(III). The magnetic moment of the compounds were found to be <u>ca</u> 5.7 μ_B.

The results of studies described in Chapters 3 and 6, and a part of the results described in Chapter 5 have been published, while rest of the results incorporated in Chapter 5 and those included in Chapter 4 are now under communication.

Chapter 3

Transition Met. Chem., 1985, 10, 333;

J. Ind. Chem. Soc., 1985, 62, 815.

Chapter 5

Inorg. Chem., 1985, 24, 2706.

Chapter 6

Inorg. Chem., 1986, 25, 3749; *Ind. J. Chem.*, 1985, 24A, 447.

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To

THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG
INDIA

DECEMBER, 1987

Dedicated
To
My Parents

Phone :
Grams : NEHU

North-Eastern Hill University
Bijni Complex
Bhagyakul, Shillong - 793003 (Meghalaya)

Department of Chemistry

Dr.Mihir K.Chaudhuri
Professor of Chemistry

I certify that the thesis entitled "STUDIES ON PEROXO AND HETERO-LIGAND-PEROXO COMPLEXES OF VANADIUM(V) AND FLUORO AND MIXED-LIGAND-FLUORO COMPLEXES OF IRON(III)", submitted by Miss Nashreen S.Islam for the Degree of Doctor of Philosophy of the North-Eastern Hill University, embodies the record of original investigation carried out by her under my supervision. She has been duly registered, and the thesis presented is worthy of being considered for the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

Mihir Kanti Chaudhuri
Signature of the Supervisor

Date: 16 December 1987

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December 16, 1987.

This is to certify that Miss Nashreen S.Islam has satisfactorily completed the following Pre-Ph.D. courses, as prescribed by the University:

1.	Organometallic Chemistry	Chem 620
2.	Solid state Chemistry	Chem 660
3.	Experimental Technique	SPS 630
4.	French Language	SPS 601

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ACKNOWLEDGEMENT

It gives me immense pleasure to place in record my heartfelt gratitude to my research guide, Professor Mihir K. Chaudhuri, Department of Chemistry, North-Eastern Hill University, Shillong for his having taken keen interest in my work and extending inspiration, guidance and constant supervision over all these years of my Ph.D. research.

I wish to thank Dr. M.N. Bhattacharjee for his suggestions and help during the course of my work. My heartfelt thanks go to my colleagues of the laboratory, Dr. S.K. Ghosh, Dr. Z. Hiese, Dr. R.N. Dutta Purkayastha, Mrs. M. Devi, Mr. B. Das, Mr. S. Purkayastha, Mr. M. Bhattacharjee, Mr. C.R. Bhattacharjee, and Mr. P. Paul, and two colleagues of the department, Mr. A. Sinha and Miss G. George for their manifold help and active co-operation over all these years.

It is my pleasant duty to acknowledge with thanks the generous co-operation extended to me by the authorities of the University, the Dean, School of Physical Sciences, the Head of the Department of Chemistry, and the Head, R.S.I.C., for kindly allowing me to use all the facilities required for my research work. I am also thankful to Professor A.L. Verma for allowing me to make use of some of the facilities available in his laboratory. I am very grateful to Professor J. Subramanian and Dr. D.T. Khathing for their interest in our work and their help.

I extend my sincere gratitude to all the faculty members of the Department of Chemistry, NEHU, for their help and good wishes.

Thanks are due to non-teaching staff of the Department of Chemistry and the technical staff of R.S.I.C. for their co-operation during this period of research.

I am thankful to the Department of Atomic Energy, Govt. of India, for financial assistance for an initial period of seven months, and the Council of Scientific and Industrial Research, New Delhi, for awarding me a Junior Research Fellowship and subsequently a Senior Research Fellowship, which enabled me to carry out this research.

I must thank Mr. R. Sadhu for taking pain in efficiently typing out the thesis.

I owe gratitude to my parents whose guidance and inspiration has been an important source for this goal. I am indebted to my sisters and brother-in-laws for their encouragement, enthusiasm, and moral support.

N. S. Islam

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The deep blue $A[V(O_2)_3].3H_2O$ (A = Na or K) reacts with SO_2(g) to generate ultimately a permanent green-blue solution (pH ca 2) from which a blue complex was obtained. The compounds were characterised as salts of triaquobis(sulphato)oxovanadate(IV) complex, $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ (A = Na or K). The molar conductances of the complexes at ambient temperatures were found to lie between 235 and 262 $\Omega^{-1}cm^2mol^{-1}$. The room temperature magnetic moment of the compounds were found to be 1.51 - 1.53 μ_B. The ESR spectra of the compounds in aqueous solution recorded at room temperature and also at 77°K showed signals characteristic of oxovanadium(IV) species. The IR and LR spectra exhibited the characteristic absorptions of co-ordinated SO_4^{2-} ligand, co-ordinated and lattice water, and the V=O stretching. The IR and LR spectral studies further showed the occurrence of SO_4^{2-} ligand bonded to the metal centre in a unidentate (C_{3v}) manner. It is evident from the compounds isolated from the reactions of $A[V(O_2)_3].3H_2O$ with $SO_2(g)$, that it is one of the co-ordinated peroxide groups which participates in an electron transfer reaction preferentially over vanadium(V), which is also otherwise known to undergo ready electron-transfer reaction.

Newer information concerning the reactivity of co-ordinated dioxygen may be anticipated from further studies on similar highly peroxygenated metal systems.

The reactions of $A[V(O_2)_3].3H_2O$ with $SO_2(g)$ conducted in the presence of alkali fluoride, AF, taken in a molar ratio between V:F as 1:2 afforded a novel blue coloured ternary complex vanadate(IV), $A_4[VO(SO_4)_2F_2(H_2O)].2H_2O$ (A = Na or K). The compounds are hygroscopic in nature and soluble in water. The molar conductances of the complexes were recorded to be 510-522 $\Omega^{-1}cm^2mol^{-1}$ The ESR spectra in aqueous solution at room temperature as well as at 77°K exhibit signals characteristic of oxovanadium(IV) species with g_{av} = 1.996. The IR and LR spectra of the compounds, $A_4[VO(SO_4)_2F_2(H_2O)].2H_2O$, resemble those of $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ closely and show absorptions of co-ordinated SO_4^{2-}, co-ordinated

H_2O, and V=O stretching. In addition, the absorption at ca 520 cm^{-1} has been attributed to ν_{M-F} of co-ordinated F^- ligands. The SO_4^{2-} ligands are co-ordinated to the vanadium(IV) centre in a unidentate (C_{3v}) manner. This reaction serves as a paradigm for the synthesis of ternary complexes of vanadyl, VO^{2+}, and may provide an easy access to such compound for further studies.

The direct synthesis of alkali-metal and ammonium hexafluoroferrates(III), A_3FeF_6 (A = NH_4, Na or K), the results of studies concerning optimum conditions for quantitative conversion of SCN^- to SO_4^{2-} through electron-transfer reaction between H_2O_2 and SCN^- along with the scope of this reaction, and a detailed account of the first reported synthesis of fluoro-(sulphato)ferrate(III) complexes, $(NH_4)_2[Fe(SO_4)F_3]$ and $K_3[Fe(SO_4)F_4]$, as well as their characterisation and structural assessment form the subject matter of Chapter 6 which is indeed the concluding Chapter of the thesis.

The reaction of iron(III) hydroxide with alkali metal or ammonium fluoride and 48% hydrofluoric acid in the presence of hydrogen peroxide,followed by the addition of ethanol, directly gives alkali metal or ammonium hexafluoroferrates(III), A_3FeF_6 (A = Na, K or NH_4), in very high yields. The compounds were characterised and their identity established from the results of chemical analyses, magnetic susceptibility measurements, and IR and LR spectroscopy.

The optimum conditions for oxidations of SCN^- to SO_4^{2-} by the reaction between SCN^- and H_2O_2 have been determined. Ammonium or potassium thiocyanate and 30% H_2O_2, in the molar ratio of SCN^- to H_2O_2 at 1:8-10 was allowed to react at pH 7-8 to yield quantitatively the corresponding sulphate. While the pH $>$ 8 reduced the yield of A_2SO_4 ($A = NH_4$ or K), the pH $<$ 6 has not been found conducive to the quantitative conversion of SCN^- to SO_4^{2-}. Likewise, the $SCN^-:H_2O_2$ molar ratio 1:6, at a pH 7-8, did not produce SO_4^{2-} in more than 90% yield, and an excess of H_2O_2 ($SCN^-:H_2O_2$ as 1: $>$ 10) was found to be redundent. The knowledge obtained from the study of this reaction has been of some practical utility in the context of the synthesis of fluoro(sulphato)ferrates(III) complexes.

An investigation of the reaction of ammonium or potassium thiocyanate and 48% HF with iron(III) hydroxide in the presence of hydrogen peroxide has been carried out. Sulphate has been obtained as the oxidation product of SCN^-, without involving reduction of iron(III), and providing an access to fluoro(sulphato)-ferrates(III) of the types $(NH_4)_2[Fe(SO_4)F_3]$ and $K_3[Fe(SO_4)F_4]$. Similar reactions with sulphates in lieu of thiocyanates, either in the presence or in the absence of H_2O_2, do not afford fluoro(sulphato)ferrates(III), however. IR and Laser Raman spectroscopy provide evidence for a chelated sulphate in each of the fluoro(sulphato)ferrates(III). The magnetic moment of the compounds were found to be <u>ca</u> 5.7 μ_B.

The results of studies described in Chapters 3 and 6, and a part of the results described in Chapter 5 have been published, while rest of the results incorporated in Chapter 5 and those included in Chapter 4 are now under communication.

Chapter 3

Transition Met. Chem., 1985, 10, 333;

J. Ind. Chem. Soc., 1985, 62, 815.

Chapter 5

Inorg. Chem., 1985, 24, 2706.

Chapter 6

Inorg. Chem., 1986, 25, 3749; Ind. J. Chem., 1985, 24A, 447.

CHAPTER 1

CHAPTER 1

INTRODUCTION

Vanadium with the outer electronic configuration $3d^34s^2$ belongs to the periodic group VB. Besides its utility as a catalyst in industrial purposes,[1] there is considerable evidence which suggests that vanadium is also an essential element for mammals[2] of an unknown biochemistry.[3-5] Further, it is established that vanadium in moderate levels has a significant impact on the function of enzymes and of biological systems.[3,6,7]

Vanadium can attain a highest oxidation state of +5. 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+} (aq) cation is probably best represented as $[VO(H_2O)_5]^{3+}$, with the oxygen occupying one co-ordination position in the octahedral complex. The VO^{3+} unit is found 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.[8] In addition, however, a number of complexes of the type $VOCl_3.L$, which appears to be five or six co-ordinated monomer have been characterised in which L can be either an oxygen donor or a nitrogen donor ligand.[9,10] Vanadium oxytrichloride also reacts[9] with ligands containing replaceable hydrogen atoms to give substitution products of the type $VO(OMe)_3$, $VOCl_2(OMe)$, $VOCl_2(OEt)$ $VOCl(OEt)_2$, $VOCl_2(acac)$, and $VOCl(acac)_2$ ($acac^-$ = acetylacetonate). The VO^{3+} entity is also very commonly encountered in peroxo-vanadium chemistry[11] and there are some X-ray crystallographic evidences for the occurrence of V=O in the peroxy-vanadate(V) compounds, viz., $(NH_4)[VO(O_2)(C_2O_4)]_2\frac{1}{2}H_2O$,[14] $[VO(O_2)_2C_2O_4]^{3-}$ (Ref.12), $(NH_4)[VO(O_2)_2bipy].4H_2O$,[12] $(NH_4)_2[VO(O_2)(C_4H_5O_4N)]$,[13] in addition to a few published earlier.[15-19] Some other complexes containing VO^{3+} include $VOCl_4^-$, VOF_4^- (Ref. 20-22) and $[VOF_3(H_2O)]$.[23]

The second oxo-vanadium(V) species, the VO_2^+ ion, is not very much characterised, but it is believed to occur discreetly in the complexes, $VO_2(NO_3)$, VO_2F, and $VO_2(SbF_6)$ and as a cis-VO_2 unit in the complexes $K_3[VO_2F_4]$ and $K_3[VO_2(C_2O_4)_2]$.[25]

Vibrational spectroscopy plays an important role in the study of oxo-vanadium compounds. The most characteristic feature of the vibrational spectra of oxovanadium complexes is the occurrence of very strong and sharp bands at 980±50 cm^{-1}. Such bands are assigned to the V=O stretching frequencies[24] and as expected it lies near the upper frequency limit for those complexes which are known, from X-ray work, to have the shortest V-O bonds.

One of the most interesting aspects of vanadium chemistry, which has also engaged the attention of several groups of contemporary researchers, is its peroxo chemistry.[28-38] Peroxo-transition metal complexes in general have received continued attention over several years because of their important roles in biological processes[26,27] as well as in catalytic oxidations.[39-41,44,84,85,87]

It has been known for over a century that characteristic colour reaction may take place when hydrogen peroxide is added to solutions of transition metal derivatives[42,43] and many peroxy transition metal compounds have been isolated in the solid state.[42] Peroxo-metal complexes besides having an intrinsic interest of their own[44-65] constitute an important class of reactive intermediates in catalytic oxidations[40,66] and are involved as potential oxygen donors in the oxygen transfer reactions to organic substrates including hydrocarbons.[40] Also, the research leading to gain an insight into the roles of peroxo-transition metal compounds in the storage and transport of oxygen and oxidase functions in biological systems is of growing interest.[15,26,27,67]

Molecular oxygen functions both as a ligand and as a reagent in transition metal chemistry. Recent interest in the chemistry of molecular oxygen has involved biochemists interested in biological oxygen transport and oxygen function as well as industrial chemists interested in developing homogeneous analogues to heterogeneous metal-catalysed oxidation reactions. The isolation and characterisation of stable dioxygen complexes and the variety of reactions that they themselves undergo arebeginning to yield general information about bonding, structure, and reactivity of co-ordinated molecular oxygen,[44,65]

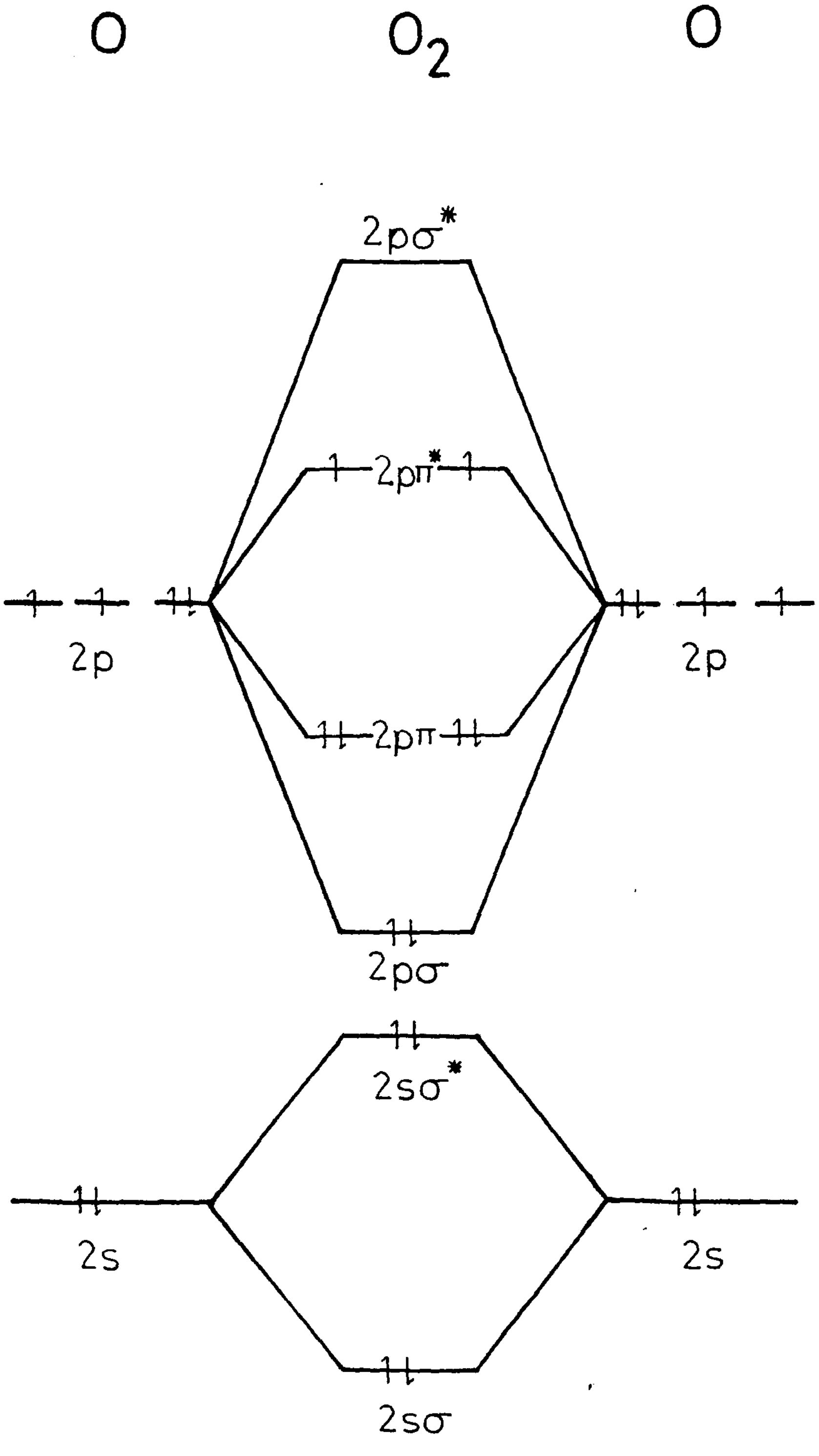


Fig.1 Molecular orbital diagram for O_2

Owing to the importance of molecular oxygen as a reagent in biological and industrial processes and also because dioxygen is an interesting ligand in its own right, current research in this area has been directed towards understanding the bonding of dioxygen to transition metal complexes and the effect of this bonding upon its reactivity towards other substrates, or in other words the extent to which the O-O bond of co-ordinated O_2 is activated.[44]

The bonding in molecular oxygen is best described by MO theory.[69] According to this theory, the valence orbitals of the two oxygen atoms ($2s^2 2p^4$) combine to give molecular orbitals whose relative energies are shown in Fig. 1. The ground state of molecular oxygen is predicted and observed to be a triplet state ($^3\Sigma$) with two unpaired electrons occupying a pair of degenerate π^* antibonding orbitals. The two lowest excited states are formed by redistributing the two electrons in these $2p\pi^*$ orbitals. The configuration and energies for the ground state and first two excited states are shown in Fig. 2.

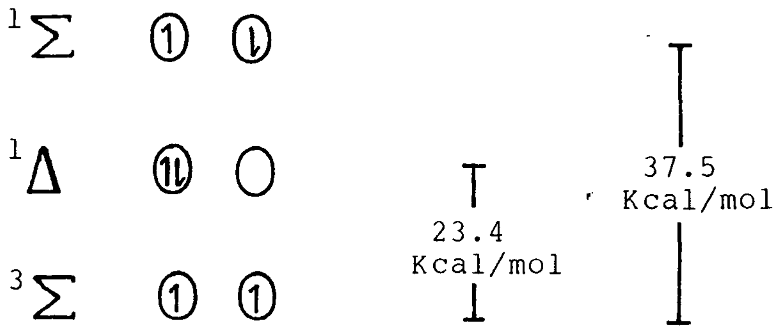


Fig.2 π^* orbital occupancy and energies of the first two electronically excited states of O_2

MO theory also predicts bond orders of 2.5, 2, 1.5, and 1 for the dioxygenyl cation O_2^+, molecular oxygen O_2, superoxide O_2^-, and peroxide O_2^{2-}, respectively. Some of the salient features for O_2^+, O_2, O_2^- and O_2^{2-} are summarised in Table 1-1.

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

	Bond Order	Compound	O-O distance(Å)[70]	Bond Energy[69] (Kcal/mol)	ν (O-O) cm^{-1}
O_2^+	2.5	O_2PtF_6	1.12	-	1905[70]
O_2	2	O_2	1.207	117.2	1554.7[71]
O_2^-	1.5	KO_2	1.28	-	1145[72]
O_2^{2-}	1	Na_2O_2	1.49	35	842[73]

Although the term molecular oxygen refers only to the free unco-ordinated O_2 molecule with the ground state configuration $^3\Sigma_g$, the term dioxygen has been used as a generic designation for O_2 moiety in any of its several forms and can be refered to O_2 in either a free or combined state.[74] 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 co-ordinated to the metal centre, and no distinction is made between neutral dioxygen in any of its reduced forms. According to the rationalisation made by Vaska,[74] transition metal peroxide involve co-valently bound dioxygen resembling O_2^{2-} in peroxo configuration. A common characteristic of these complexes is the O-O distance, which occurs between 1.4 and 1.52Å (1.49 for O_2^{2-}), and the corresponding infrared frequency ν (O-O) which lies between 800 and 950 cm^{-1} (802 cm^{-1} for O_2^{2-}). 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 co-ordinated peroxo groups and one or more monodentate or polydentate ligands. Heteroligands may range from monodentate ions to bulky porphyrins[27] (F^-,Cl^-,NH_3,$C_2O_4{}^{2-}$,$SO_4{}^{2-}$,$CO_3{}^{2-}$,NTA,EDTA,bipy,o-phen, oxine, porphyrins, pyridine-2, 6-dicarboxylic acid etc).

The stability of peroxo complexes is generally enhanced by specific heteroligand combinations. Many simple 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[42] but many heteroligand peroxo complexes, on the other hand, survive recrystallisation from boiling aqueous solutions, heating <u>in vacuo</u>, and remain unchanged for prolong periods in closed containers.[75] The biochemical significance of peroxo metal complexes has been emphasised in recent literatures.[26,27,30,48] The reactivity of peroxides[64,76-81,85,87] and the lability of metal-oxygen bonds in special heteroligand environments in solutions are of particular interest to biochemistry although not easy to measure directly.

A comparison between the peroxo and unreduced dioxygen heteroligand complexes reflects that the chemistry of the two is very different owing to the presence of two extra electrons in the antibonding O-pπ^* orbitals of the peroxide ion.[27] The electron rich O_2^{2-} ion therefore preferably forms complexes with metal ion of low d^n including d^o, and also f^o electronic configurations, while the neutral dioxygen molecule favours higher d^n metal acceptors. However, there are at least two things that these oxygen species have in common, viz., both are stabilised by specific heteroligand spheres and both are of importance in biochemistry.

The way in which peroxo group is expected to co-ordinate to metals can range from symmetrical bidentate to a terminal monodentate position, including all the possible angles in between them. The structural classification of dioxygen complexes, rationalised by Vaska[74] can be represented as shown in Fig. 3. The bridging peroxo could vary from cis-planar and trans-planar to trans-nonplanar configuration. An unusual symmetrical double bridging was also found,[82,83] however, such complexes are very rare. Deviations from the ideal symmetry are also observed very often. In the cases of heteroligand fields they are due to the inherent symmetry of different donor atoms. Additional pπ^* electron delocalisation to the metal ion is anticipated, which could therefore favour d^o/f^o or low d^n metal ion configuration. The stereochemical polyhedra in heteroligand peroxo complexes are often fairly predictable. In oxoperoxo heteroligand surroun-

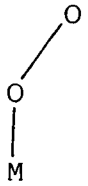
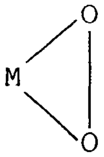
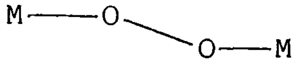
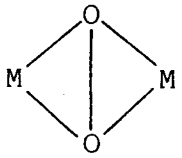
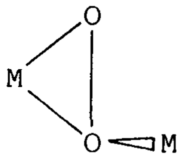
Structural type	Structural designation	Vaska Classification
	η^2 dioxygen	Type a (superoxo)
	η^2 dioxygen	Type IIa (peroxo)
	η^1: η^1 dioxygen	Type Ib (superoxo)
	η^1: η^1 dioxygen	Type IIb (peroxo)
	η^2: η^2 dioxygen	-
	η^1: η^2 dioxygen	-

Fig.3. Structural Classification of dioxygen complexes

ding, the pentagonal bypiramidal arrangement is most common[12,13] for transition metal complexes, usually with two co-ordinated peroxo groups in cis position. There is also an interesting non-octahedral example of co-ordination number 6 for a peroxy-vanadium complex.[19]

Infrared spectra are essential for the characterisation of complexes containing peroxo groups. For, a bidentate peroxide, regarded as a C_{2v} unit, three IR active modes are expected,[25] the peroxo stretching (A_1) and symmetric and asymmetric $M-O_2$ stretching A_1 and B_2. The ν (O-O) band is the most sensitive and intense one and characteristically occurs between 800 and 950 cm^{-1}, but generally observed below 900 cm^{-1}. The frequency of this band remains fairly independent of the heteroligand environment but is effected by the mass of the central metal ion, indicating some degree of coupling of the ν (O-O) with $M-O_2$ vibrations. Although, peroxide may bind metal centres in different manners as mentioned earlier in this Chapter, the most familiar way of bonding of O_2^{2-} groups is a triangular bidentate manner which is similar to the one proposed by Griffith[86] for the bonding of O_2 in oxyheamoglobin, and the ν (O-O) values, which are similar to that observed for O_2^{2-} ions. While the importance of infrared spectroscopy in this field has been emphasised, the usefulness of Raman spectroscopy should not be underestimated. All the three IR active modes as mentioned above are also Raman active. Thus the results of Raman spectral studies not only complement the IR results but also augment them. Moreover, Raman spectroscopy can also be easily applied to solutions, and the results of which provide further information concerning identity and structure of a complex species in solutions.

The importance of neutral dioxygen complexes in biochemistry is well known,[26] but the biochemical connection of the metal peroxy complexes with biological processes is not very well understood. The metals, Sc, Ti, V, Cr, Y, Zr, Nb, Mo, La, Hf, Ta, W,[27] and U[88] form stable heteroligand peroxy complexes and there is increasing evidence that vanadium has a significant biological role.[2,6,89-91] It is reasonable to assume that the participation of vanadium will depend upon parameters such as pH, and the availability of inorganic or organic species that can act as heteroligands.

The behaviour of vanadium(V) in hydrogen peroxide solution is not analogous to its congeners niobium(V) and tantalum(V) under similar conditions. Unlike niobium and tantalum, vanadium has a strong tendency to form oxoperoxo species. Oxodiperoxovanadate complexes have been reported previously[25,28,42] and by composition they correspond to some chromium(VI), molybdenum(VI) and tungsten(VI) peroxo complexes which exhibit co-ordination number of 6 or 7.[28] Heteroligand complexes of niobium and tantalum are rather easily formed and they commonly exhibit eight co-ordination with a dodecahedral co-ordination polyhedron.[28,92] Although, some information concerning peroxo, oxoperoxo and heteroligand peroxo complexes of vanadium(V) are now available,[36,42,102] nevertheless some fundamental aspects of peroxo-vanadium chemistry still seem to be unattended to.

Vanadium-hydrogen peroxide system appears to be complicated owing to the formation of a number of different complexes with a small change of pH of the reaction solutions.[32,42,93] The addition of aqueous H_2O_2 to (i) V_2O_5,[97] (ii) an acid solution of a metavanadate[98], (iii) a vanadium(V) salt in a weakly acid solution,[99] (iv) or a decavanadate[100] produces in each case a red colour which was believed to be due to the formation of a monomeric monooxoperoxovanadate(V) cation $[VO(O_2)]^+$. The red colour thus obtained is stable in moderately acid media. However, very recently it has been shown that red colouration of the vanadium-hydrogen peroxide system owes its origin to the formation of a peroxovanadate(IV) complex.[34,101] In an excess of H_2O_2 the red species is converted to the yellow oxodiperoxovanadate(V) anion[99,100] $[VO(O_2)_2]^-$.

The yellow colour produced by the addition of aqueous hydrogen peroxide to a dilute solution of a metavanadate was shown to be due to a diperoxo anion by cryoscopy[95] as well as by thermochemical studies[96] more than a few decades ago. There was, however, some controversy as to how the anion should be formulated although the results of cryoscopic and photometric studies were interpreted in terms of the anion $[VO(O_2)_2]^-$. Various attempts made in the past to ascertain the existance of this species through isolation in the solid state were unsuccessful thereby leaving some doubt regarding its actual composition. Therefore it was considered quite imperative to synthesise this species in solid state and to ascertain its composition.

The reaction of concentrated alkali hydroxide with a concentrated solution of vanadium pentoxide (V_2O_5) in aqueous hydrogen peroxide at low temperature (0° or below 0°C) gives a deep blue solution owing to the formation of tetraperoxy vanadate(V) species,[42] $[V(O_2)_4]^{3-}$. The salts of the complex $[V(O_2)_4]^{3-}$ ion were obtained by the addition of ethanol to such a solution. The salts are stable only at low temperatures, and their stability decreases with increasing cation size.[42] The potassium salt, $K_3[V(O_2)_4]$, which is isomorphous with $K_3[Cr(O_2)_4]$,[94] presumably having a dodecahedral structure, has a magnetic moment of 0.6 μ_B, consistent with the presence of vanadium(V). Albeit the tetraperoxovanadate(V) species is evidently a blue complex, it was not known until recently as to what is the minimum number of O_2^{2-} bonded to vanadium(V) centre, required for the formation of the blue colouration of vanadium —— H_2O_2 systems leaving some fundamental questions unanswered.

The notable point[42] emerged out of the earlier studies include the following:

(i) The number of peroxy groups per vanadium atom increases with alkalinty.

(ii) Increasing acidity increases polymerisation and decreases the peroxy groups per vanadium atom.

(iii) Increasing concentration of H_2O_2 decreases the degree of polymerisation.

Studies involving vanadium peroxo complexes are of special interest because the actual function of vanadium in living cell is unknown.[2] From the biochemical point of view, the most interesting aspect of peroxy-vanadium chemistry remains the experimental approach to measuring the reactivity of the co-ordinated peroxo group in an environment of various heteroligand fields. An essential factor in the biochemical activity of peroxo-heteroligand vanadates is the heteroligand.[27] Recently, a few peroxo-vanadates of the type, $M_4[O(VO(O_2)_2)_2]$, $M^1_3[VO(O_2)_2C_2O_4]$ and $M^1[VO(O_2)L]$ (L = malate, citrate, iminodiacetate, nitrilotriacetate and EDTA), have been tested for toxicity and antitumour activity and such activity of peroxovanadates(V) has been shown to depend upon the type of heteroligand present.[102] Peroxo-heteroligand vanadates(V) behave differently from analogous non-peroxo complexes. The heteroligands determine the biological activity of these complexes, presumably because it can shift the V(V)/V(IV) redox potential ($E^\circ_{298} = 1.00V$) towards the point where an intramolecular electron-transfer could occur within the [V(V)-peroxo] moiety. Such a process reduces vanadium(V) to vanadium(IV) and oxidises peroxo group to superoxide radical. Consequent upon this bonds to co-ordinated dioxygen ligand weaken, and superoxide ion generated in the process could trigger further biological events.[102] This is further supported by the fact that peroxo heteroligand complexes of niobium(V) and tantalum(V) do not exhibit analogous bio-activity[102] because the metal ion does not allow intramolecular electron transfer probably due to unfavourable M(V)/M(IV) redox potential. These observations cause one to infer that the

[V(V)-peroxo] moiety is unique. It has also been suggested that the tendency of vanadium(V) to form stable heteroligand complexes could be extended to vanadium chemistry in the cell or membranes where complexes of this type may form wherever vanadium happens to accumulate.[102] Apart from their biological activity peroxovanadium compounds, like some other similar compounds of transition metals play a significant role in catalytic oxidation reactions.[15] It has been reported, from the results of limited studies, that they are highly active and stereoselective in the oxidation of various organic substrates.[15] In a very recent report Mimoun et. al. have given a good account of the synthesis of oxo-[N-(2-oxodiphenyl)salicylidenaminato]vanadium(V) alkyl peroxides, their use in the selective epoxidation of olefines, and discussed the results in relation to the mechanism of Halcon epoxidation process.[84] However, much remains yet to be explored.

In view of the importance of heteroligand peroxovanadates, in biochemistry as well as in catalysis, it appeared that, suitably chosen heteroligands may give rise to peroxo-vanadium complexes which are of interest in biochemistry. Amino acids are the alphabet of protein structure and determine many of the important properties of proteins. The increasing interest in metal-amino acid systems is attributed to their potentials as models for understanding biologically important molecules. To us it appears that peroxo-amino acid complexes of vanadium(V) will be of interest because they would contain three biological important components: peroxo group, α-amino acid and vanadium(V). Besides, possibility of their exhibiting catalytic properties cannot be ruled out. According to a recent report[103] some attempts to synthesise peroxo-amino acid complexes of vanadium(V) were unsuccessful. We, however, considered it worthwhile to reinvestigate this aspect of vanadium chemistry and to work out appropriate experimental conditions leading to the synthesis of heteroligand peroxo-vanadium(V) compound containing an amino acid.

Added to all that have been mentioned so far regarding the peroxo-vanadium chemistry, there remains another important point which deserves a due consideration. This addresses to the nature and mode of bonding of SO_4^{2-} with oxodiperoxovanadate(V) in the complex species formed in the reaction of vanadium(V) with hydrogen peroxide in the presence of SO_4^{2-}. This reaction is of considerable practical importance in the context of spectrophotometric determination of vanadium.

It may be infered from the above non-exhaustive discussion, that the chemistry of peroxovanadates(V) in general embraces a fascinating, rewarding and worthwhile area of investigation. Also it is evident that the synthesis and structural assessment of well defined peroxovanadate(V) complexes are above all prerequisites following which other aspects can be developed in this field of chemistry.

Accordingly, such studies were undertaken as a major part of the present Ph.D. programme. Following selective aspects of peroxovanadium(V) chemistry have been identified for the present research:

(i) isolation in the solid state of oxodiperoxovanadate(V) complexes, $A[VO(O_2)_2]$ (A = alkali metal or NH_4);

(ii) reactions of vanadium(V) with alkali sulphate or thiocyanate and hydrogen peroxide;

(iii) synthesis and characterisation of heteroligand-oxodiperoxovanadate(V) complexes containing an amino acid (e.g. glycine(GlyH) as the heteroligand; and

(iv) synthesis and structural assessment of alkali triperoxovanadates(V) and studies of their reactivity.

Chapter 3 of the present thesis describes the first isolation in the solid state of the yellow complex, $[VO(O_2)_2]^-$, its characterisation and structural assessment. Two reactions highlighting the scope for the use of the compounds in synthesis are also included. Also reported in this Chapter are the results of the studies involving the reactions of vanadium(V) and H_2O_2 in the presence of SO_4^{2-} or SCN^-.

Chapter 4 presents the synthesis, characterisation and structural assessment of peroxo complexes of vanadium(V) having amino acid (e.g. glycine) as a heteroligand.

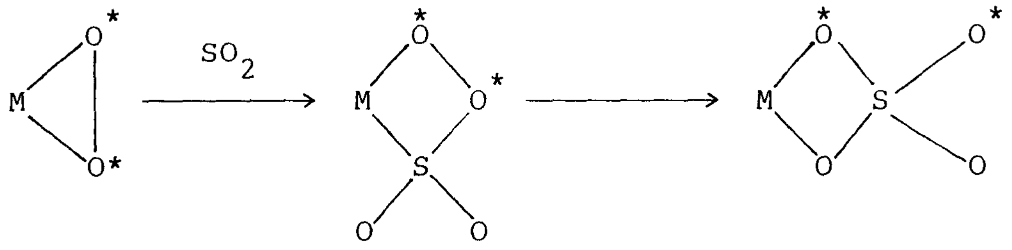
Studies of reactivity of a co-ordinated dioxygen of low valent transition metal compounds have received considerable attention in the recent years.[44,74,104,105,121] The nature of metal-dioxygen bonding was the subject of several theoretical studies[106-109] as well. The various studies indicate that the reactivity of dioxygen increases upon co-ordination for which three possible explanations were advanced.[44]

(i) Co-ordinated dioxygen (Type IIa) is in general diamagnetic; therefore reactions with diamagnetic substrates to form diamagnetic products are not hindered by the requirement for spin conservation.

(ii) The metal may hold dioxygen and the substrate in cis positions, lowering the activation energy for oxidation of the substrate.

(iii) Co-ordinated dioxygen is, in most cases, partially reduced since a considerable charge is transfered to the O_2 ligand and increased electron density on the O_2 may activate it.

Information concerning the reactivity of O_2 bonded to metals has relevance in understanding the processes involved in the activation of molecular oxygen by metallo-enzymes in biological systems. The reactivity of low valent, group VIII transition metal complexes with respect to their ability to oxidise organic and inorganic substrates, viz., olefines,[104,110-112] acetylenes,[104] carbonyls,[113,114] CO_2,[114,115] SO_2,[64,116-120] NO[119,120] etc. have been studied to a certain extent, in recent years. As a case in point, for example, it is evident from the literature, that in most cases co-ordinated dioxygen behaves as a nucleophile and reaction of SO_2 with such complexes leads to the corresponding sulphato complexes, which is generated from the insertion of SO_2 into a $M-O_2$ bond as evidenced by the isotopic IR study.[44,117] This has been further supported by theoretical studies based on MO theory.[109]



However, the the best of our knowledge, no work, except for the one involving a peroxo-titanium[64] compounds, has been reported on the reactions of SO_2 with non group VIII transition metal peroxo compounds, leaving curiosity regarding the course of such reactions under similar conditions, and the nature of the products obtained thereof. Moreover, it is relevant to mention that none of the earlier investigations relating to SO_2 reactions with peroxo-metal compounds seem to have involved compounds containing more than one peroxo group per metal centre thereby leaving some questions unanswered in this context.

In view of the above, it was considered imperative to study the reaction between inorganic polar species, SO_2, with higher valent vanadium compounds containing more than one peroxo groups. The results of which might enable one to rationalise the reaction sequence of the peroxo groups in the parent compounds. An additional interest adhered to this was to find out whether the co-ordinated peroxide or the high valent metal centre would react with SO_2 in preference over the other particularly when both are susceptible to attack by SO_2. Such studies may also provide an access to synthesis of newer ternary compounds of vanadium when carried out in presence of suitable ligands.

In line with the contention such a study was undertaken as a part of the whole programme. Alkali-metal triperoxovanadates(V), $A[V(O_2)_3].3H_2O$ (A = Na or K), have been synthesised and their structural assessment made, thereby enabling us to ascertain the minimum number of peroxide groups necessary for the formation of blue peroxovanadates(V). Making use of alkali-metal triperoxovanadates(V) as the precursors, reactions of SO_2(g) in an aqueous medium were carried out. In addition, similar reactions were also conducted in the presence of F^- leading to the synthesis of newer ternary complexes of vanadium(IV).

A detailed account of the synthesis, structural assessment and the reactivity of alkali triperoxovanadates(V) constitutes the subject matter of Chapter 5.

Quite apart from the vanadium chemistry, research involving chemistry of fluoro-containing transition metal compounds appears to be one of the areas of contemporary interest.[122-139] Interest in this field of chemistry seem to be never diminishing. Studies of the fluoro-compounds of different metals are interesting not only for the sake of science but also for use in practice. Inorganic fluoro compounds are successfully used in optical instrument making, laser technology, microelectronics, in the production of pure metals by thermal reduction, in the manufacture of electrochemical cells with solid electrolytes and in some other fields of technology.[140] Quite exciting is also to draw attention to a recent development in the history of fluorine chemistry is the chemical synthesis of elemental fluorine (F_2) from a fluoro complex of transition metal.[139] However, over and above the utility of metal-fluorides in various fields of science and technology, fluoride ions are also subjected to much controversy. "Fluoride ions, despite their similarity to the biologically ubiquitous chloride ions, and the necessary role that they play in various biological systems, are also blamed by some, for several biologically harmful processes, including cancer".[141,142]

Three main factors mostly explain why the chemistry of fluorine is different from that of other halogens.[143] These are:

(i) the low dissociation energy of the fluorine molecule [$D(F_2) = 37.7$ Kcal/mol];

(ii) relatively high strength of bonds formed between fluorine and metallic or non-metallic elements; and

(iii) the relatively small ionic size of the fluorine atom and the fluoride ion.

With most transition metals a variety of stoichiometries are possible, leading to a versatility of structures and physical properties. Metal fluorides are generally well behaved, with structure depending largely on stereochemical factors. Further, as a result of high electronegativity of the fluoride ion, metal-fluoro complexes are generally insulators or large band gap semiconductors. The lack of electron delocalisation leads to a certain simplicity in the interpretation of physical properties such as magnetism, and in consequence metal fluorides have often been studied as model systems.[144]

The ready dissociation of fluorine into atom is at the root of its high reactivity. The overall energy release in the formation of a fluoride is considerably greater than the other halides.[143] The fundamental properties of fluorine, viz., its extreme electronegativity and small ionic size render it suitable for stabilising higher oxidation states of metals, and knowledge on fluoro-compounds of transition metals has been increasing considerably,mainly because fluorine itself has ceased to be a laboratory curiosity as a result of simplification of its preparation and purification. New materials and improved techniques have made newer synthetic methods very effective.[122,127,146-152] Although much of the very recent activity in this area of fluoro-metal chemistry is devoted to studies related to kinetics[153] and magnetic properties,[154-157] a great deal of effort is still required for the search for direct, and easier to manipulate,synthetic procedures for the synthesis of novel fluoro and mixed-fluoro species,

Success has been achieved by other workers in the laboratory where the present work has been carried out in searching out simple and direct methods for the synthesis of fluoronickelates(II),[151,158] fluoromanganates(III),[122,127] and mixed fluoromanganates(III),[135,149] fluoro and mixed fluorocobaltates(II)[159] and also their structural assessment have been made. However, such aspects of iron chemistry were unattended to. As a sequel of studies on fluoro and mixed-fluoro complexes of transition metals, and fluoro compounds of non-metals, viz., boron,[162] phosphorus[160,161] etc. as a part of a general programme of the laboratory, it was considered worthwhile to undertake such studies on iron so that the information obtained thereof would enrich the existing wealth of knowledge of fluoro metalate chemistry.

It is known that iron is the first row group VIII transition metal, fourth most abundant element in the earth's crust, occurring to the extent of ~ 5.1%.[163] Besides its various utilities in industrial purposes, iron is by far the most widespread and important transition metal also with intrinsic functional role in living systems.[164] Iron containing proteins participate in two main processes: oxygen transport and electron-transfer. Iron ~~ins~~ in the animal body is present as heme proteins which include heamoglobin in the blood, myoglobin and the heme enzymes, and in non-heme proteins as transferrin, ferritin, and hemosiderin. Iron also occurs in conjunction with molybdenum in enzymes that catalyse nitrogen fixation.[165]

The metal has the ground state electronic configuration $[Ar]3d^6 4s^2$ which can attain oxidation states ranging from -2 to +6. The lower oxidation states are generally found in the carbonyl, nitrosyl and organometallic derivatives of iron.[166] Rather surprisingly the higher oxidation states of iron Fe(IV) d^4, Fe(V) d^3 occur when iron is in combination with oxygen but generally not with fluorine.[167]

In aqueous solution, the principally occurring oxidation states of iron are +2 and +3. These two states of iron are the two important and relatively more studied oxidation states of the metal. Iron in its +3 state forms a large number of complexes, mostly octahedral ones, and the octahedron may be considered its characteristic co-ordination polyhedron.[171] Iron (III) also forms complexes with co-ordination number ranging from 3 to 8 with various geometries.

The metal in its +3 oxidation state has the free ion electronic configuration in the ground state of $3d^5$. Most of the iron(III) complexes are high spin and in high-spin complexes (S = 5/2) this gives rise to ^6S free ion ground term. Since this is the only sextuplet term arising from d^5 and since this is not split in a crystal field all the terms of higher energy are of a different spin multiplicity to the ground term. All the electronic transitions are thus spin forbidden so that the ligand field bands in the spectra of these complexes are very weak. The magnetic properties of high spin iron(III) complexes of cubic symmetry are fairly straightforward. As the ground term is $^6A_1$, the magnetic moments are expected to be close to the spin only value of 5.92 μ_B and to be independent of temperature and this is found to be the case experimentally for magnetically dilute complexes.[168]

It has been established that like some other transition metals iron(III) also forms binary fluoro complexes. The affinity of iron(III) for F^- is quite high as shown by equilibrium constants,[169] which may also be accounted for by the hard acid hard base concept.[170] Three principal types of binary fluoro complexes have been reported, viz., $M^1_3FeF_6$, $M^1_2FeF_5.H_2O$, and M^1FeF_4.[172] Typical members of the series are $NH_4[FeF_4]$, $(NH_4)_2[FeF_5]$, $(NH_4)_3[FeF_6]$. The corresponding salts of the alkali metals and certain of the heavy metals, e.g. Tl, Co, Ni are also known.[145] In some cases salts of these types form hydrate, but in others water molecules make up part of the complex, e.g. $Ag_2[FeF_5.H_2O].2H_2O$, $Tl_2[FeF_5.H_2O].2H_2O$.[145] Also the pentafluoroferrates(III) have shown very interesting magnetic properties.[154] The ready formation of stable fluoroferrate complexes has important applications in analytical chemistry.[145] If a solution containing fluoride ions is added to a solution containing a coloured ferric compound such as ferric thiocyanate the colour of the latter decreases in intensity owing to the formation of the stable $[FeF_6]^{3-}$ ion. In addition the position of the absorption bands is shifted to shorter wavelengths and are broadened. The decrease in colour intensity is proportional to the fluoride concentration and this bleaching effect forms the basis of a colorimetric method for the determination of fluoride.[145]

In the context of synthesis of the fluoro-compounds of iron(III), the tetrafluoroferrates(III) are obtained from aqueous hydrofluoric acid solutions by using 1:1 mole ratios of the univalent cation and iron(III) fluoride.[172] The pentafluoroferrate(III) is the most easily accessible. The reactions between iron(III) hydroxide and alkali-metal fluorides in aqueous hydrofluoric acid yields principally the aquopentafluoroferrate(III), e.g. $Na_2[FeF_5.H_2O]$.[173]

The hexafluoroferrate(III) compounds are magnetically dilute high spin complexes with room temperature magnetic moment of $\sim 5.9\,\mu_B$. The ammonium salt is cubic, while the potassium salt, K_3FeF_6, has a slightly distorted cubic unit cell.[174] To obtain the cryolite like hexafluoroferrate(III), the recommended method[174] requires first the synthesis of the $[FeF_5]^{2-}$ complex, which on treatment with molten alkali-metal hydrogen fluoride, AHF_2,yields the corresponding hexafluoroferrate(III), $A_3[FeF_6]$. Moreover, it is mentioned in the literature[175] that cryolite like compounds in general are difficult to obtain in a pure state directly from aqueous solution probably owing to the contamination of hydrates such as $A_2MF_5.H_2O$.[175]

It is evident from the above discussion on fluoroferrates(III) chemistry that no direct and simple route to hexafluoroferrate(III) seems to be available thus limiting their accessibility. The currently used methods involve steps which require high temperature heating.[174] Thus it is imperative and necessary to improvise suitable methods for the synthesis of alkali metal hexafluoroferrate(III).

When a solution contains a metal ion and at least two different ligands, there exists always a finite possibility of formation of a mixed-ligand complex. In view of the potential donating ability of many counter anions and solvents, there are very few cases indeed when this possibility is out of consideration.[176] Various types of mixed-ligand complexes of different metals have been studied, methods regarding the determination of their stability constants have been worked out in details, and their importance in chemical[177,178] and by biosystems[179,180] have been emphasised by others. The relationship between the stability of a mixed-ligand complex and its parent complex has been long disputed and it was thought that the mixed-ligand complexes are always more stable that could be expected on statistical grounds, but there are now many examples of the opposite behaviour. Statistically however mixed-ligand complex formation is always favoured,[181] which has been later supported[177] by elementary electrostatic consideration, steric effect and back co-ordination. A survey of literature shows that mixed ligand complexes of iron in its different oxidation states are known. However, one finds that there is a paucity of information regarding mixed-fluoro complexes of iron not only in its +3 but also in +2 oxidation states of the metal. It appears, therefore, that studies directed to mixed ligand fluoro complexes of iron(III) may generate some valuable information rendering it to be a rewarding aspect of investigation. A planning of synthetic strategies and working out of appropriate experimental conditions are important prerequisites for this.

Sulphate was thought to be an appropriate ligand for this purpose, because SO_4^{2-} is an important spectroscopic probe amenable to direct structural assessment by IR and Raman spectroscopy. Also the corresponding fluoro-sulphato compounds of manganese(III) and cobalt(II), viz.,$A_2[MnF_3(SO_4)]$[149] $A[CoF(SO_4)(H_2O)_2]$,[159] respectively, synthesised in the laboratory where the present work was carried out, have shown some interesting physical properties different from those of the corresponding parent binary fluoro complexes.

Strategically three different reaction pathways may be considered for the synthesis of fluoro(sulphato)iron(III) complex from an aqueous medium. These are:

(i) Direct reaction of sulphate and fluoride with iron(III) in an acidic medium.

(ii) In situ generation of SO_4^{2-} by reacting H_2O_2 in the medium with $SO_2(g)$ and reaction of this with iron(III) and F^- ion, already made available in the reaction solution.

(iii) Chemical oxidation of SCN^- to SO_4^{2-} by H_2O_2 in the presence of F^- ions and iron(III).

In case strategy (iii) has to be exploited in the context of synthesis of fluoro-sulphato complexes of iron(III), evaluation of the optimum conditions for the hydrogen peroxide oxidation of thiocyanate to sulphate is the pre-requisite. It was known that hydrogen peroxide oxidation of thiocyanate in solution to yield sulphate is an electron-transfer reaction[182] but the optimum conditions like pH, molar ratio between SCN^- and H_2O_2 etc. required for the quantitative oxidation have not been known so far.

Accordingly, in line with the scope highlighted in the above discussion, studies involving fluoro and mixed-ligand fluoro complexes of iron(III) were undertaken as the other part of the research programme. A new and direct method for the synthesis of $A_3[FeF_6]$ (A = NH_4, Na or K) from aqueous solution has been developed. Mixed-ligand fluoro-ferrate(III) compounds of the type $K_3[Fe(SO_4)F_4]$ and $(NH_4)_2[Fe(SO_4)F_3]$, have been synthesised for the first time and their structural assessment has been made by various physico-chemical techniques. Since a direct interaction of fluoride and SO_4^{2-} with iron(III) did not lead to success, an indirect reaction involving the oxidation of SCN^- with hydrogen peroxide in the presence of F^- and iron(III) had to be adopted. In order to utilise the reaction of hydrogen peroxide oxidation of thiocyanate to SO_4^{2-} in the context of synthesis of the afore mentioned complexes, optimum conditions for the quatitative conversion of SCN^- into SO_4^{2-} have been worked out. The knowledge obtained from this reaction was made use of for the synthesis of the above mentioned mixed-ligand fluoro complexes of iron(III), and the synthesis of the desired mixed-ligand complexes has been achieved from the reaction of SCN^- and F^- with iron(III) hydroxide and hydrogen peroxide. Chapter 6, indeed the concluding Chapter of the thesis contains the results of the afore-mentioned studies.

Chapters 3 to 6 present interpretative accounts of the results of studies on peroxo- and hetero-ligand-peroxovanadates(V) and fluoro and mixed-ligand fluoro complexes of iron(III). Each of these Chapters has been so designed as to make it a self-contained one with a brief introduction, sections on experimental, and results and discussion followed by relevant bibliography. Most of the new results have been published, while the rest are under communication.

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CHAPTER 2

CHAPTER 2

Methods of Elemental Analyses and Particulars of Instruments/Equipment Used for Characterisation and Structural Assessment

The details of the methods used for quantitative determination of various constituents, and the relevant particulars of the instruments/equipment used for the characterisation and structural assessment of the newly synthesised compounds are described in this Chapter.

Elemental Analyses

Vanadium[1]

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, after removing peroxide, was treated with a stream of sulphur dioxide for ca 10 min, and then with a stream of carbon dioxide to expel any excess of sulphur dioxide. The vanadium(IV) solution thus obtained was cooled at ca 80°C, and finally titrated with a standard potassium permanganate solution.[1]

Active Oxygen(Peroxo Oxygen)[2-4]

(i) Permanganometry[2]

An accurately weighed amount of a peroxovanadate(V) compound was dissolved in 7N sulphuric acid containing ca 4g of boric acid. Boric acid was used to form perboric acid to prevent any loss of active oxygen. The resulting solution was then titrated with a standard potassium permanganate solution.

$$1\ \text{cm}^3 \text{ of } 1\text{N } KMnO_4 \equiv 0.01701\text{g of } H_2O_2$$

This method is suitable for determination of peroxide contents in peroxovanadium(V) compounds.

(ii) Iodometry[3]

To a freshly prepared 2N sulphuric acid solution, containing an appropriate amount of potassium iodide ($\sim$1g in 100cm^3) was added an accurately weighed amount of a peroxovanadate(V) compound with stirring. The mixture was allowed to stand for ca 15 min in CO_2 atmosphere in the dark. The amount of iodine liberated was then titrated with a standard sodium thiosulphate solution, adding 2 cm^3 of freshly prepared starch solution, when the colour of the iodine was nearly discharged.

$$1\ \text{cm}^3 \text{ of } 1\text{N } Na_2S_2O_3 \equiv 0.01701\text{g of } H_2O_2$$

This method gives the total amount of peroxide plus vanadium present in the compound. On deduction of the contribution of vanadium(V) from the total amount of iodine liberated, the net peroxide content of the compound is evaluated.

(iii) Determination of peroxide (O_2^{2-}) content by titrating with a standard Ce^{+4} solution[4]

An accurately weighed amount of a peroxyvanadate(V) compound was dissolved in a 2N sulphuric acid solution in the presence of an excess of boric acid. Peroxide was then determined by titrating with a standard Ce^{+4} solution. Vanadium(V) does not interfere in this method.

Sulphate[5]

A known amount of sulphato compound of vanadium was dissolved in about 25 cm^3 of water, and 0.6 cm^3 of concentrated hydrochloric acid was added to it. The solution was diluted to 200 cm^3, and then boiled for nearly 40 min. A warm solution (10-12 cm^3) of 5% barium chloride (5g $BaCl_2.2H_2O$ in 100 cm^3 of water) was added from a burette or pippette drop by drop with continuous stirring, and the resultant precipitate was allowed to settle for ca 2 min. The supernatant liquid was tested for complete precipitation by adding a few drops of barium chloride. The process was repeated until a slight excess of barium chloride was present in the mixture to ensure complete precipitation. The mixture was kept covered over a steam-bath for 1h in order to allow time for complete precipitation of $BaSO_4$. The precipitated barium sulphate was filtered through a previously weighed sintered glass crucible (grade 4) using a gentle suction. The precipitate was washed with warm water until the filtrate gave no precipitate with a few drops of silver nitrate solution. The crucible with its content was dried at ca 110°C, and heated for 10-15 min at a higher temperature (ca 600°C) followed by cooling in a desiccator. The heating process was continued until a constant weight was attained.

The sulphate content of the sample was finally weighed as $BaSO_4$,

The estimation of sulphate in fluoro(sulphato)ferrate(III) complexes required decomposition of the compound prior to the estimation of SO_4^{2-}. A weighed amount of the compound was treated with 25 cm^3 of water, and dissolved completely by the addition of a few drops of dilute nitric acid. The solution was then treated with 30% solution of aqueous ammonia in order to decompose the compound, and to separate iron(III) as iron(III) hydroxide. The solution was filtered, the residue washed thoroughly with water, and the filtrate and washings were collected for the estimation of sulphate.

The solution was concentrated by boiling and then neutralised with dilute nitric acid. An amount of 2 cm^3 of concentrated hydrochloric acid was added to the solution and the whole was boiled for nearly 40 min. The sulphate content in the resulting solution was then determined gravimetrically as barium sulphate following the procedure described in the case of sulphate estimation in sulphato compounds of vanadium.

Fluoride[6]

An accurately weighed amount of a fluorosulphatovanadate(IV) or a fluoroferrate(III) compound was dissolved in water. While the fluoride estimation in the fluorovanadate compounds could be made directly from their aqueous solutions, the estimation of fluoride in the fluoroferrates(III) required decomposition of the compound prior to the estimation of fluoride. The fluoroferrate(III) compound was decomposed by treating with 30% aqueous ammonia and the mixture was heated over steam bath for ca 10 min to ensure complete decomposition. The hydrated iron(III) oxide formed due to the addition of aqueous ammonia was separated out by filtration and washed several times with water. The filtrate and washings were collected together for fluoride estimation.

To the above solution 2 to 3 drops of bromophenol blue indicator and 3 cm^3 of 10% sodium chloride solution were added, and the whole was diluted to ca 250 cm^3. Dilute nitric acid was added to it until colour changed to just yellow, followed by the addition of dilute sodium hydroxide solution until the colour ultimately just changed to blue. The mixture was then treated with 1 cm^3 of concentrated hydrochloric acid and 5.0g of lead nitrate, and then heated on a steam bath. After all the lead nitrate had dissolved, 5.0g crystallised sodium acetate was added to the solution and the solution was digested on a steam bath for about half an hour with occassional stirring, and then allowed to stand overnight.

For the gravimetric estimation, the precipitated lead chloride fluoride, PbClF, was filtered through a weighed Gooch crucible (grade 4) and weighed as PbClF after drying at 140-150°C to constant weight.

In the volumetric estimation, the precipitate PbClF was quantitatively collected by filtration through a Whatman 542 filter paper and washed once with cold water, then 3 to 4 times with saturated solution of lead chloride fluoride, and finally once more with cold water. The precipitate was then dissolved in 100 cm^3 of 5% (v/v) nitric acid by heating over steam bath for 4-5 min. A known excess of saturated 0.1N silver nitrate solution was then added to it, followed by digestion on a steam bath for 30 min, and then cooled at room temperature in the absence of light. The precipitated silver chloride was filtered through a sintered glass crucible and washed with cold water. The unreacted silver nitrate in the filtrate and washings was titrated with a standard 0.1N potassium thiocyanate solution using 1 cm^3 of ferric ion indicator until one drop of thiocyanate solution produced a permanent faint brown colour. The amount of silver nitrate in the filtrate, thus found, was subtracted from that originally added, and the content of fluoride was then calculated from the amount of silver nitrate consumed.

$$1\ cm^3 \text{ of } 1N\ AgNO_3 \equiv 0.0190g \text{ of } F.$$

Carbon, Hydrogen, and Nitrogen

Carbon, hydrogen and nitrogen were estimated by micro analytical methods. The results of analyses were obtained from Micro Analytical Laboratories, Regional Sophisticated Instrumentation Centre (RSIC), Central Drug Research Institute, Lucknow, and also from Micro Analytical Laboratories, RSIC, NEHU, Shillong.

Iron[7]

A weighed amount of the iron(III) compound was dissolved in 30 cm^3 of 5N hydrochloric acid solution and heated in a steam bath. To the hot solution a concentrated solution of tin(II) chloride (solution was made as per standard procedure) was added dropwise from a burette, with stirring, until the yellow colour of the solution has nearly disappeared. The reduction of iron(III) to iron(II) was then completed by diluting the concentrated solution of tin(II) chloride with 2 volumes of dilute hydrochloride acid, and adding the dilute solution dropwise, with stirring after each addition, until the liquid attained a faint green colour, quite free from any tinge of yellow. The solution was then rapidly cooled under the tap, with protection from the air, and the slight excess of tin(II) chloride present removed by adding 10 cm^3 of a saturated solution (5% at 25°C) of mercury(II) chloride rapidly in one portion and with thorough mixing; a slight sikly white precipitate of mercury(I) chloride was obtained.

After the addition of mercury(II) chloride solution, the whole was allowed to stand for 5 min. Dilute (1M) sulphuric acid (200 cm^3) was added to it and then titrated with standard potassium dichromate solution using N-phenyl-anthranilic acid as internal indicator, until the colour changed from green to violet-red.

$$1\ cm^3 \text{ of } 1N\ K_2Cr_2O_7 \equiv 0.05585g \text{ of } Fe$$

Sodium and Potassium

Sodium and potassium contents were determined by flame photometry. A solution containing sodium or potassium ions was acidified with hydrochloric acid. The acidified solution thus obtained was used for flame photometry.

Particulars of Instruments/Equipment used

pH Measurement

pH of the reaction solutions, whenever required, were measured by using a Systronics Type 335 digital pH meter and also by BDH indicator paper.

Molar Conductance

Molar conductance measurements were made using Philips PR 9500 conductivity bridge. Conductivity grade water was used for the purpose.

Magnetic Susceptibility

The Gouy method was used to measure magnetic susceptibilities of the complexes. The compound $Hg[Co(NCS)_4]$ was used as the standard for calibration.

Electronic Spectra

Electronic spectral measurements of solutions were made on Beckman model UV-26 and Cary model 2300 Spectrophotometers.

Infrared Spectra

Infrared spectra were recorded in KBr on the following spectrophotometers:

(1) Perkin-Elmer model 297

(2) Perkin-Elmer model 983

Laser Raman Spectra

Laser Raman(LR) spectra were recorded on a SPEX Ramalog model 1403 Raman spectrometer. The 4880Å laser line from spectra-physics model 165-09 Argon laser and 6471Å laser line from coherent model Innova 90K Krypton ion laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube, followed by photon-count processing system.

The sample was held either in a quartz capillary or in the form of a pressed pellet. The solution LR spectra were recorded by taking the sample solution in quartz capillary. The recording was done at ambient temperatures.

ESR Spectra

ESR spectra of polycrystalline solids as well as those of aqueous solutions of the compounds were recorded using a Varian E109, X-band ESR spectrometer with 100 Kc field modulator.

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CHAPTER 3

CHAPTER 3

Alkali Oxodiperoxovanadate(V) Complexes $[VO(O_2)_2]^-$. First Isolation in the Solid State, Characterisation and Structural Assessment

And

Reactions of Vanadium(V) with Alkali Sulphate or Thiocyanate and Hydrogen Peroxide. Evidence for the Formation of Oxodiperoxovanadate(V) Complexes Containing Ionic Sulphate*

The importance of peroxovanadium chemistry has been emphasised in Chapter 1. It is evident from the contemporary chemistry literature that studies of peroxovanadium chemistry have generated considerable current interest,[1-11] probably owing to the special biochemical significance of peroxo transition metal compounds,[12-18] and their involvement in the catalytic oxidation processes,[9,14,19-22] particularly the activation and transfer of molecular oxygen to organic substrates including hydrocarbons.[14,19,20] The synthesis of well defined peroxovanadium compounds followed by the study of their different properties provide a means in understanding the chemistry of such compounds. It has been known that vanadium — hydrogen

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*The results described in this Chapter have been published:
<u>J.Ind.Chem.Soc</u>., 1985, <u>62</u>, 815.
<u>Trans.Met.Chem</u>., 1985, <u>10</u>, 333.

peroxide system gives different colour reactions under slightly varying pH of the reaction medium[23-25] and it is believed that the yellow colour of the vanadium(V) — H_2O_2 solution owes its origin to the formation of a diperoxovanadate(V) anion, $[VO(O_2)_2]^-$ (Ref. 24,25). However, various attempts to ascertain the existance of this species through isolation in the solid state led to failure, thereby leaving some doubt regarding its actual composition. Thus, it was felt imperative to settle this issue and also to investigate the synthetic potentiality of such compounds in the synthesis of heteroligand peroxovanadates having '$[VO(O_2)_2]^-$' frame work.

Moreover, inspite of the continued interest in the field of peroxovanadates, within the context of the synthesis, isolation in the solid state, characterisation, and structural assessment of peroxovanadium compounds, there are several points which have not been attended to. One is the mode of bonding of sulphate with vanadium(V) in the complex formed in the reaction with hydrogen peroxide in the presence of SO_4^{2-}, a reaction used in the spectrophotometric determination of vanadium. Accordingly, we were interested in the synthesis of peroxovanadates(V) compounds containing SO_4^{2-}, to characterise the peroxo compound formed, and to evaluate the nature of bonding between sulphate and the vanadium(V) centre.

Chapter 3 of the thesis presents the first successful synthesis, characterisation and structural assessment of the yellow alkali oxodiperoxovanadates(V), $A[VO(O_2)_2]$ (A = NH_4, Na or K). Two reactions involving the potassium salt, $K[VO(O_2)_2]$, which highlight the scope for the use of these compounds in synthesis, are included in this Chapter. Also presented herein an interpretative account of the results of our studies involving the reactions of vanadium(V) and hydrogen peroxide in the presence of SO_4^{2-} or SCN^-.

Experimental

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

Synthesis of alkali oxodiperoxovanadates(V) $A[VO(O_2)_2]$ (A = NH_4, Na or K)

As the methods of synthesis of the $A[VO(O_2)_2]$ compounds are similar, only a representative procedure is described.

Powdered V_2O_5 and 30% hydrogen peroxide were mixed in the concentration ratio of $V_2O_5:H_2O_2$ as 1:41.8. Alkali metal hydroxide or aqueous ammonia was slowly added to the above mixture under slow but continuous magnetic stirring, until the whole amount of V_2O_5 was dissolved to just produce a clear yellow solution with its pH lying between 7 and 8. While aqueous ammonia was added in the form of its concentrated solution (specific gravity 0.9), sodium hydroxide or potassium hydroxide was added in the solid form. The resulting solution was cooled in an ice-water bath for ca 30 min, and then an excess of pre-cooled ethanol was added to it until yellow coloured microcrystalline $A[VO(O_2)_2]$ compound ceased to appear. The compound was separated by centrifugation, washed four times with cold ethanol and finally dried in vacuo over P_4O_{10}. The amounts of reagents used and yields of the products are given in Table 3-1.

Reactions of Potassium Oxodiperoxovanadate(V), $K[VO(O_2)_2]$ with KF, or 2,2′-bipyridine(bipy)

To a concentrated aqueous solution of $K[VO(O_2)_2]$ was added an aqueous solution of KF, or an ethanolic solution of 2,2′-bipyridine(bipy) with the concentration ratio between $K[VO(O_2)_2]$ and KF or bipy maintained at 1:1. The resulting solution was stirred for ca 15 min at an ice-bath temperature followed by the addition of cold ethanol until the precipitation of yellow microcrystalline product was complete. It was allowed to stand at ice-bath temperature for ca 30 min, and the product was isolated by centrifugation, purified by washing with ethanol, and finally dried in vacuo over P_4O_{10}.

Reaction of V_2O_5 with H_2O_2 and A_2SO_4 (A = NH_4, Na or K). Synthesis of $A[VO(O_2)_2].A_2SO_4$

In a typical reaction V_2O_5 and alkali sulphate, A_2SO_4, were intimately mixed in a 1:2 ratio, and the mixture dissolved

Table 3-1. Amounts of Reagents Used and Yields of $A[VO(O_2)_2]$ (A = Na, K or NH_4)

Compound	Yield g(%)	Amount of V_2O_5 g(mmol)	Amount of 30% H_2O_2 cm^3(mmol)	Amount of AOH (mmol)
$NH_4[VO(O_2)_2]$	0.7(85)	0.5(2.7)	13(114.6)	2.1 (25% soln, sp.gr. 0.9) (15)
$Na[VO(O_2)_2]$	0.8(94)	0.5(2.7)	13(114.6)	0.72(18)
$K[VO(O_2)_2]$	0.8(85)	0.5(2.7)	13(114.6)	0.82(14.6)

in an excess of 30% H_2O_2 (V_2O_5:H_2O_2::1:32) with stirring. The solution was filtered to remove any traces of undissolved impurity, and the filtrate cooled in ice-water. Alkali hydroxide solution was added dropwise with constant stirring until the solution became permanent yellow and attained pH 7-8. The solution was stirred for a further period of ca 10 min. An excess of ethanol was added to the above solution with occassional stirring until the yellow coloured microcrystalline product, $A[VO(O_2)_2].A_2SO_4$, ceased to appear. The product was filtered, washed four times with ethanol and finally dried in vacuo over P_4O_{10}.

The amounts of reagents used and yields of the products are given in Table 3-2.

Reaction of V_2O_5 with H_2O_2 and ASCN (A = NH_4, or K). Synthesis of $A[VO(O_2)_2].A_2SO_4$

In a representative procedure, a mixture of V_2O_5 and ASCN (A = NH_4 or K), in a 1:2 molar ratio was dissolved in an excess of 30% H_2O_2 (V_2O_5:H_2O_2::1:42.5). The resultant solution was cooled in ice-water for ca 15 min, followed by the addition of aqueous ammonia or potassium hydroxide, drop by drop with continuous stirring until the solution became yellow with the pH lying between 7 and 8. The whole was cooled for ca 30 min, and an excess of ethanol was added until precipitation was complete. The yellow microcrystalline product, $A[VO(O_2)_2].A_2SO_4$, was isolated as described under the preceeding reaction.

Table 3-2. Amounts of Reagents Used and Yields of $A[VO(O_2)_2].A_2SO_4$ (A = NH_4, Na or K)

Compound	Yield g(%)	Amount of V_2O_5 g (mmol)	Amount of A_2SO_4[a] or ASCN[b] g (mmol)	Amount of 30% H_2O_2 cm^3 (mmol)
$NH_4[VO(O_2)_2].(NH_4)_2SO_4$	2.8(90)	1.0(5.5)	1.45[a](11)	20(176.4)
$Na[VO(O_2)_2].Na_2SO_4$	2.7(82)	1.0(5.5)	1.56[a](11)	20(176.4)
$K[VO(O_2)_2].K_2SO_4$	3.4(89)	1.0(5.5)	1.92[a](11)	20(176.4)
$NH_4[VO(O_2)_2].(NH_4)_2SO_4$	2.9(94)	1.0(5.5)	0.84[b](11)	26.5(233.7)
$K[VO(O_2)_2].K_2SO_4$	3 (91)	1.0(5.5)	1.1[b] (11)	26.5(233.7)

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[a] A_2SO_4 salts. [b] ASCN salts.

The amounts of reagents used and yields of the products are given in Table 3-2.

Elemental Analyses

Quantitative estimation of vanadium, sulphate, peroxide, nitrogen, and alkali-metals were made by the methods described in Chapter 2.

The analytical data are given in Tables3-3 and 3-4.

Structurally significant IR bands and their assignments are reported in Tables3-5 and 3-6.

Results and Discussion

It is generally believed that the yellow colouration which is formed between pentavalent vanadium and hydrogen peroxide is owing to the formation of the complex species $[VO(O_2)_2]^-$ in solution. However, the complex could not be isolated in the solid state despite many attempts made in the past.[25] It was expected that the complex could be synthesised by suitable adjustment of the experimental conditions. Accordingly, a clear yellow solution was prepared by the careful addition of alkali hydroxide, to a solution of V_2O_5 in an excess of hydrogen peroxide, until the pH of the solution was found to lie between 7 and 8. Addition of ethanol to the afore mentioned solution afforded the yellow alkali metal oxodiperoxovanadate(V) complexes, $A[VO(O_2)_2]$ (A = NH_4, Na or K). The role of ethanol was to facilitate precipitation.

Table 3-3. Analytical Data and Molar Conductance Values of $A[VO(O_2)_2]$ (A = NH_4, Na or K)

Compound	Molar Conductance $\Omega^{-1}cm^2mol^{-1}$	Found % (Calcd. %)		
		A	V	O[a]
$NH_4[VO(O_2)_2]$	140	9.2[b] (9.4)[b]	34.4 (34.19)	42.5 (42.96)
$Na[VO(O_2)_2]$	135	15.3 (14.94)	33.6 (33.09)	41.7 (41.58)
$K[VO(O_2)_2]$	130	22.7 (23.0)	30.3 (29.96)	37.2 (37.64)

[a] Peroxo-oxygen. [b] Analysis for N

Table 3-4. Analytical Data and Molar Conductance Values of $A[VO(O_2)_2].A_2SO_4$ (A = NH_4, Na or K)

Compound	Molar Conductance $\Omega^{-1}cm^2mol^{-1}$	Found % (Calcd. %)			
		A	V	O^a	SO_4
$NH_4[VO(O_2)_2].(NH_4)_2SO_4$	380	15.2^b $(14.95)^b$	17.8 (18.1)	23.1 (22.8)	34.8 (34.2)
$Na[VO(O_2)_2].Na_2SO_4$	370	22.8 (23.3)	17.9 (17.2)	22.1 (21.6)	32.9 (32.5)
$K[VO(O_2)_2].K_2SO_4$	355	33.6 (34.1)	14.2 (14.8)	19.2 (18.6)	27.2 (27.9)

[a] Peroxo oxygen. [b] Analysis for N.

It is worthwhile to mention that pH 7-8 of the reaction medium is very conducive to the synthesis.

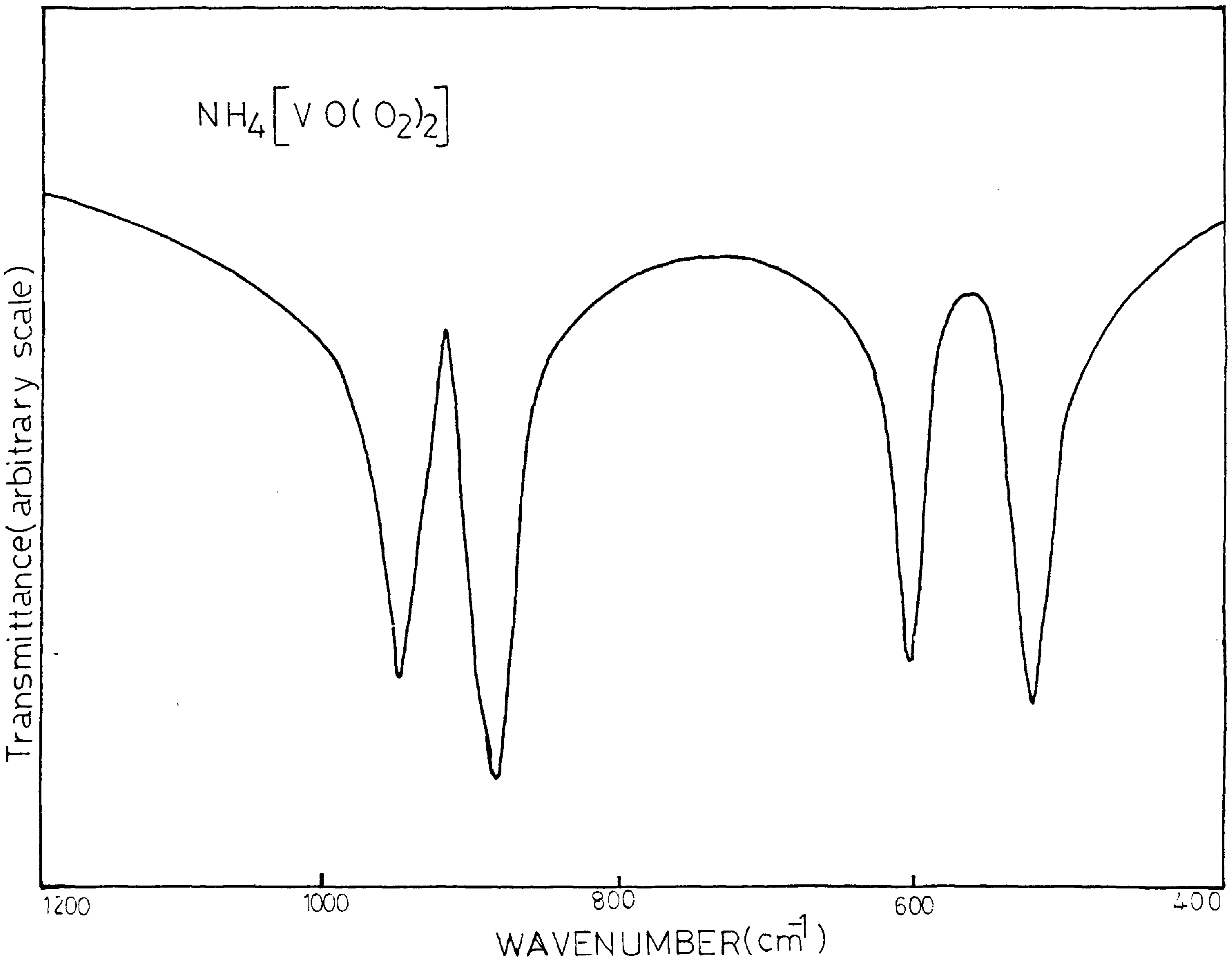
The yellow alkali metal oxodiperoxovanadates(V), $A[VO(O_2)_2]$ (A = NH_4, Na or K), are soluble in water, and they permit molar conductance measurements. The molar conductances of the newly synthesised compounds were found to lie in the range 130-140 $\Omega^{-1}cm^{2}mol^{-1}$ (Table 3-3) suggesting an 1:1 electrolytic nature of each of them in agreement with their formulae. The diamagnetic nature of the compounds, as evidenced from the results of magnetic susceptibility measurements, is in conformity with the view that vanadium occurs in its +5 oxidation state (d°) in each of them.

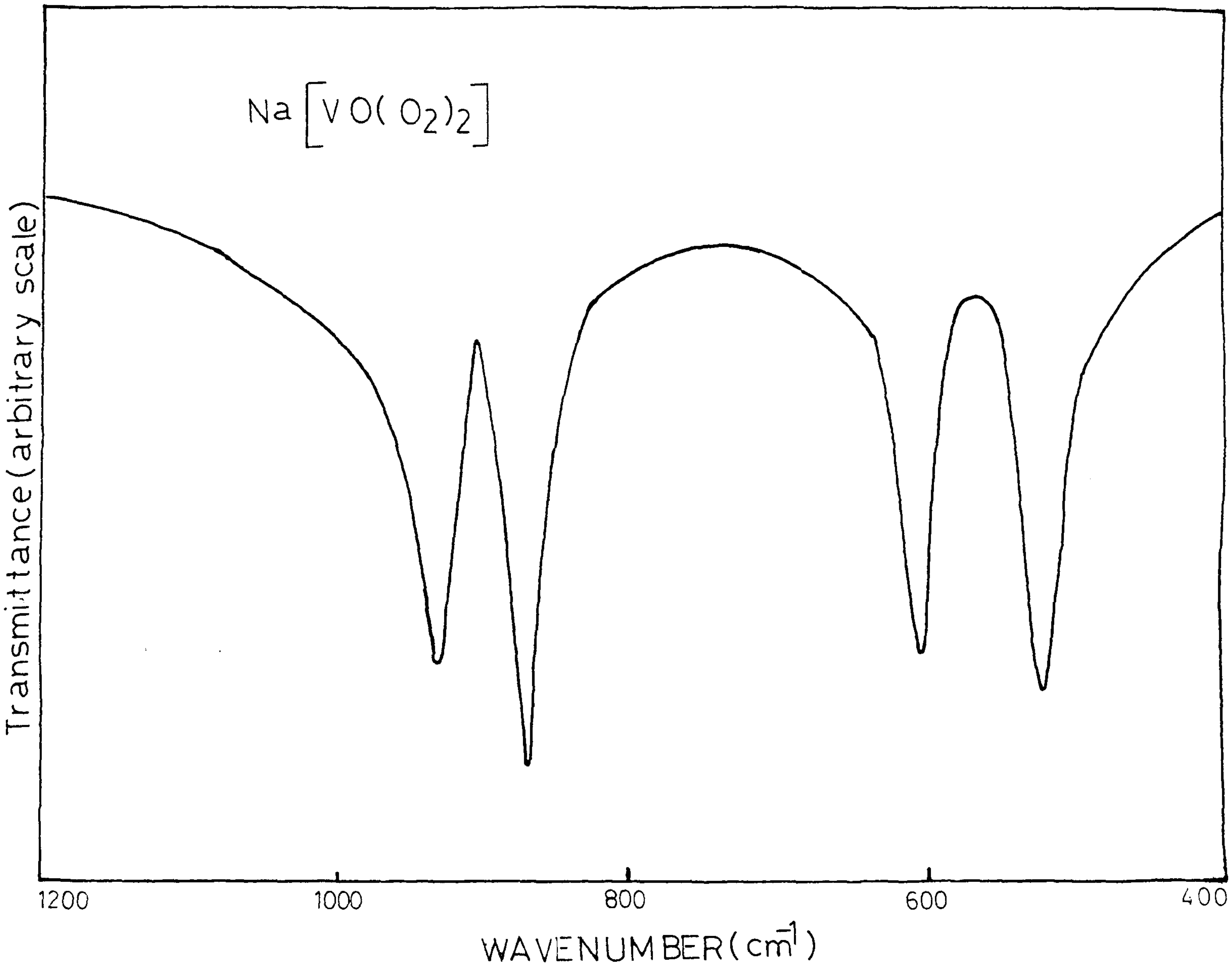
The compounds can be stored in sealed sample tubes, and their stability can be ascertained by the estimation of peroxide periodically. Peroxide estimation, in such compounds, must be considered very important in order to fix the number of O_2^{2-} groups co-ordinated to the metal centre. The peroxide content was determined by redox titrations involving standard Ce^{4+} solution, and also separately by standard potassium permanganate solution as mentioned in Chapter 2. The titration was carried out in each case in the presence of boric acid to prevent any loss of active oxygen, and the results conspicuously suggested the occurrence of two peroxo groups per vanadium atom in each of the compounds.

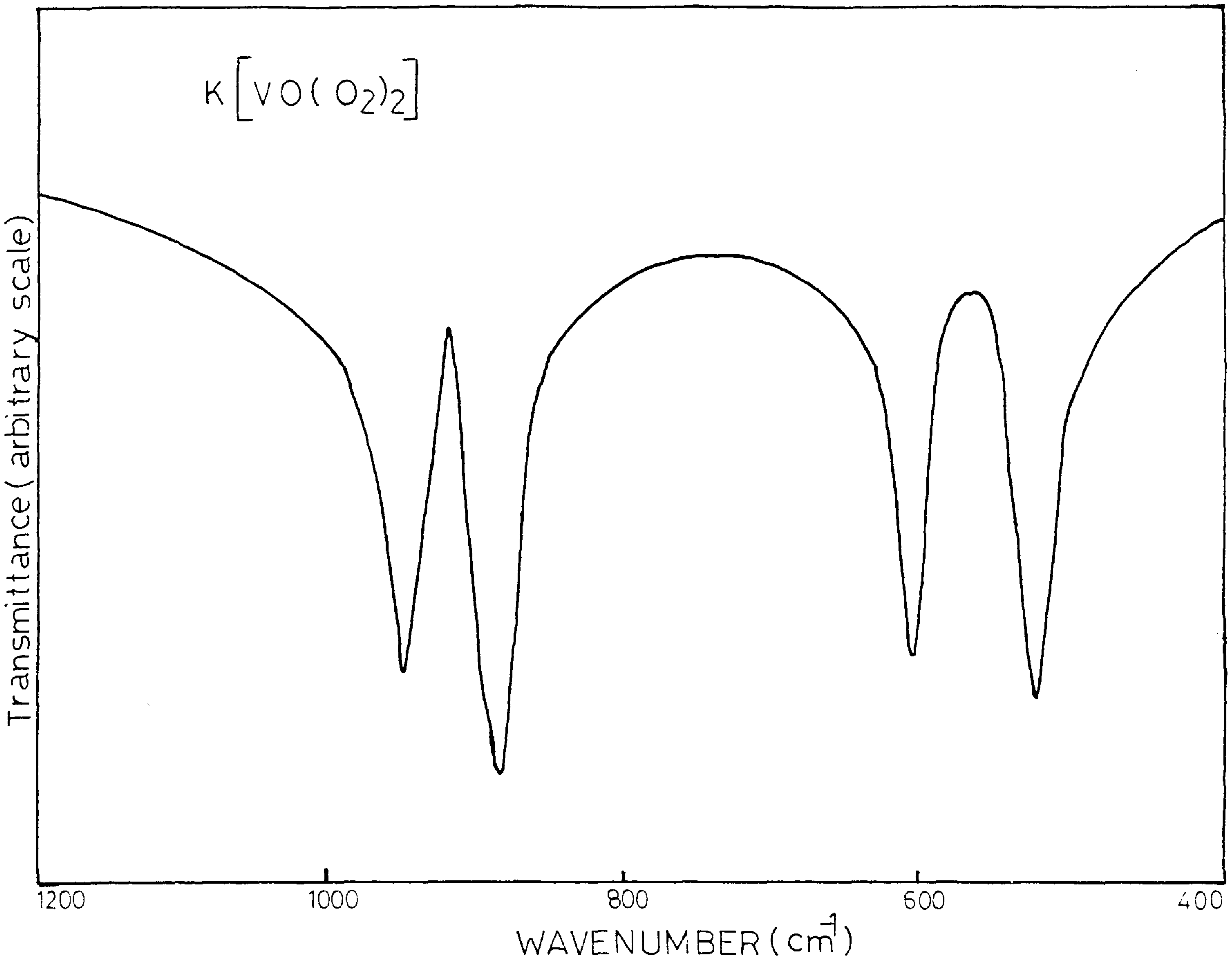
The infrared and laser Raman (lR) spectra of the oxodiperoxovanadates(V), $A[VO(O_2)_2]$ (A = NH_4, Na or K), are quite characteristic. Both IR and laser Raman spectra show bands at ca 950, ca 880, ca 610, and ca 530 cm^{-1} which have been assigned to ν (V=O),[26] ν (O-O)(ν_1),[27,28] ν ($V-O_2$)(ν_3),[27,28] and ν ($V-O_2$)(ν_2)[27,28] modes, respectively. The O-O and metal-O_2 bands are important spectroscopic probes for molecular structure determination, and are amenable to infrared and Raman spectroscopic studies. The observed positions of ν (O-O) and ν ($V-O_2$) modes, and the number of such vibrations correspond to those which one would expect to observe for a triangularly bonded peroxide ligand,[28] and accordingly it is argued that the peroxide ligands are bonded to the vanadium(V) centre in a triangular bidentate (C_{2v}) manner in each of the newly synthesised compounds. The distinction between ν_2 and ν_3 modes of ν ($V-O_2$) was made on the basis of the fact that the ν ($V-O_2$) band at ca 530 cm^{-1} was comparatively more sharp and intense than that of the ν ($V-O_2$) at ca 610 cm^{-1}, and polarised as observed in the LR spectra. The ν_1 mode is well separated from the ν_2 and ν_3 modes and the band at ca 880 cm^{-1} is unambiguously assigned to the ν_1(ν_{O-O}) mode of the co-ordinated peroxide (O_2^{2-}). The strong absorption at ca 950 cm^{-1} owes its origin to the presence of a terminally bonded oxygen atom. It is on account of the large polarisability changes involved in the V=O bond that the ν (V=O) appears as a strong band in the laser Raman spectra, and is quite

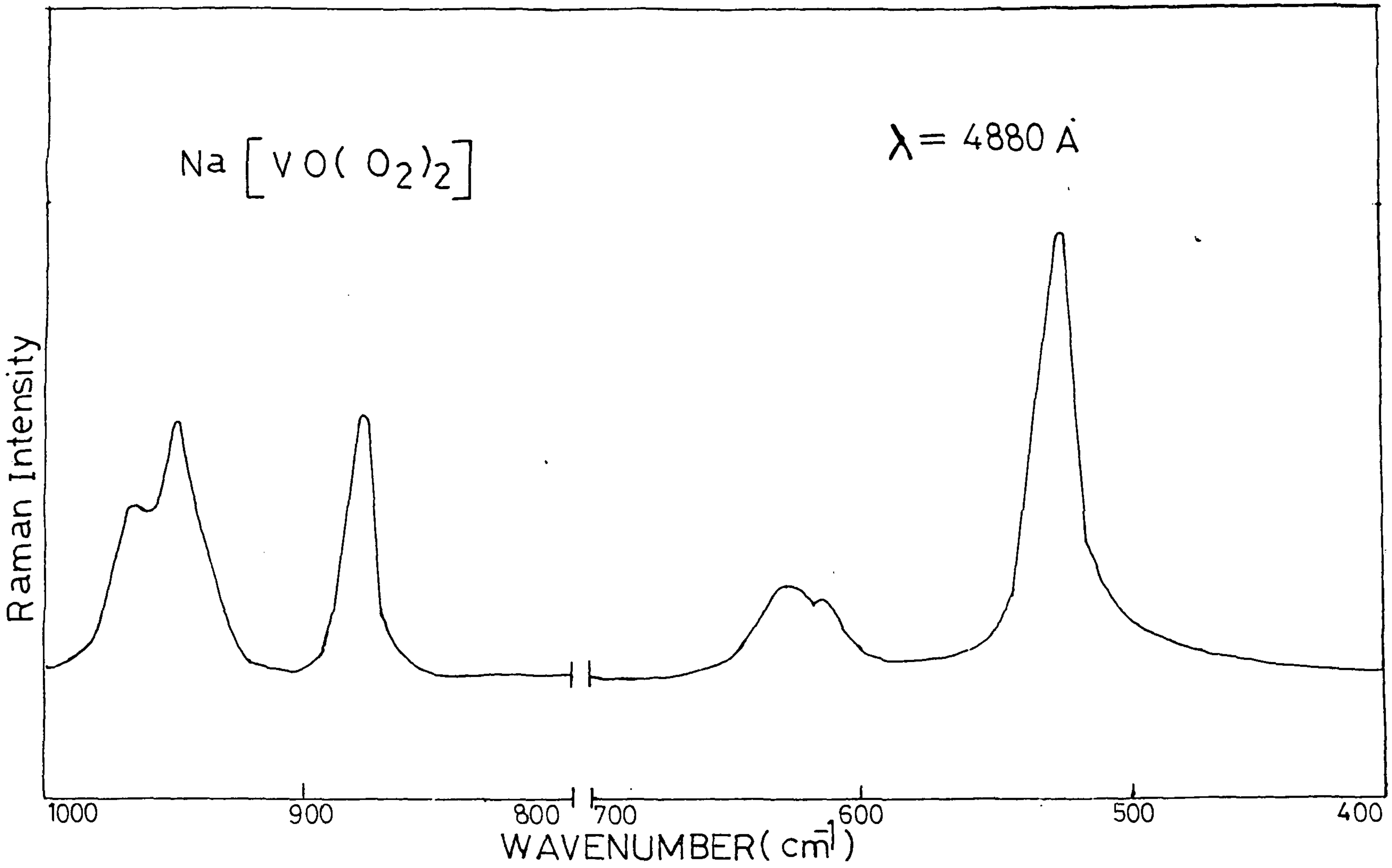
Table 3-5. Structurally Significant IR and Laser Raman (LR) Bands of $A[VO(O_2)_2]$ (A = NH_4, Na or K)

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$NH_4[VO(O_2)_2]$	950s	945	ν (V=O)
	885s	880	ν (O-O) ν_1
	605s	610	ν $(V-O_2)$ ν_3
	525s	530	ν $(V-O_2)$ ν_2
$Na[VO(O_2)_2]$	935s	950	ν (V=O)
	870s	880	ν (O-O) ν_1
	605s	600	ν $(V-O_2)$ ν_3
	530s	530	ν $(V-O_2)$ ν_2
$K[VO(O_2)_2]$	960s	945	ν (V=O)
	885s	875	ν (O-O) ν_1
	605s	615	ν $(V-O_2)$ ν_3
	530s	525	ν $(V-O_2)$ ν_2


$NH_4[VO(O_2)_2]$
Transmittance(arbitrary scale)
1200
1000
800
600
400
WAVENUMBER(cm^{-1})


Na$[VO(O_2)_2]$
Transmittance (arbitrary scale)
1200
1000
800
600
400
WAVENUMBER (cm^{-1})


K[VO(O2)2]
Transmittance (arbitrary scale)
1200
1000
800
600
400
WAVENUMBER (cm-1)


Na $[VO(O_2)_2]$
$\lambda = 4880$ Å
Raman Intensity
1000
900
800
700
600
500
400
WAVENUMBER(cm^{-1})

characteristic for the newly synthesised compounds. In order to explore the possibility of any change in the structure of the complex anion $[VO(O_2)_2]^-$ in solution, laser Raman spectra of the freshly prepared solutions of alkali metal oxodiperoxovanadates(V) were recorded at ambient temperatures. The solution spectra neither showed any new band nor any appreciable change in positions of the peaks observed in the corresponding solid state spectra. The only notable difference was that the solution laser Raman peaks, especially the ν (V=O), ν (O-O)(ν_1) and ν (V-O_2)(ν_2) modes, were found to be relatively sharper. This, therefore, leads us to infer that the complex species $[VO(O_2)_2]^-$ most probably retains its identity both in the solid state as well as in solutions.

The reaction of $K[VO(O_2)_2]$ with KF yielded the product , which was characterised as $K_2[VO(O_2)_2F]$,[29] while the product obtained from the reaction of $K[VO(O_2)_2]$ with bipyridine was identified as $K[VO(O_2)_2bipy].4H_2O$.[4,5] The results of elemental analyses, molar conductance values, IR and Raman band positions of these complexes were similar to those reported earlier.[4,5,29] The type of products obtained from the reaction of $K[VO(O_2)_2]$ separately with KF and bipy adduce further evidence regarding the identity of the $[VO(O_2)_2]^-$ species. Moreover, these reactions highlight the synthetic potentiality of $A[VO(O_2)_2]$ compounds as precursors for the synthesis of heteroligand peroxo complexes of vanadium(V). The facile reactions of potassium oxodiperoxo vanadate(V) suggest that the co-ordinatively unsaturated vanadium(V) centre, in the $[VO(O_2)_2]^-$ ion, readily co-ordinates with suitable ligands and a host of heteroligand peroxovanadium(V) compounds may be easily accessible through similar routes.

Reactions of Vanadium(V) with Alkali Sulphate or Thiocyanate and Hydrogen Peroxide

As a sequel of our studies involving the syntheses and structural evaluation of complex peroxovanadates,[3,29-32] we thought it worthwhile to extend such studies to the synthesis of peroxovanadate(V) compounds containing SO_4^{2-} and to make an assessment of their structure and mode of bonding. Accordingly, vanadium pentoxide was allowed to react with hydrogen peroxide in the presence of alkali sulphate at a pH 7-8 maintained by the addition of the corresponding alkali hydroxide to give a yellow solution. Addition of an excess of ethanol, which facilitated precipitation gave a yellow microcrystalline product.

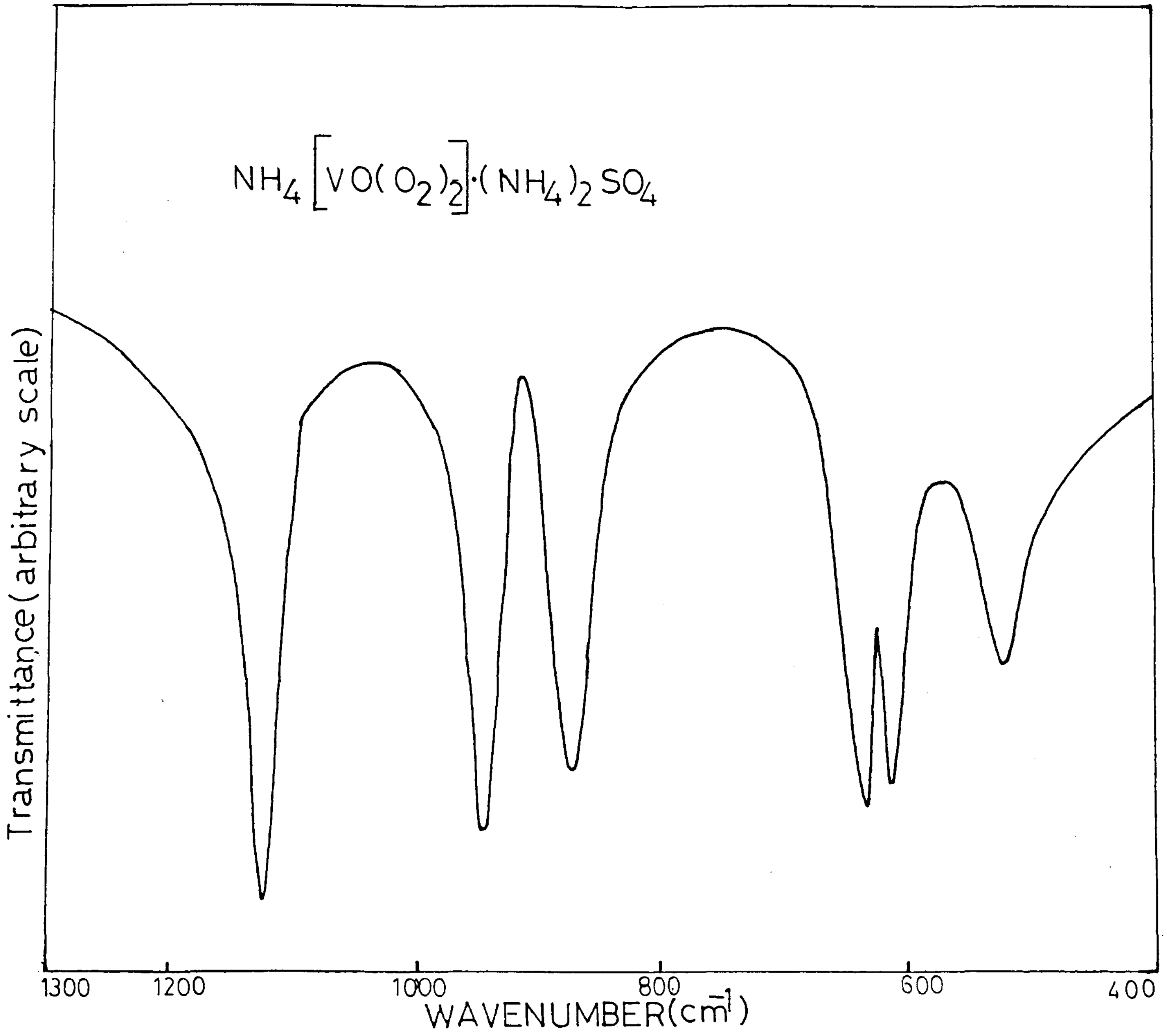
The yellow product was found to be stable for prolonged period and completely soluble in water. The results of chemical analyses suggest the $A:V:O_2^{2-}:SO_4^{2-}$ as 3:1:2:1 stoichiometry. The molar conductances, based on the molecular weight calculated from the results of elemental analyses were found to lie in the 350-380 $\Omega^{-1}cm^2mol^{-1}$ range suggesting that the products may be formulated as $A_3[VO(O_2)_2SO_4]$, or, as well, as $A[VO(O_2)_2].A_2SO_4$. The magnetic susceptibility measurements shows the diamagnetic nature of the compounds, which suggest that vanadium is present in each of the compounds in its +5 oxidation state. This is further supported by the absence of any signals in the E.S.R. spectra.

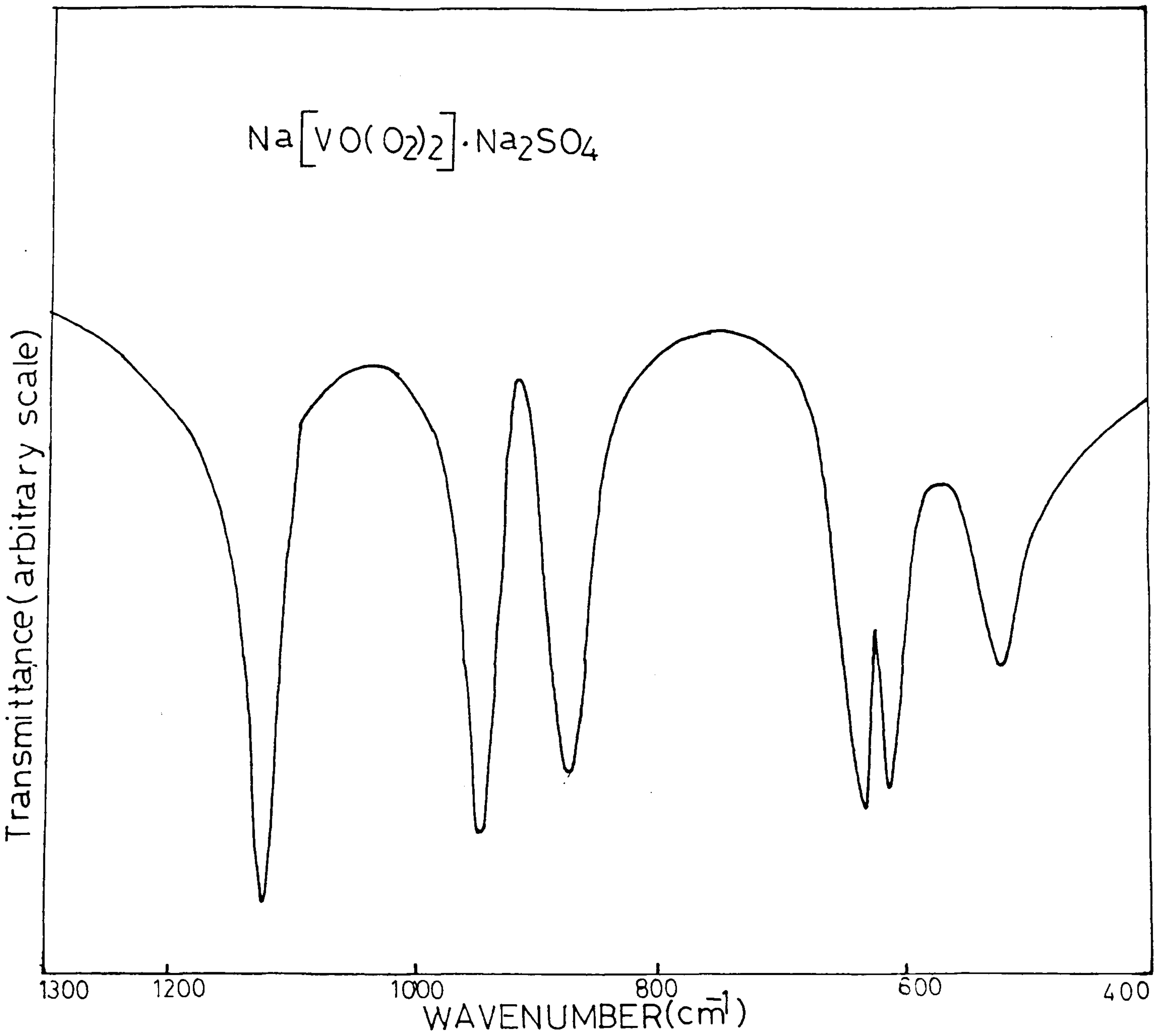
The IR spectra of the compounds resemble each other very closely except for the additional cation modes in NH_4^+ salts, suggesting that the compounds are structurally similar. The absorptions in the IR spectra at ca 950s due to ν (V=O) and ca 870s, ca 630s, and ca 525m cm^{-1} are assigned to ν(O-O) and ν (V-O_2) modes, respectively, of co-ordinated peroxide group. Since the ν (O-O) and the complementary ν (V-O_2) modes are observed in the positions stipulated for a triangularly bonded O_2^{2-} group, it may be infered that peroxide groups are bonded to the vanadium(V) in a triangular bidentate (C_{2v}) manner.

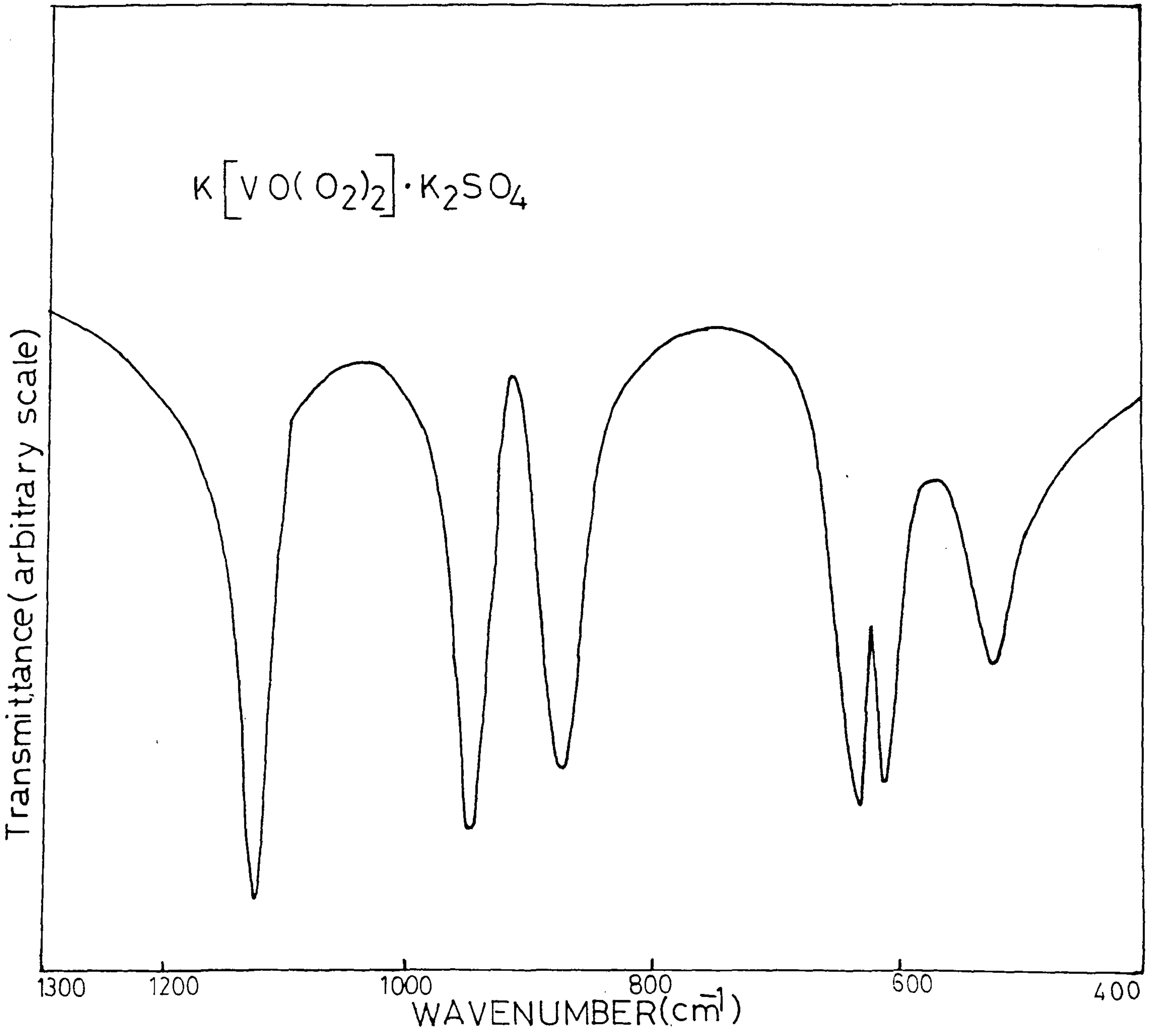
Free sulphate ion has T_d symmetry. It has four fundamental vibrations of which ν_3 and ν_4 are IR active. When the sulphate ion is co-ordinated to a metal, its IR spectrum changes drastically.[33,34] While the SO_4^{2-} ligand is bound in a monodentate fashion, its symmetry is lowered to C_{3v} due to which ν_3 and ν_4 are split into two bands each and both ν_1 and ν_2 appear with medium intensity. However, if sulphate occurs as a bidentate ligand (C_{2v} symmetry), ν_3 and ν_4 are split into three bands each, while ν_1 and ν_2 still appear with medium Intensity. In the case of the compounds synthesised by us, the two absorptions in the spectra at ca 1120vs and ca 615s cm^{-1} are attributed to ν_3 and ν_4 modes, respectively,

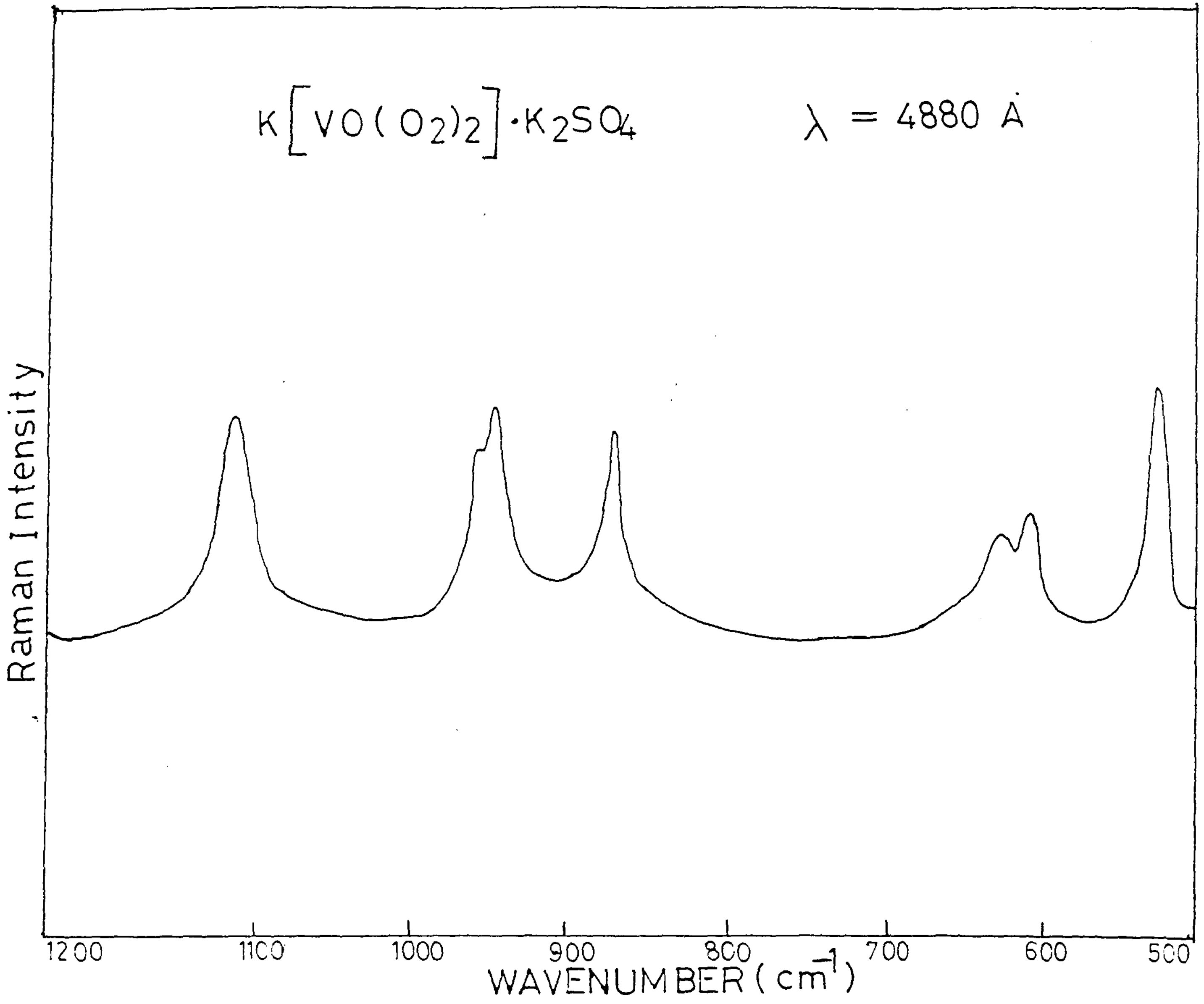
Table 3-6. Structurally Significant IR and Laser Raman (LR) Bands of $A[VO(O_2)_2].A_2SO_4$ (A = NH_4, Na or K)

Compound	IR cm^{-1}	Raman cm^{-1}	Assignments
$NH_4[VO(O_2)_2].(NH_4)_2SO_4$	950s	950	ν (V=O)
	875s	880	ν (O-O)
	630s	625	ν $(V-O_2)(\nu_3)$
	525m	520	ν $(V-O_2)(\nu_2)$
	1125vs	1105	ν (S-O) (ν_3)
	615s	600	ν (S-O) (ν_4)
	3045s		ν_1 N-H
	3160m		ν_3
	1400s		ν_4
$Na[VO(O_2)_2].Na_2SO_4$	960s	950	ν (V=O)
	870s	875	ν (O-O)
	635s	620	ν $(V-O_2)(\nu_3)$
	525m	525	ν $(V-O_2)(\nu_2)$
	1120vs	1110	ν (S-O) (ν_3)
	610s	600	ν (S-O) (ν_4)
$K[VO(O_2)_2].K_2SO_4$	950s	960	ν (V=O)
	870s	880	ν (O-O)
	630s	620	ν $(V-O_2)(\nu_3)$
	520m	520	ν $(V-O_2)(\nu_2)$
	1120vs	1105	ν (S-O) (ν_3)
	610s	600	ν (S-O) (ν_4)


$NH_4[VO(O_2)_2]\cdot(NH_4)_2SO_4$
Transmittance (arbitrary scale)
1300
1200
1000
800
600
400
WAVENUMBER(cm^{-1})


$Na[VO(O_2)_2]\cdot Na_2SO_4$
Transmittance (arbitrary scale)
1300
1200
1000
800
600
400
WAVENUMBER(cm^{-1})


K[VO(O2)2]·K2SO4
Transmittance (arbitrary scale)
1300
1200
1000
800
600
400
WAVENUMBER(cm-1)


K[VO(O2)2]·K2SO4
λ = 4880 Å
Raman Intensity
1200
1100
1000
900
800
700
600
500
WAVENUMBER (cm-1)

of SO_4^{2-}. Since these bands fall in the regions typical of an ionic sulphate (T_d) it may be safely assumed that SO_4^{2-} is not co-ordinated to the vanadium centre.

These observations were further augmented by the results of laser Raman spectroscopic studies. These showed ν (V=O) peak at ca 950, ν (O-O) peak at ca 880 (ν_1) and ν ($V-O_2$) peaks at ca 620 (ν_3) and at ca 520 (ν_2) cm^{-1}. The ν_3 and ν_4 modes of ν (S-O), arising from the ionic sulphate were observed at ca 1105 and ca 610 cm^{-1}, respectively.

These results show that the compounds synthesised are oxodiperoxovanadate(V) complexes containing ionic sulphate and the compounds can be best formulated as $A[VO(O_2)_2].A_2SO_4$ ($A = NH_4$, Na or K).

In our attempts to explore the possibility of co-ordination of SO_4^{2-} to vanadium(V) in the presence of peroxide, the reaction of V_2O_5 and alkali thiocyanate, ASCN ($A = NH_4$ or K), was performed in the presence of an excess of hydrogen peroxide at pH 7-8 maintained by the addition of the corresponding AOH. The strategy was that SCN^- would be oxidised to SO_4^{2-} in situ by H_2O_2, and remain co-ordinated to produce mixed ligand peroxo-sulphato compound. Here again yellow microcrystalline products were obtained, and the chemical analysis, IR and Raman spectroscopic studies showed that the compounds were the same, viz., $A[VO(O_2)_2].A_2SO_4$, as those obtained from the reaction of V_2O_5 with H_2O_2 and A_2SO_4 at pH 7-8.

It may be inferred from our above studies that the long searched for yellow alkali metal oxodiperoxovanadates(V), $A[VO(O_2)_2]$ (A = NH_4, Na or K), can be obtained in the solid state under the appropriate experimental conditions. The pH 7-8, of the reaction medium has been found to be conducive to the synthesis. The $[VO(O_2)_2]^-$ ion, in an aqueous solution, undergoes facile addition reactions with F^- and (2,2′-bipy), respectively.

Further, it is evident from the results of our experiments involving vanadium(V), hydrogen peroxide, and SO_4^{2-} or SCN^- that SO_4^{2-} does not co-ordinate to the metal centre at least in the presence of peroxide instead, oxodiperoxovanadates(V) containing ionic SO_4^{2-} are obtained as the end products.

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CHAPTER 4

CHAPTER 4

Synthesis and Characterisation of Glycine Oxodiperoxovanadate(V) Monohydrates, $A[VO(O_2)_2GlyH].H_2O$ (A = NH_4 or K)

Peroxo hetero-ligand transition metal complexes, besides having an intrinsic biological relevance,[1-6] constitute an important class of reactive intermediates in catalytic oxidations,[1,5-10] and are involved as potential oxygen donors in the oxygen transfer reactions to organic substrates including hydrocarbons.[1,8] Because of their important role in biological processes and importance in oxidation chemistry, there has been a recent upsurge in interest in peroxovanadium chemistry and consequently it has emerged as one of the active areas of current research.[8,11-17] As mentioned in Chapter 1, vanadium has been identified as an essential element for mammals.[18,22-24] However, its actual function does not seem to be completely understood.[19,20] In addition, it has been reported recently that some heteroligand peroxovanadate(V) compounds have shown 'antitumour activity'.[21] A perusal of various reports[3,21] clearly indicates that an essential factor in the biochemical activity of peroxoheteroligandvanadates is the heteroligand and also that peroxoheteroligandvanadates(V) behave differently from the corresponding non-peroxo complexes.[21] Thus, a systematic study involving heteroligand peroxovanadium(V) complexes is extremely important.

For more than half a decade our group has engaged its attention to devise synthetic strategies and to make systematic studies of some heteroligand peroxovanadate(V) complexes. The heteroligands ranging from highly electronegative F^- (Ref. 13) or Cl^-, (Ref. 13) CO_3^{2-} (Ref. 25) to bidentate amine ligands[26] have been incorporated into peroxovanadium(V) systems to obtain the corresponding heteroligandperoxovanadates by other workers of the group. As a part of the programme, it was, therefore, imperative to extend such studies to heteroligands which have some biological implications, such as α-amino acids. There has been an increasing interest[27-29] in metal-amino acid complexes which is attributed to their potentials as models for understanding biologically important molecules. It may be pertinent to mention at this stage, as evident from one of the recent reports,[27] that the attempts to synthesise peroxo-α-amino acid complexes of vanadium(V) were unsuccessful. The peroxo α-amino acid vanadium complexes may be considered to be of interest in biochemistry, because it contains three biologically important components: peroxo group, α-amino acid, and vanadium(V). Apart from this they may also show catalytic properties similar to some other peroxovanadium(V) compounds.[1,8]

Accordingly, in a continuation of the work on peroxovanadates(V) described in Chapter 3, it was decided to investigate such complexes containing amino acid as a heteroligand in terms of their method of synthesis, mode of co-ordination of both peroxide as well as the heteroligand, and their stability.

This Chapter presents an account of the synthesis and characterisation of hitherto unreported compounds, alkali glycine-oxodiperoxovanadate(V) monohydrates, $A[VO(O_2)_2GlyH].H_2O$ (A = NH_4 or K).

Experimental

Chemicals used were all reagent grade (SISCO, S.D's, Sarabhai M. Chemicals, Glaxo) products.

Synthesis of Ammonium and Potassium Oxodiperoxoglycine-vanadate(V)Monohydrates, $A[VO(O_2)_2GlyH].H_2O$ (A = NH_4 or K)

As the methods of synthesis of $A[VO(O_2)_2GlyH].H_2O$ compounds are similar, only a representative procedure is described.

Glycine (1.65g, 21.97 mmol) was first dissolved in 30% hydrogen peroxide (20ml, 176.3 mmol). To this was added V_2O_5 (1g, 5.5 mmol) under constant stirring, maintaining the concentration ratio of V : glycine : H_2O_2 as 1 : 2 : 32. Before V_2O_5 was completely dissolved, a small amount of powdered alkali metal hydroxide or aqueous ammonia was added very carefully with stirring until the pH of the solution was adjusted to 3-4. A clear yellow solution was obtained at this stage. The reaction solution was stirred for a further period of ca 10 min to allow the reaction to be complete. The reaction was conducted at an ice-bath temperature. Addition of pre-cooled ethanol to the reaction solution obtained as above caused precipitation of an yellow oily mass which was separated by decantation. The separated mother liquor was treated repeatedly with ethanol to obtain another crop of the yellow oily product. The two lots of yellow oily mass thus obtained were combined together, treated repeatedly with acetone-ethanol (3:1) mixture until it became solid. The solid alkali oxodiperoxoglycinevanadate(V)monohydrate, $A[VO(O_2)_2GlyH].H_2O$ ($A = NH_4$ *or* K), compound was separated by centrifugation, washed with ethanol, and dried in vacuo over conc. sulphuric acid.

The yields of $NH_4[VO(O_2)_2GlyH].H_2O$ and $K[VO(O_2)_2GlyH].H_2O$ were 1.8g (67%) and 2.1g (72%), respectively.

Elemental Analyses

Quantitative estimations of vanadium, peroxide, carbon, hydrogen, nitrogen, and potassium were accomplished by the methods descibed in Chapter 2. The analytical data of the compounds are summarised in Table 4-1.

Results and Discussion

The reaction of vanadium with hydrogen peroxide is highly pH dependent, and a small variation of pH of the reaction solutions leads to the formation of peroxovanadium complexes of varied compositions. The importance of pH, for the successful synthesis of peroxo-metal compounds as mentioned in Chapter 3, has been

Table 4-1. Analytical Data of $A_2[VO(O_2)_2GlyH].H_2O$ (A = NH_4 or K)

Compound	Found % (Calcd. %)				
	V	O[a]	C	H	N
$NH_4[VO(O_2)_2GlyH].H_2O$	20.85 (21.07)	26.13 (26.44)	10.04 (9.92)	4.33 (4.54)	11.92 (11.57)
$K[VO(O_2)_2GlyH].H_2O$	18.92 (19.39)	24.14 (24.33)	9.26 (9.12)	2.61 (2.66)	5.39 (5.32)

[a] Peroxo-oxygen

emphasised in the literature.[13,30] In the present synthesis, the suitable pH for bringing about co-ordination of both peroxide and the amino acid with oxovanadate(V) centre was ascertained to be 3-4. It is imperative to mention that the products isolated at relatively higher pH do not show the presence of glycine which indicates that $pH > 4$ is not conducive to the desired synthesis. It is also equally important to mention that the order of addition of the reactants as mentioned in the experimental section is necessary to maintain in order to achieve success. Reactions carried out starting from a hydrogen peroxide solution of V_2O_5 followed by the addition of glycine (GlyH) and maintaining the other conditions similar to those described herein did not produce the compounds searched for. Thus the reaction of V_2O_5 with H_2O_2 and glycine (GlyH) at pH 3-4 of the reaction solution, maintained by the addition of potassium hydroxide or aqueous ammonia, followed by the addition of ethanol (vide Experimental) afforded alkali oxodiperoxoglycinevanadate(V) complexes. The reaction was monitored by isolating a small amount of the product from the reaction solution and recording its IR spectrum. Appearance of a strong band at ca 860 cm^{-1} due to the ν (0-0) mode of co-ordinated peroxide (O_2^{2-}), and the bands due to the occurrence of glycine indicates the formation of the complex species. The role of ethanol is similar to that explained in Chapter 3. Our attempts to synthesise sodium salt of the complex $[VO(O_2)_2GlyH]^-$ ion have not been successful so far.

The $A[VO(O_2)_2GlyH].H_2O$ ($A = NH_4$ or K) compounds are yellow microcrystalline products, and are hygroscopic in nature. The compounds are soluble in water at ambient temperatures, but the dissolution is accompanied by simultaneous decomposition and their molar conductance measurements were thus precluded. Unlike some other heteroligand peroxovanadate(V) compounds,[13,26] the peroxovanadium(V) complexes containing an amino acid as the heteroligand are not very stable for a prolonged period.

In an attempt to find out the possibility of removal of lattice water of $A[VO(O_2)_2GlyH].H_2O$ compounds, pyrolysis of the compounds were carried out at 100°C. Unfortunately the compounds started undergoing decomposition involving the simultaneous loss of both peroxide (O_2^{2-}) and H_2O, thus a genuine dehydration was not possible.

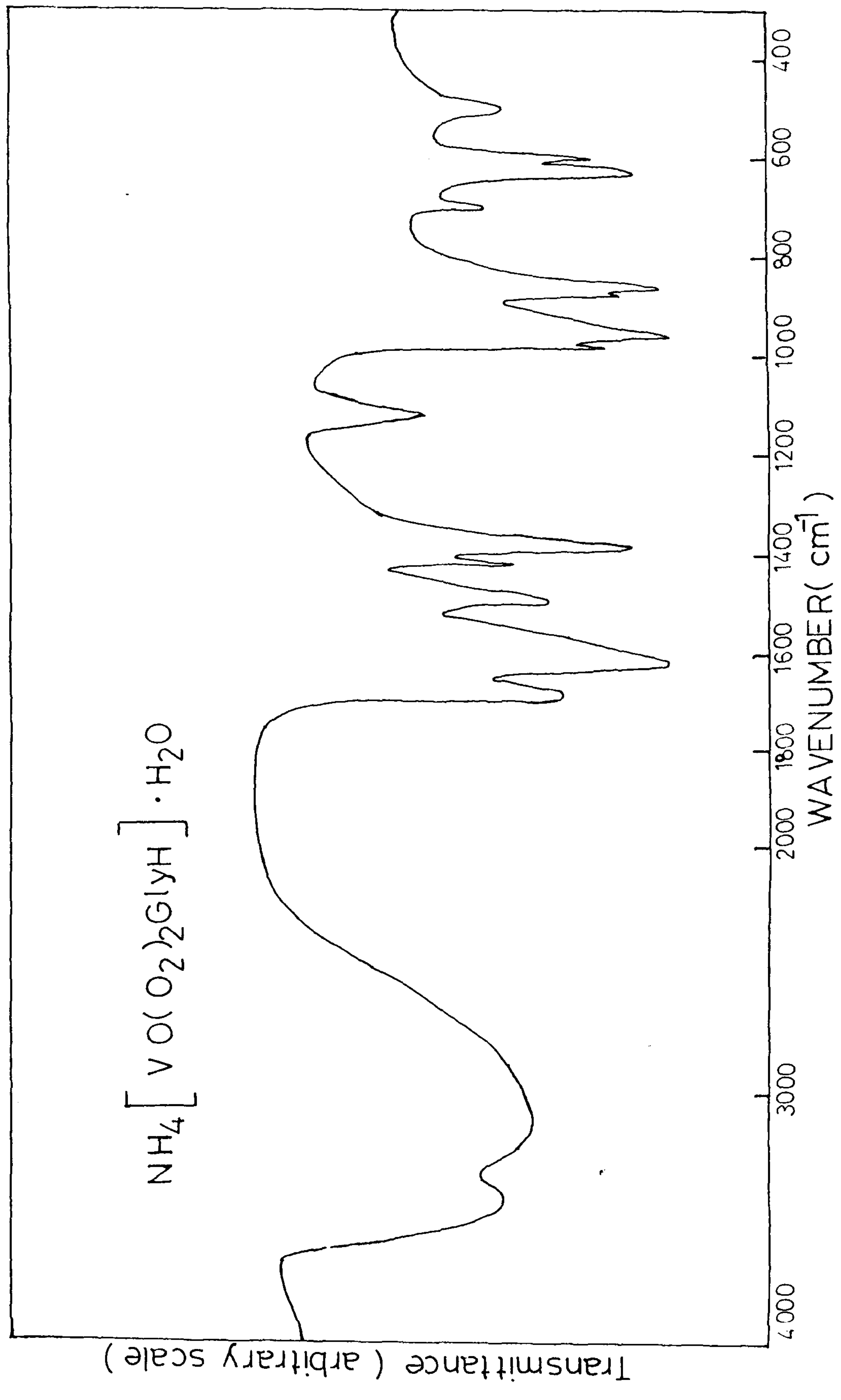
The $A[VO(O_2)_2GlyH].H_2O$ compounds were diamagnetic in nature, as evident from the results of magnetic susceptibility measurements, in conformity with the occurrence of vanadium(V) in each of them. The compounds were also ESR silent. The peroxide estimation were accomplished by redox titrations separately involving standard potassium permanganate and Ce^{4+} solutions by following the procedures described in Chapter 2. The results obtained thereof conspicuously suggest the presence of two peroxides per vanadium(V) centre in each of the newly synthesised compounds.

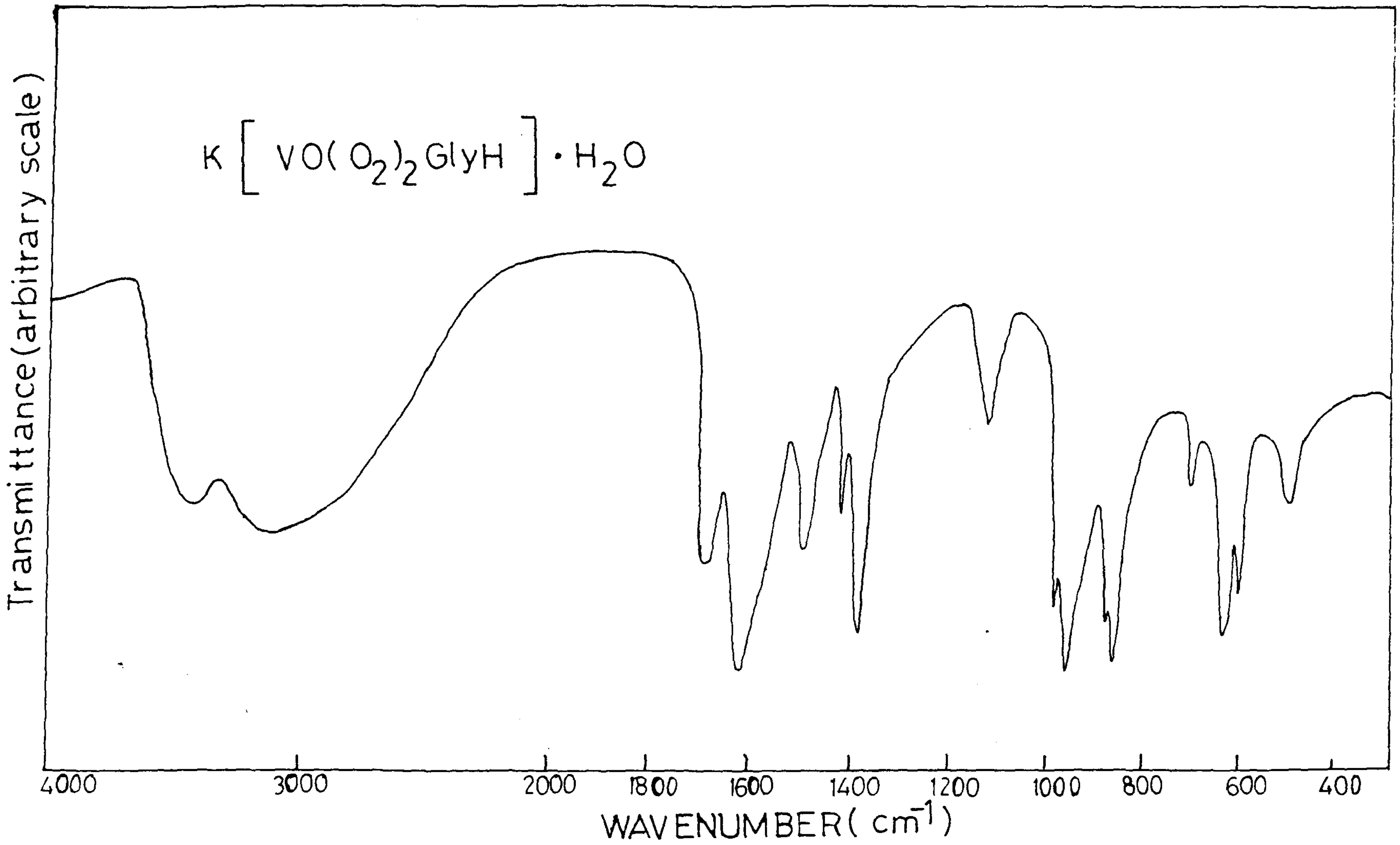
The significant features of the IR spectra of the $A[VO(O_2)_2GlyH].H_2O$ ($A = NH_4$ or K) compounds involve absorptions due to ν (V=O), co-ordinated peroxide, and co-ordinated glycine

(GlyH) ligands. The strong bands at *ca* 960 cm^{-1} has been assigned to ν (V=O) arising from the terminally bonded V=O group. The bands at *ca* 850, *ca* 605, *ca* 510 cm^{-1} owe their origins to the co-ordinated peroxide groups.[31] The typical pattern of the spectra suggests that each of the O_2^{2-} ligands is bonded to the vanadium centre in a triangular bidentate (C_{2v}) manner. Amino acids are known to form complexes with metals in either the neutral zwitterionic form or in the anionic form, however, the anionic form is by far the most common among the published monomeric solid structure. The frequencies observed at *ca* 1630s, *ca* 1395s, *ca* 1120m, *ca* 690m, and *ca* 595 cm^{-1} are due to $\nu_{as}(COO^-)$, $\nu_s(COO^-)$, $\rho_r(NH_3^+)$, $\rho_w(COO^-)$, and $\delta(COO^-)$ modes, respectively, of the co-ordinated glycine.[29,32] Notably important are the (i) increase in $\nu_{as}(COO^-)$, (ii) decrease of $\nu_s(COO^-)$, and (iii) unaltered positions of N-H stretching frequency as compared to an unco-ordinated glycine. The observations in the present case as stated above cause us to state that glycine in the $A[VO(O_2)_2GlyH].H_2O$ compounds occurs in the zwitterionic form ($NH_3^+CH_2COO^-$), and is bonded to the metal centre through its carboxylic oxygen.[29,33] Thus although glycine can act as a bidentate ligand, in the present case it appears that this ligand acts as a monodentate one being bonded in a fashion described above. The chelation is probably prevented due to steric requirements. This kind of bonding of glycine via oxygen, and their co-ordination as zwitterions, which is an interesting structural feature in these complexes, is not very common, however, is not unprecendentate in chemical literature.[27,29,33]

Table 4-2. Structurally Significant IR Bands of $A[VO(O_2)_2GlyH].H_2O$ (A = NH_4, K)

Compound	IR cm^{-1}	Assignment
$NH_4[VO(O_2)_2GlyH].H_2O$	955s	ν (V=O)
	850s	ν (O-O) ν_1
	605s	ν (V-O_2) ν_3
	510m	ν (V-O_2) ν_2
	1630s	ν_{as}(COO^-)
	1495s	δ_s(NH_3^+)
	1430s	δ (CH_2)
	1390s	ν_s (COO^-)
	1125m	ρ_r (NH_3^+)
	680m	ρ_w (COO^-)
	590s	δ (COO^-)
	1650m	δ (H-O-H)
	3395s	ν (O-H)
$K[VO(O_2)_2GlyH].H_2O$	960s	ν (V=O)
	855s	ν (O-O) ν_1
	600s	ν (V-O_2) ν_3
	510m	ν (V-O_2) ν_2
	1630s	ν_{as}(COO^-)
	1500s	δ_s (NH_3^+)
	1427s	δ (CH_2)
	1395s	ν_s (COO^-)
	1120m	ρ_r (NH_3^+)
	700m	ρ_w (COO^-)
	597s	δ (COO^-)
	1658m	δ (H-O-H)
	3420s	ν (O-H)


$NH_4[VO(O_2)_2GlyH] \cdot H_2O$
Transmittance (arbitrary scale)
WAVENUMBER(cm^{-1})
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400


K [VO(O2)2GlyH] · H2O
Transmittance (arbitrary scale)
WAVENUMBER (cm-1)
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400

This may be explained in terms of a high stability of the oxodiperoxovanadate(V) moiety, due to which it probably directs the selection and orientation of additional heteroligand attached to the vanadium(V) centre displaying preference for oxygen over nitrogen.

The two additional bands at ca 1658 and ca 3410 cm^{-1} in each of the ammonium and potassium salts resemble in their shapes and positions those commonly observed for the unco-ordinated water and have been assigned to δ(H-O-H) and ν (O-H) modes, respectively. The region in which the ν (O-H) band has been observed in the present case is rather typical of lattice water.[34] These observations clearly suggest that the water molecule is not co-ordinated to the metal centre.

We conclude from our results that heretofore unknown glycineperoxovanadates(V) of the type $A[VO(O_2)_2GlyH].H_2O$ can be synthesised directly from the reaction of V_2O_5 with glycine and hydrogen peroxide at pH 3-4. The pattern of the IR spectra, due to the co-ordinated peroxide (O_2^{2-}), and the co-ordinated glycine ligands, renders it certain that peroxide (O_2^{2-}) ligand is co-ordinated to the vanadium(V) centre in a chelated (C_{2v}) fashion, whereas glycine binds the vanadium(V) as zwitterions via oxygen. The complex $[VO(O_2)_2GlyH]^-$ ion may have a distorted octahedral structure.

It may be mentioned here that further studies on synthesis and reactivity of peroxo α-amino acid complexes are in progress and will be reported elsewhere.

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CHAPTER 5

CHAPTER 5

Synthesis and Structural Assessment of Alkali Triperoxovanadates(V), $A[V(O_2)_3]$ (A = Na or K)

And

Reactions of $A[V(O_2)_3].3H_2O$ (A = Na or K) with an Inorganic Polar Substrate $SO_2(g)$*

The importance of and the interests in peroxo transition metal compounds which rendered them the focus of one of the active areas of contemporary research have been emphasised in the literature[1-9] and highlighted in Chapter 1, as well as in Chapters 3 and 4. Many transition metals, of which vanadium is not an exception, give colour reactions with hydrogen peroxide owing to the formation of complex peroxo-metal species in solutions. Unfortunately not many of them were obtained in the solid state probably because of their instability as solids or might as well be due to the lack of suitable synthetic methods. It is evident from the literature[10,11] that under varying pH conditions of solutions vanadium forms at least four different peroxovanadate(V) species, viz., $[VO(O_2)]^+$, $[VO(O_2)_2]^-$, $[VO_2(O_2)_2]^{3-}$ and $[VO(O_2)_3]^{3-}$. A blue tetraperoxovanadate(V) complex, $K_3[V(O_2)_4]$ has been known[12] only in the solid state, presumably having a dodecahedral structure analogous to

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*A part of the work described in this Chapter has been published: Inorg.Chem., 1985, 24, 2706.

that of $K_3[Cr(O_2)_4]$ compound.[13] However, there seems to be no reported evidence in regard to the formation of blue vanadium(V)-peroxide species in solutions.[14-19] First in 1982[20] and then in 1984,[21] it has been shown by isolating in the solid state, that quinquevalent vanadium can form blue peroxo compounds in the presence of a heteroligand like F^- or Cl^- containing three peroxo groups and one F^- or Cl^-, co-ordinated to vanadium(V) per formula unit. The question regarding the minimum number of peroxo groups required for the formation of a blue peroxovanadate(V) remained unanswered. We felt that the synthesis and isolation of blue $[V(O_2)_3]^-$ species will not only provide a piece of fundamental information in the field of peroxo-vanadium chemistry but also will offer an unequivocal answer to the question refered to above.

Further, any information concerning the reactivity of co-ordinated dioxygen is highly relevant in understanding the processes involved in the activation of molecular oxygen by metalloenzymes in biological systems. The synthesis of well defined transition metal peroxides followed by the study of their oxidising properties also provide a heuristic approach to the understanding of catalytic oxidation reactions. The reactivity of co-ordinated dioxygen ligand in low-oxidation state transition metal (especially group VIII transition metals) complexes have been investigated in recent years,[22-33] particularly their reactions with carbonyl compounds,[34,35] olefins,[36-39] carbon dioxide[35] and sulphur dioxide.[23-30,33,36] In most of these reactions the co-ordinated dioxygen behaves as a nucleophile.[36] It is evident from the earlier reports that the reaction of SO_2 with the co-ordinated peroxo group in the above type of complexes show a characteristic reactivity, i.e. they react with SO_2 to give sulphate.[23,33,36] Theoretical investigations were also carried out on the mechanistic details of the steps involved in the ultimate formation of co-ordinated sulphate.[32] However, to the best of our knowledge, except for Ti,[33] no work in this field seems to have been reported concerning non group VIII transition metal complexes leaving some fundamental questions, like their ability to oxidise similar substrates, mode of bonding of the oxidised substrate to the metal etc., still open. Behaviour of other potential peroxo metal complexes like those of vanadium with similar reagents under varying experimental conditions have not received much attention. Also, all such reactivity studies involve complexes which contain not more than one peroxo group co-ordinated to the metal centre. It therefore appeared logical to us to study the reactivity of the inorganic polar species, SO_2 with vanadium compounds containing more than one peroxo groups, which may enable one to rationalise the sequential reactions of the peroxo groups in the parent compound. The interest was also to see whether the co-ordinated peroxide or the metal centre reacted with SO_2 in preference, when both were susceptible to attack by SO_2. Such studies might also provide scope for synthesis of newer compounds of vanadium having heteroligand systems.

As an extension of the above mentioned reactivity studies we thought it relevant also to carry out the aforesaid type of reactions in presence of suitable ligand, viz., F^- in order to explore the feasibility of formation of ternary complexes of vanadium.

The present Chapter reports the synthesis, isolation in the solid state, and characterisation of the blue alkali-metal triperoxovanadate(V), $A[V(O_2)_3]$ (A = Na or K). Also reported in this Chapter are the results of the studies of reactivity of $SO_2(g)$ with $A[V(O_2)_3].3H_2O$. The reactions of SO_2 with $A[V(O_2)_3].3H_2O$ in aqueous solution have been shown to afford newer information, and the products isolated from such reactions have been identified as the salts of $[VO(O_2)_2.H_2O]^-$ and $[VO(SO_4)_2(H_2O)_3]^{2-}$ species. Similar reaction when carried out in the presence of AF (A = Na or K) afforded the synthesis of novel ternary complexes of VO^{2+}, $A_4[VO(SO_4)_2F_2(H_2O)].2H_2O$.

Experimental

The chemicals used were all analytical/guaranted reagents (SISCO, Thomas Baker, Glaxo).

(i) Synthesis of Alkali Metal Triperoxovanadates(V), $A[V(O_2)_3]$ (A = Na or K)

As the methods of syntheses of the $A[V(O_2)_3]$ compounds are similar, only a representative procedure is described.

To finely powdered V_2O_5 was added an excess of 30% hydrogen peroxide, with slow stirring, in the molar ratio of $V_2O_5:H_2O_2$ as 1:42.5. Solid alkali metal hydroxide, AOH, was slowly added to the above mixture under continuous stirring until a blue colour was developed (molar ratio $V_2O_5:H_2O_2$:AOH as 1:42.5:(10-12)). The blue solution was then cooled in an ice-water bath for *ca* 10 min, followed by the addition of an excess of precooled ethyl alcohol until the blue microcrystalline $A[V(O_2)_3]$ ceased to appear. The blue compound was separated by centrifugation, washed four or five times with cold ethanol and finally dried *in vacuo* over P_4O_{10}. When the compounds were dried *in vacuo* over conc. H_2SO_4 the hydrated complex, $A[V(O_2)_3].3H_2O$ was obtained. The reaction was monitored by IR spectroscopy. The complete disappearance of the sharp band at *ca* 950 cm^{-1} due to ν (V=O), in the product isolated from a small amount of the blue solution, indicates completion of the reaction.

The amounts of the reagents used and yields of the products are given in Table 5-1.

Table 5-1. Amounts of Reagents Used and Yields of $A[V(O_2)_3]$ (A = Na or K)

Compound	Yield g(%)	Amount of V_2O_5 g (mmol)	Amount of 30% H_2O_2 cm^3(mmol)	Amount of of AOH (mmol)
$Na[V(O_2)_3]$	0.8(86)	0.5(2.7)	13(114.6)	1.1(27.5)
$K[V(O_2)_3]$	0.9(90)	0.5(2.7)	13(114.6)	1.8(32)

(ii) Reaction of $A[V(O_2)_3].3H_2O$ (A = Na or K) with $SO_2(g)$

(a) Isolation of Yellow $K[VO(O_2)_2.H_2O]$

The deep blue microcrystalline $K[V(O_2)_3].3H_2O$ (1.5g. 6.25 mmol) was dissolved in 10 cm^3 of water. $SO_2(g)$ was slowly bubbled through the blue solution with occassional shaking of the contents of the flask until the solution attained a uniform yellow colour (ca 10 min) and thwarting out a yellow microcrystalline product. The pH of the solution recorded at this stage was 6-7. The compound was separated by filtration, washed repeatedly with ethanol and finally dried in vacuo over concentrated H_2SO_4. The product was analysed as $K[VO(O_2)_2.H_2O]$.

Yield of the compound was noted to be 0.8g (70%).

(b) Isolation of Blue $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ (A = Na or K)

$A[V(O_2)_3].3H_2O$ (6.6 mmol) was dissolved in 10 cm^3 of water. Bubbling of $SO_2(g)$ through this solution over a period of ca 20 min resulted in different colour changes. First, the solution changes colour from deep blue to yellow, then to deep green and ultimately to a blue colour which does not undergo anymore colour change on further bubbling of $SO_2(g)$. The pH of the solution at this stage was recorded to be ca 2. Bubbling of $SO_2(g)$ was stopped and the solution was filtered to remove any undissolved residue. To the clear solution ethanol was added slowly until the formation of a blue oily mass was observed. Addition of an excess of ethanol is detrimental as this gives rise to the contamination of the product with white alkali metal sulphate, A_2SO_4. The blue oily mass was separated by decantation and treated several times with ethanol-acetone (1:1) mixture, and finally dried in vacuo over concentrated H_2SO_4 to afford blue solid $A_2[VO(SO_4)_2(H_2O)_3].H_2O$.

Yields of $Na_2[VO(SO_4)_2(H_2O)_3],H_2O$ and $K_2[VO(SO_4)_2(H_2O)_3].H_2O$ were 1.2g (48%) and 1.3g (51%), respectively.

The reaction was monitored by ESR spectrometry. Whereas the deep blue solution of $A[V(O_2)_3].3H_2O$ was completely ESR silent as expected, the ultimate blue solution, obtained after SO_2(g) reaction, was ESR active giving characteristic signals of vanadium(IV).

(iii) Reaction of $A[V(O_2)_3].3H_2O$ (A = Na or K) with SO_2(g) in the Presence of AF (A = Na or K) and Synthesis of Ternary Complexes $A_4[VO(SO_4)_2F_2(H_2O)].2H_2O$ (A = Na or K)

$A[V(O_2)_3].3H_2O$ (6.6 mmol) and AF (13.3 mmol) were dissolved in about 15 cm^3 of water maintaining the molar ratio between V:F at 1:2, SO_2(g) was bubbled through this solution in a manner similar to that described under the preceding reaction. The colour changes were also similar to those observed therein. Here again, the ultimate blue solution was found to be ESR active (cf. vanadium(IV)). The blue solution was worked up in an analogous manner as described earlier for the isolation of $A_2[VO(SO_4)_2(H_2O)_3].H_2O$. The products obtained in the present reactions have been analysed as blue $A_4[VO(SO_4)_2F_2.H_2O].2H_2O$.

Yield of $Na_4[VO(SO_4)_2F_2(H_2O)].2H_2O$ and $K_4[VO(SO_4)_2F_2(H_2O)].2H_2O$ were found to be 1.5g (52%) and 1.6g (49%), respectively.

Elemental Analyses

The quantitative estimations of vanadium, peroxide, sulphate, fluoride, sodium and potassium were made by the methods described in Chapter 2. The analytical data of the compounds are summarised in Tables 5-2 and 5-3.

Results and Discussion

Although there has been a continued interest in the peroxovanadium chemistry,[3,4,7,8,14-19] there seems to be a paucity of information on synthesis, isolation in the solid state, characterisation, and structural assessment of peroxovanadate compounds. From our studies on peroxovanadates it is evident that the judicial addition of the alkaline media to a vanadium(V) —— H_2O_2 mixture gives rise to the formation of both yellow (Chapter 3) and blue coloured peroxovanadate(V) species (reported in this Chapter) in solution. The synthesis of blue alkali metal triperoxovanadates(V), $A[V(O_2)_3]$ (A = Na or K), has been achieved from the reaction of V_2O_5 with 30% H_2O_2 in the presence of a relatively large concentration of alkaline medium with molar ratio of $V_2O_5:H_2O_2:AOH$ being maintained at 1:42.5:(10-12). A high concentration of AOH is necessary for and conducive to the formation and then isolation of $A[V(O_2)_3]$ compounds. Although the vanadium(V) —— H_2O_2 solution assumes a blue colour

Table 5-2. Analytical Data and Molar Conductance Values of $A[V(O_2)_3]$ (A = Na or K)

Compound	Molar Conductance $\Omega^{-1}cm^2mol^{-1}$	Found % (Calcd %)		
		A	V	O^a
$Na[V(O_2)_3]$	135	13.8 (13.53)	30.4 (29.98)	55.8 (56.49)
$K[V(O_2)_3]$	140	21.2 (21.02)	27.8 (27.38)	52.1 (51.6)

[a] Peroxo Oxygen

Table 5-3. Analytical Data and Molar Conductance Values of $K[VO(O_2)_2(H_2O)]$, $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ (A = Na or K), and $A_4[VO(SO_4)_2F_2(H_2O)].2H_2O$ (A = Na or K)

Compound	Molar conductance $\Omega^{-1}cm^2mol^{-1}$	Found % (Calcd. %)				
		A	V	O^a	SO_4	F
$K[VO(O_2)_2(H_2O)]$	135	20.33 (20.74)	26.92 (27.13)	33.88 (34.04)	-	-
$Na_2[VO(SO_4)_2(H_2O)_3].H_2O$	262	12.36 (12.20)	13.24 (13.52)	-	51.18 (50.92)	-
$K_2[VO(SO_4)_2(H_2O)_3].H_2O$	255	18.88 (19.07)	12.12 (12.46)	-	47.3 (46.94)	-
$Na_4[VO(SO_4)_2F_2(H_2O)].2H_2O$	522	20.39 (20.76)	11.43 (11.51)	-	43.81 (43.34)	8.61 (8.57)
$K_4[VO(SO_4)_2F_2(H_2O)].2H_2O$	510	31.01 (30.8)	9.89 (10.06)	- -	37.2 (37.86)	7.6 (7.49)

at a relatively lower concentration of AOH, the IR spectrum of the product isolated from it shows a band at ca 950 cm^{-1} owing to ν (V=O) in addition to those expected for the co-ordinated O_2^{2-}. This suggests that the formation of the triperoxovanadate(V), $[V(O_2)_3]^-$, complex is not complete; thus it is required to add a further amount of alkali-metal hydroxide after the first appearance of blue colour, however, not beyond the stipulated limit (vide Experimental). It may be noted that the change of colour of vanadium — H_2O_2 solution with the increase in concentration of alkaline medium from yellow to blue clearly indicates that the complex $[VO(O_2)_2]^-$ is first formed and then ultimately converted to the $[V(O_2)_3]^-$ complex. The complete disappearance of the ν (V=O) at ca 950 cm^{-1} in the IR and LR spectra of the compound isolated from the reaction solution ensures completion of the reaction. The fact that a very high concentration of the alkaline medium leads to the formation of the triperoxo species $[V(O_2)_3]^-$ while the relatively lower concentration of alkaline medium produces $[VO(O_2)_2]^-$ (vide Chapter 3) suggests that a very high alkaline medium probably helps replacement of the last oxygen from the $[VO(O_2)_2]^-$ by a O_2^{2-} group, thereby favouring the formation of $[V(O_2)_3]^-$, or that the oxo oxygen of the $[VO(O_2)_2]^-$ species is converted to the third peroxy ligand by abstracting an oxygen of hydrogen peroxide. It is difficult for us to say, in the absence of any direct evidence, which of the two mechanisms is more probable. However, the fact that oxygen exchange on vanadium(V) is very slow[18] and the strength of the V—O multiple bond is high, as evident from the IR spectroscopic studies of oxovanadium(V) complexes,[22,40] indicates that the latter mechanism may be more likely. The $A[V(O_2)_3]$ compounds were obtained by the addition of ethanol to the reaction solution. Attempts to synthesise $NH_4[V(O_2)_3]$ were futile. Although a transitory blue solution was obtained by the addition of aqueous ammonia (specific gravity 0.9), the colour was practically discharged, with brisk evolution of oxygen, during work up. It is worthwhile to mention that the tetraperoxovanadate(V), $[V(O_2)_4]^{3-}$ complex, as opposed to the triperoxo species, is formed only at temperatures below 0°C presumably in the presence of a relatively higher amount of alkaline medium.

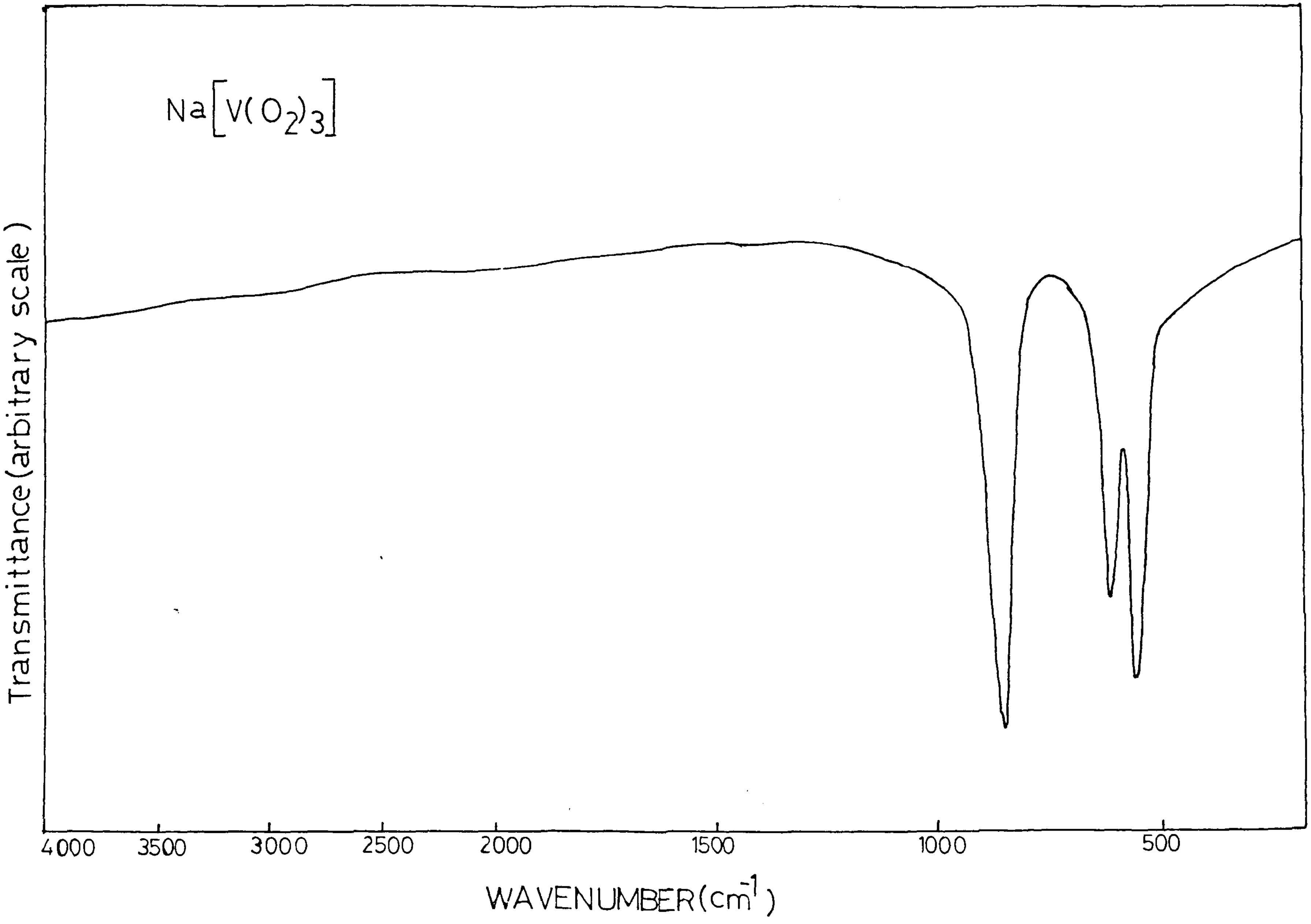
The blue triperoxovanadates(V), $A[V(O_2)_3]$ (A = Na or K) are diamagnetic and ESR silent in line with the occurrence of quinquevalent vanadium and, unlike the $A_2[V(O_2)_3X]$ ($X = F^-$ or Cl^-)[20,21] and $A_3[V(O_2)_4]$[12] compounds, are stable in water. Whereas $A_2[V(O_2)_3X]$ and $A_3[V(O_2)_4]$ do not permit molar conductance measurements, the values for the $A[V(O_2)_3]$ compounds, at ambient temperatures, were found to lie in the range 130-140 $\Omega^{-1}cm^2mol^{-1}$, suggesting their 1:1 electrolytic nature, in complete agreement with the formula. The chemical determination of active oxygen contents in such compounds is extremely important and this has been emphasised in the preceding Chapters. The results of peroxide determination accomplished in similar ways as mentioned in Chapters 2 and 3, conspicuously suggested the occurrence of three peroxide groups per vanadium(V) centre in each of the new compounds.

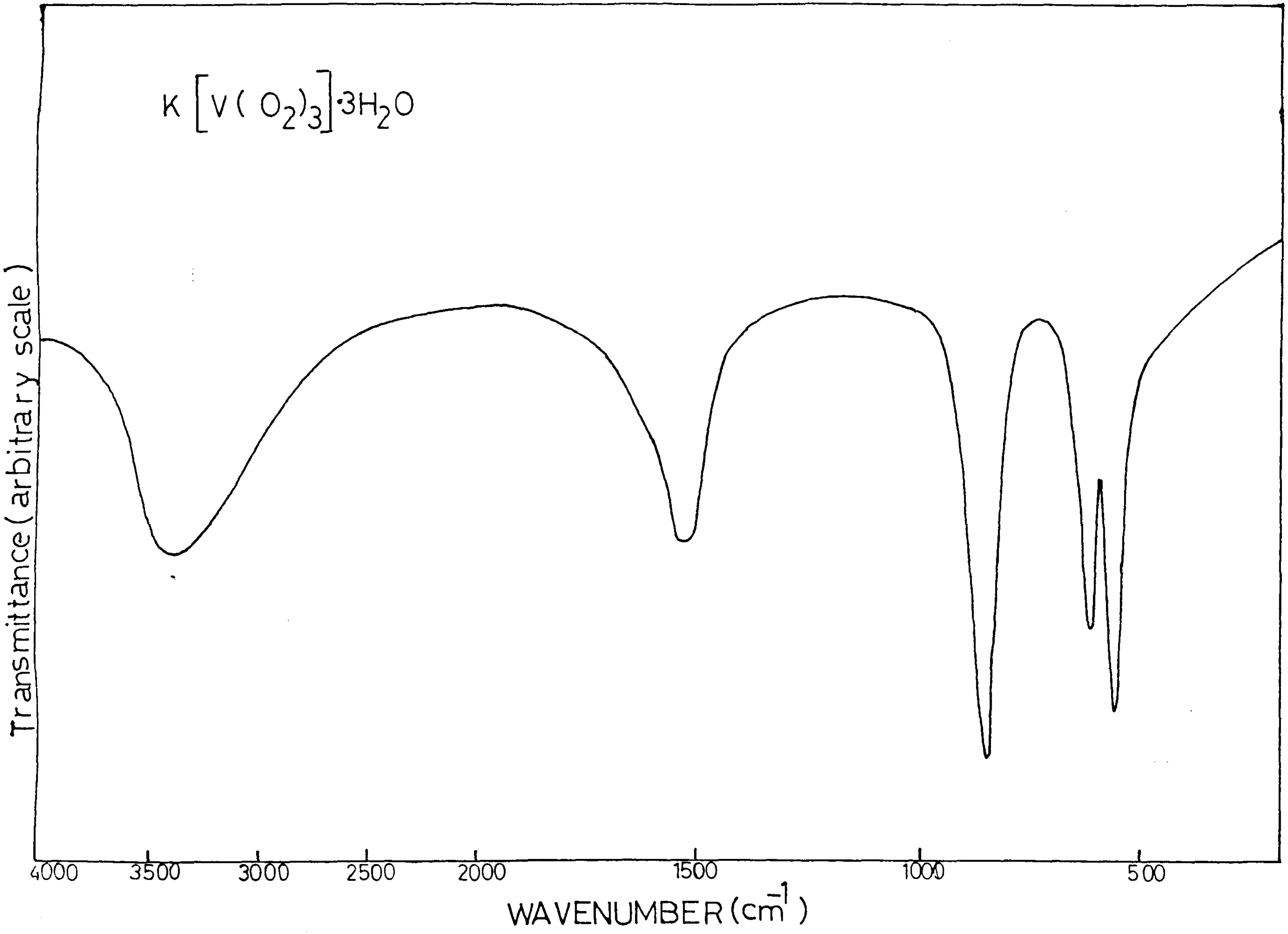
The UV-vis spectra of the solutions recorded before isolation of the compound and that obtained by redissolving the compound were similar and showed absorptions at 560 and 192 nm with molar absorption co-efficients being 84.3 and 1.04 x 10^4, respectively. This indicates that the complex species formed in solution and that isolated in the solid state are identical. The electronic spectral data for $[V(O_2)_4]^{3-}$ are not available in the literature, thus precluding comparison with those of $[V(O_2)_3]^-$.

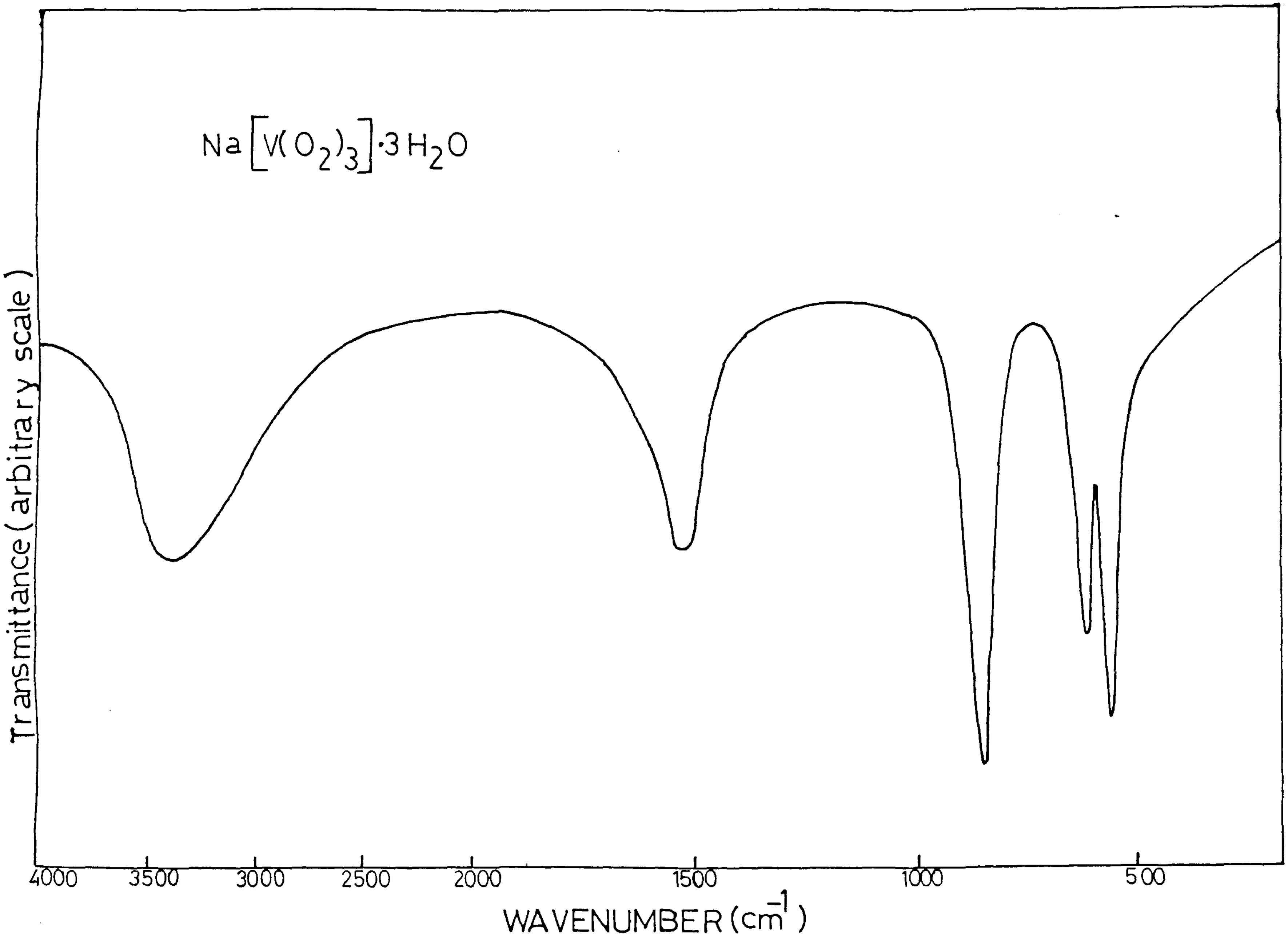
The characteristic features of the IR and LR (Table 5-4) are the absorptions at ca 850 cm^{-1} owing to ν (O-O)[41,42] and the two absorptions at ca 600 and ca 530 cm^{-1} due to ν $(V-O_2)$[41,42] with all three originating from the co-ordinated peroxide groups. The typical pattern of the spectra suggests that each of the O_2^{2-} ligands is bonded to the vanadium(V) centre in a triangular bidentate manner. Considering C_{2v} to be the local symmetry of a co-ordinated O_2^{2-} group, three vibrations, viz., ν (O-O)ν_1, ν $(V-O_2)\nu_2$ and ν $(V-O_2)\nu_3$ are expected to be both IR and Raman active, with the ν_1 and ν_2 modes being polarised in the latter and appearing comparatively more sharp and intense than the ν_3 mode. Accordingly, the LR signals at ca 850s, ca 530, and ca 600 cm^{-1} have been assigned, respectively, to the ν_1, ν_2 and ν_3

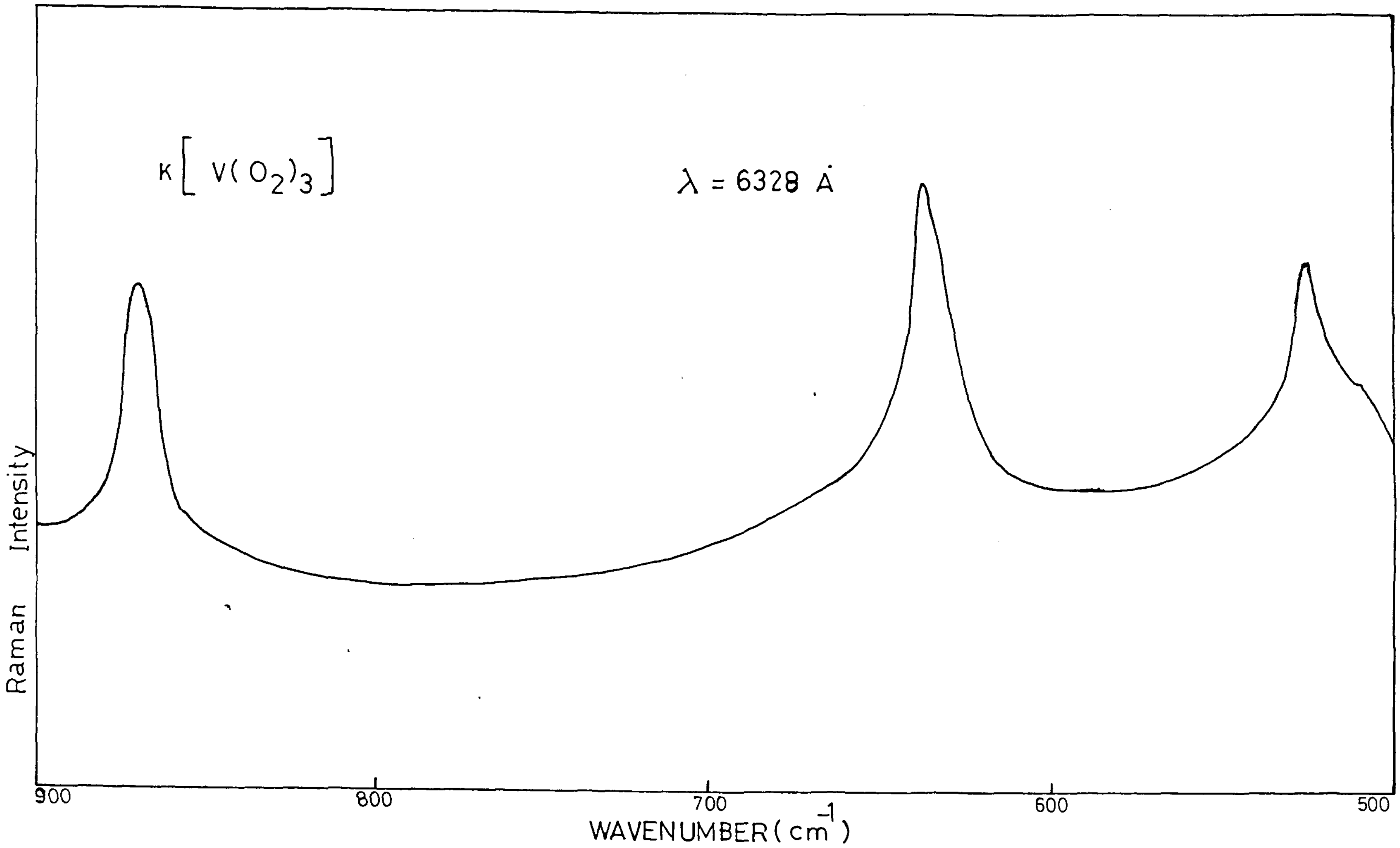
Table 5-4. Structurally Significant IR and Raman Bands of $A[V(O_2)_3]$ (A = Na or K)

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$Na[V(O_2)_3]$	855s 610s 525s	850 600 530	ν (O-O) ν_1 ν $(V-O_2)$ ν_3 ν $(V-O_2)$ ν_2
$K[V(O_2)_3]$	855s 610s 530s	860 610 530	ν (O-O) ν_1 ν $(V-O_2)$ ν_3 ν $(V-O_2)$ ν_2


Na$[V(O_2)_3]$
Transmittance (arbitrary scale)
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER (cm^{-1})


K $[V(O_2)_3]\cdot 3H_2O$
Transmittance (arbitrary scale)
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER (cm^{-1})


Na[V(O2)3]·3H2O
Transmittance (arbitrary scale)
4000
3500
3000
2500
2000
1500
1000
500
WAVENUMBER (cm-1)


K[V(O₂)₃]
λ = 6328 Å
Raman Intensity
900
800
700
600
500
WAVENUMBER (cm⁻¹)

modes of the co-ordinated O_2^{2-} ligands. The absence of any band at 950 cm^{-1} due to ν (V=O), especially in the LR spectra in which it would be strong on account of large polarisability changes involved in the V-O bond, renders it certain that the complex does not contain any V=O group.

Reactions of $A[V(O_2)_3].3H_2O$ (A = Na or K) with $SO_2(g)$

As a part of our research programme involving peroxo-vanadium chemistry we were interested to study the reactivity of the above peroxo-vanadium(V) complex with $SO_2(g)$ and to follow up the reaction sequence through the isolation of compounds at various stages of the reactions. It may be recalled that the metal centre in the present case (vanadium(V)) is also susceptible to attack by the chosen inorganic polar system, SO_2. Of some concern was also to explore the possibility of synthesising mixed-ligand peroxo-sulphato compounds of vanadium(V), assuming that SO_2 would undergo insertion reaction[23,32,36] into the O-O bond of peroxo group whereas M-O bond will remain intact giving rise to *in situ* oxidation of SO_2 to SO_4^{2-} and its co-ordination to the metal centre.

Strategically the reactions were conducted in an aqueous medium because most of the earlier studies,[23,33] as evident from the previous reports by other workers, were carried out in non-aqueous medium presumably owing to the problems of solubility and stability of the compounds in aqueous solution. Fortunately, triperoxovanadate(V) compounds are not only soluble in water but also they are stable at least under our experimental conditions.

The deep blue $A[V(O_2)_3].3H_2O$ complexes dissolved in water reacted readily with SO_2(g) which was evident from the colour changes of the solution from deep blue to yellow and ultimately to a green-blue colour. At each stage of colour change the flow of SO_2(g) was stopped and attempt was made to isolate the reaction product in the solid state.

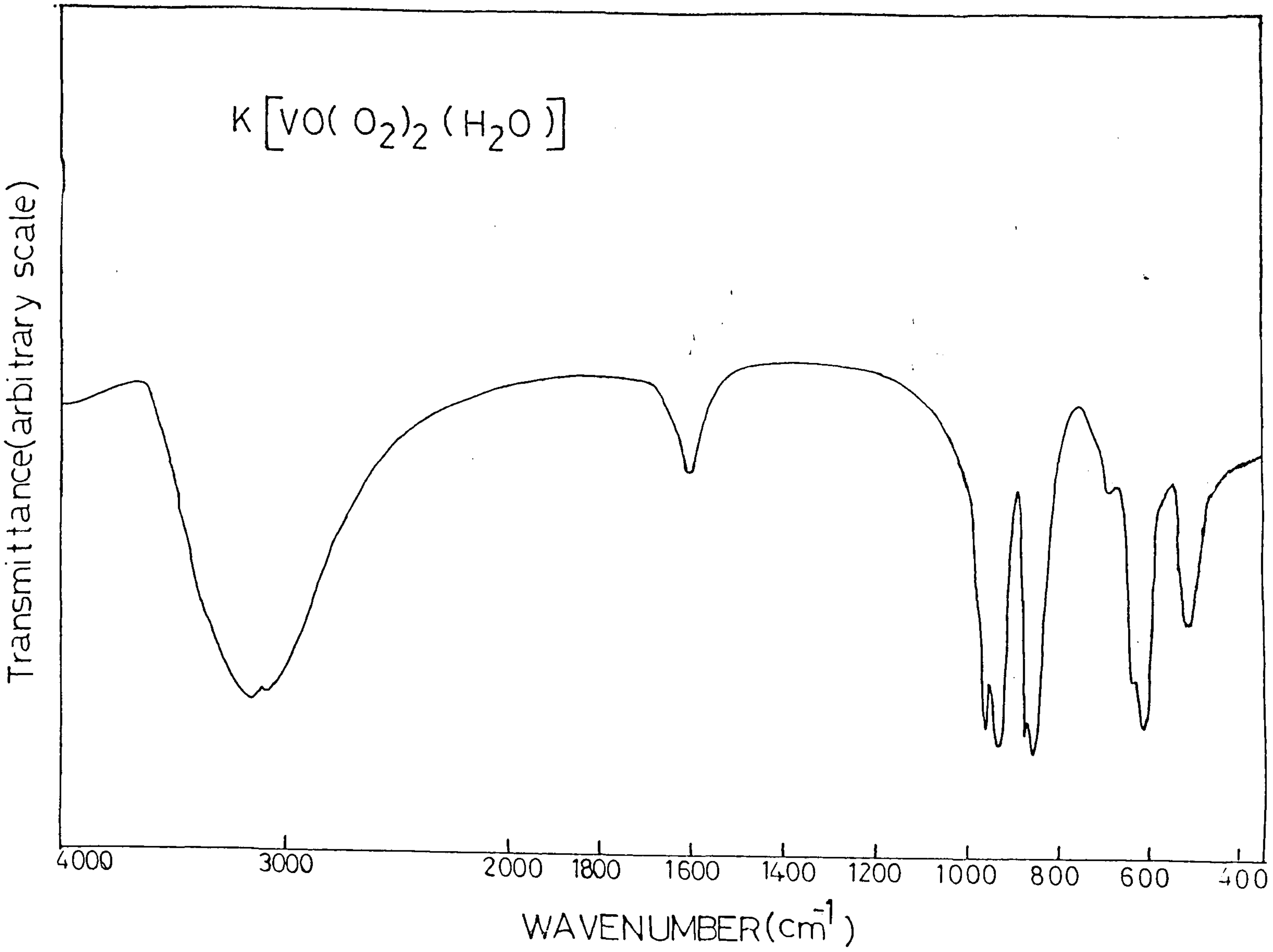
From the reaction of the complex $K[V(O_2)_3].3H_2O$ with SO_2(g), when the solution changed colour from deep blue to yellow, a yellow microcrystalline solid precipitated out spontaneously from the solution which permitted isolation. The pH of this yellow solution was noted to be 7-8. The product was found to be highly soluble and stable in water and it permits conductivity measurement. However, in the case of $Na[V(O_2)_3].3H_2O$ reaction, although the deep blue to yellow colour change was observed but the attempt to isolate the yellow intermediate in the solid state was unsuccessful.

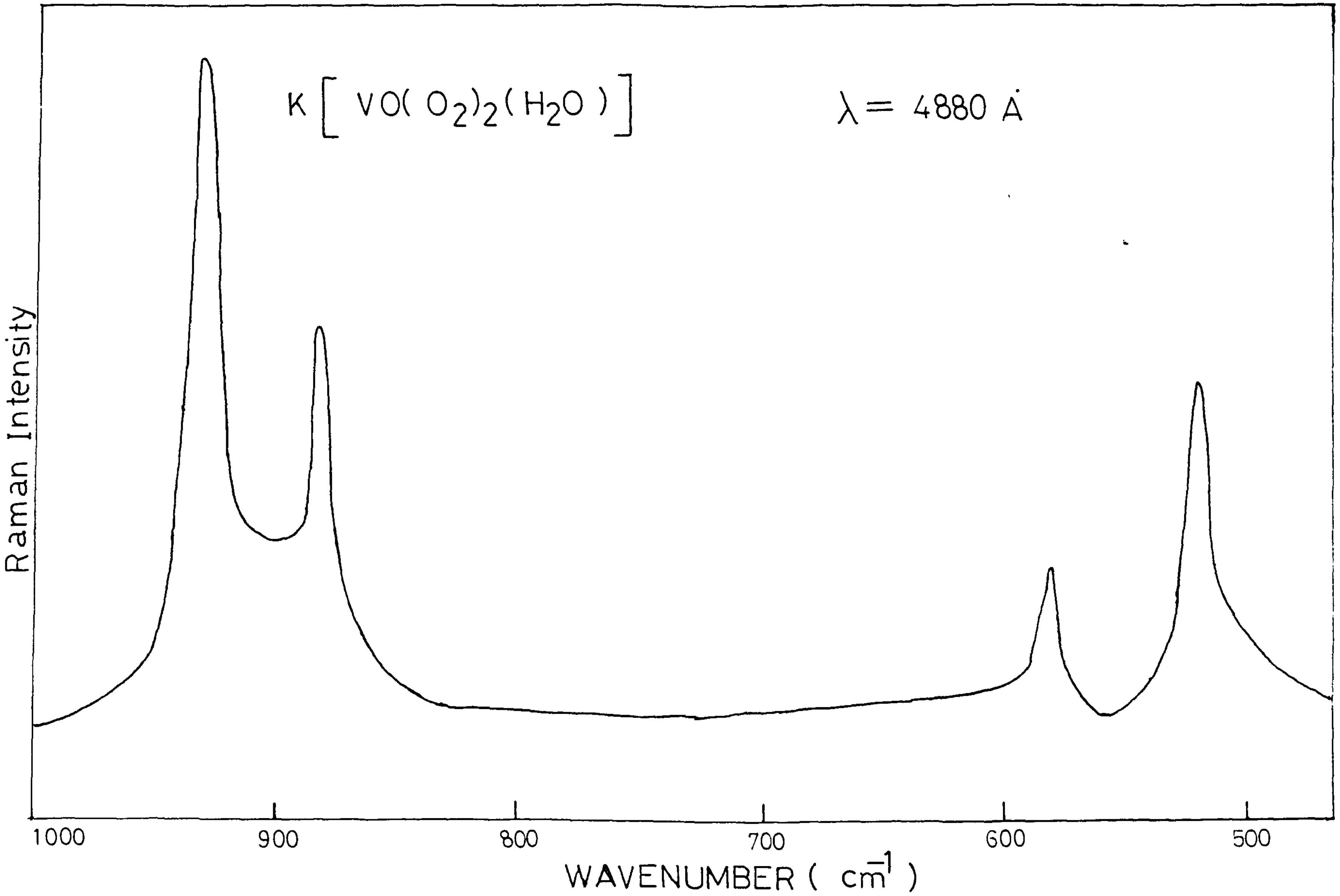
Quite significant is that the ESR spectra of the yellow reaction solution and also an aqueous solution of the compound made after isolation showed no observable signals suggesting beyond doubt that the metal centre did not undergo any reduction so far or in other words the yellow compound is definitely a vanadium(V) complex.

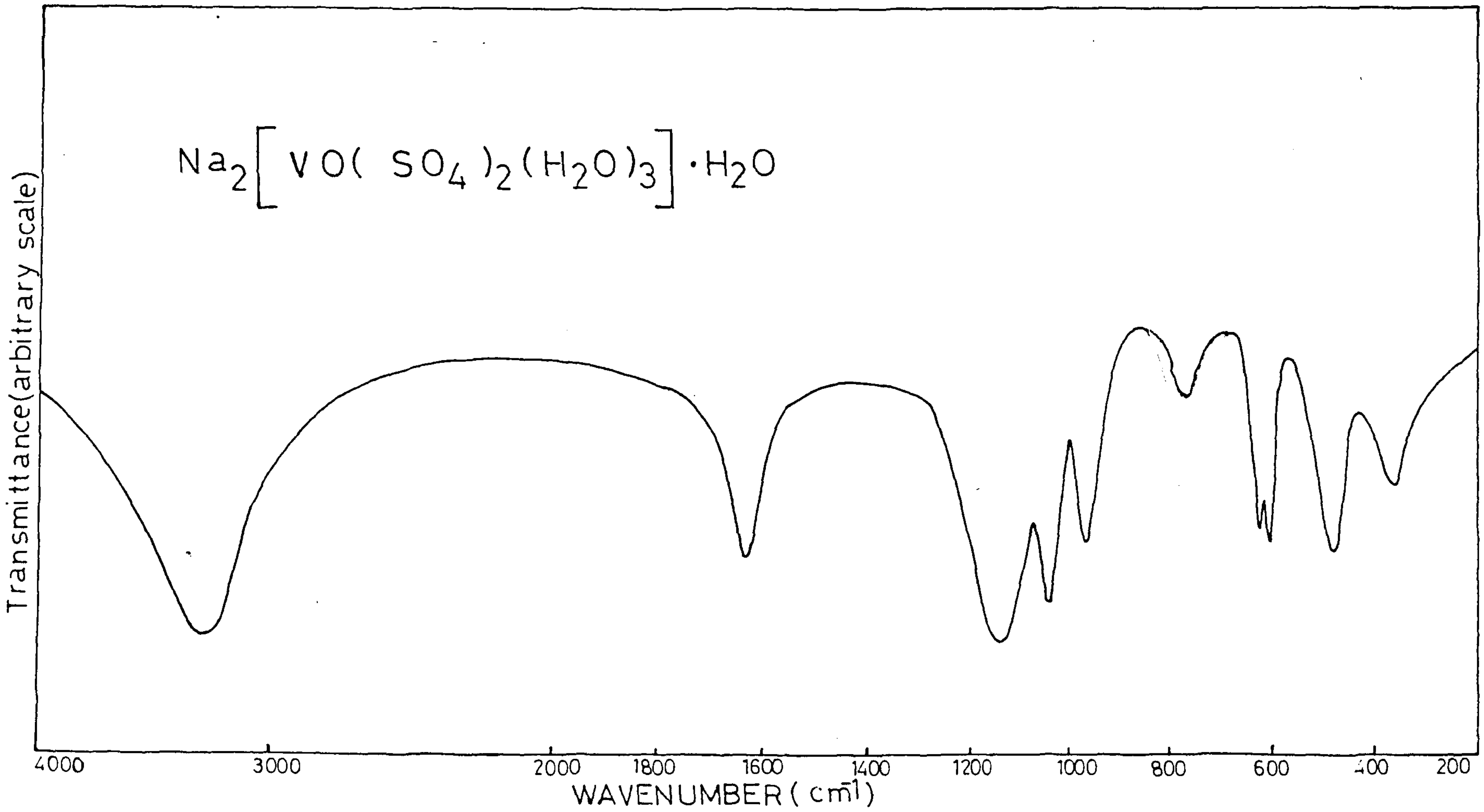
The significant feature of IR spectrum of the yellow reaction product involve the bands due to co-ordinated peroxide, co-ordinated water and V=O stretching. Interestingly, no characteristic bands for co-ordinated or ionic sulphate have been observed in the spectrum, leading us to believe that SO_4^{2-} did not get co-ordinated to the metal centre. This is an unusual kind of observation, because all such studies reported so far involving reactions of co-ordinated peroxide group with SO_2 lead to the insertion of SO_2 into O-O bond of peroxide group thereby getting oxidised to SO_4^{2-} which remains co-ordinated to the metal centre.[23-33] In the present case, however, instead of S-O modes of co-ordinated SO_4^{2-}, a strong band appears at <u>ca</u> 950 cm^{-1} in both IR and LR spectra which was assigned to ν (V=O) mode. The bands at 860 cm^{-1} owing to ν (O-O)[21] and the two absorptions at 605 cm^{-1} and 520 cm^{-1} due to ν $(V-O_2)$[21] modes are characteristi for O_2^{2-} group bonded to the metal in a triangular bidentate (C_{2v}) manner and this mode of bonding is analogous to that of most of the peroxovanadium complexes including that of the parent triperoxovanadate(V) complex. The signals in the LR spectrum of the solid at 870, 590, and 528 cm^{-1} are assigned to the ν_1, ν_2 and ν_3 modes, respectively, of co-ordinated O_2^{2-} lending further support to the presence of bidentate O_2^{2-} groups having (C_{2v}) geometry. The presence of co-ordinated water was ascertained from the distinct appearance of ν (O-H) and δ(H-O-H) modes,

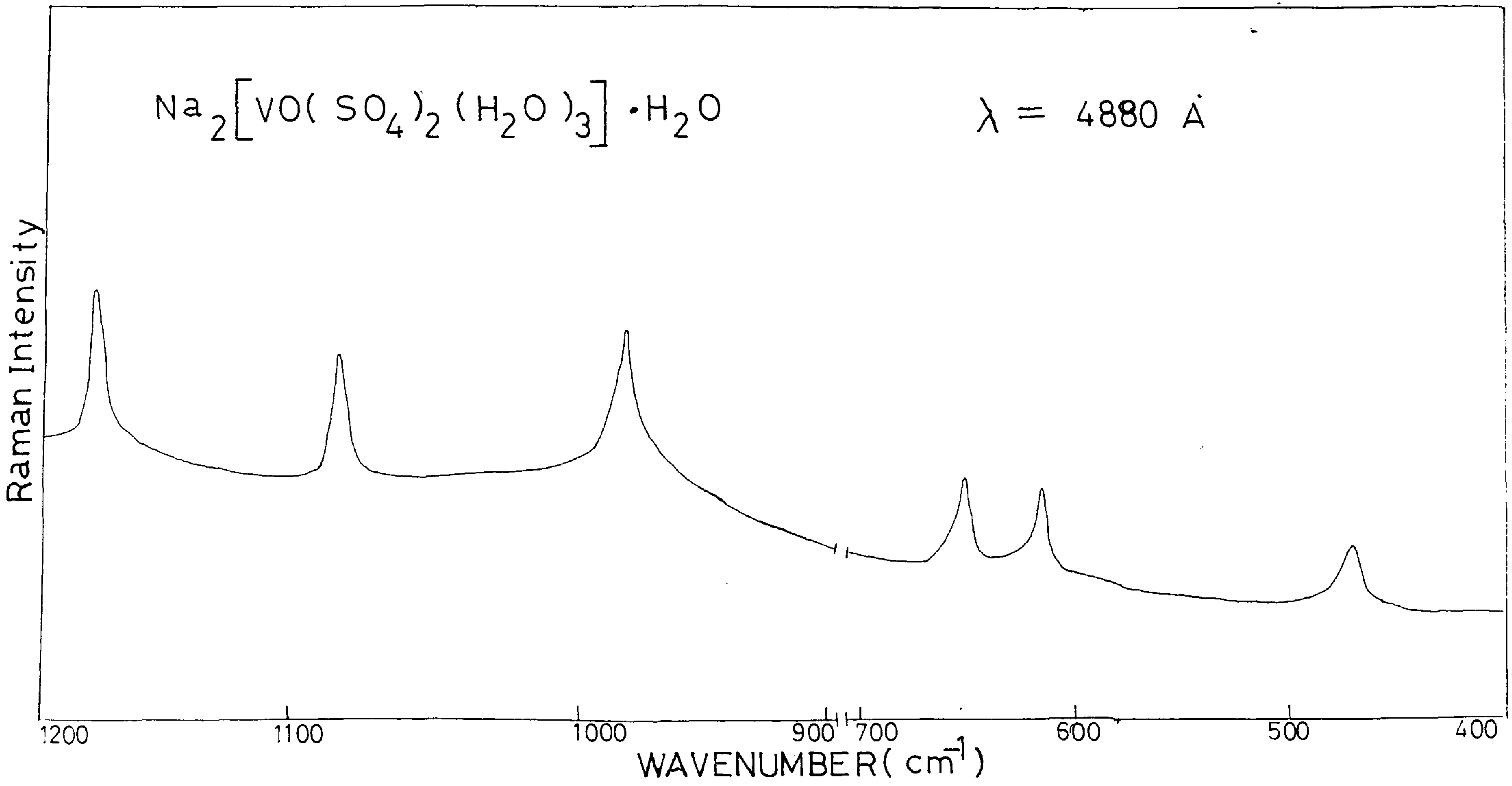
Table 5-5. Structurally Significant IR and Raman Bands of $K[VO(O_2)_2(H_2O)]$ and $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ (A = Na or K)

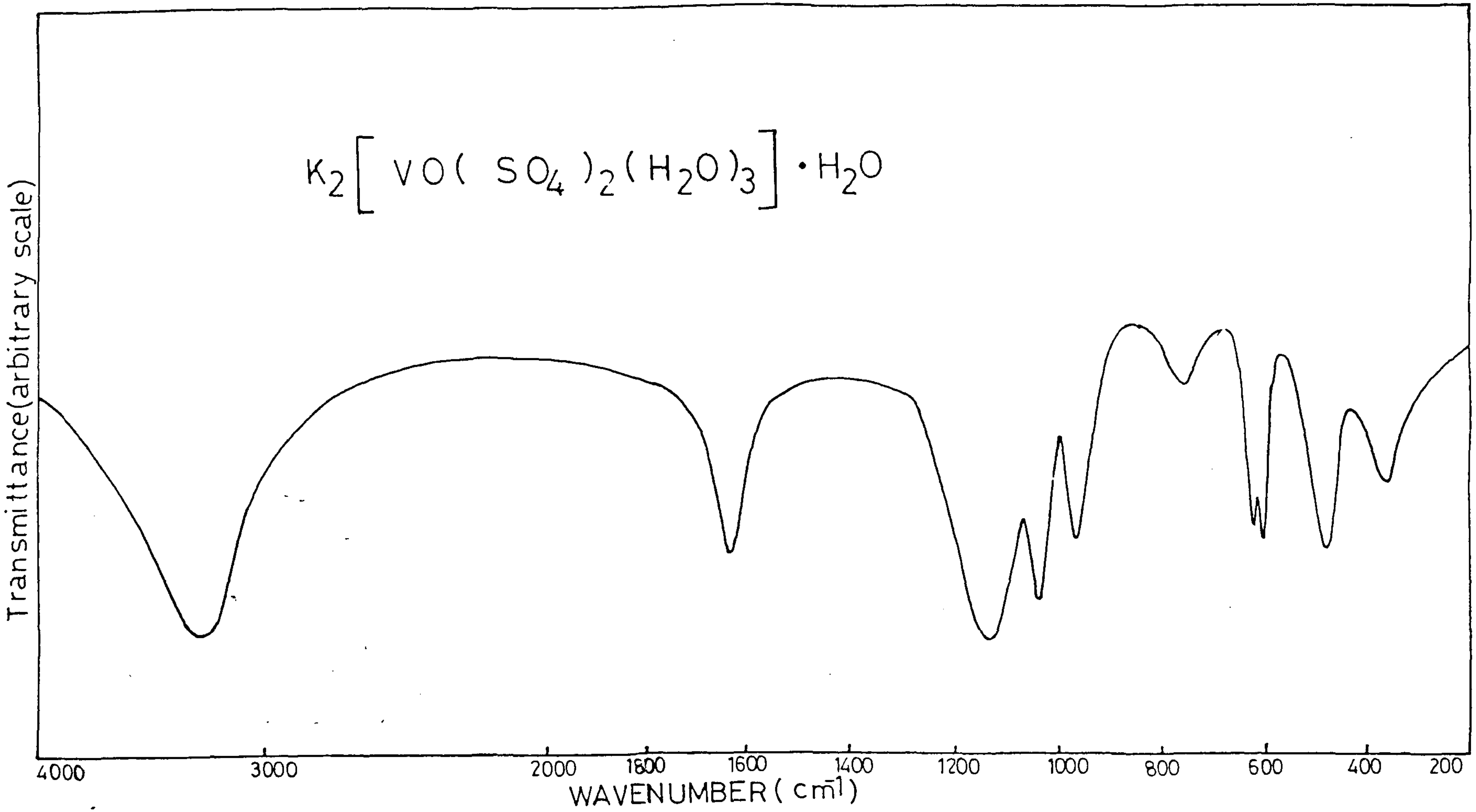
Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$K[VO(O_2)_2(H_2O)]$	950s	936	ν (V=O)
	860s	870	ν (O-O) ν_1
	605s	590	ν $(V-O_2)$ ν_3
	520s	528	ν $(V-O_2)$ ν_2
	1620m		δ(H-O-H)
	3120m		ν (O-H)
$Na_2[VO(SO_4)_2(H_2O)_3].H_2O$	970s	978	ν (V=O)
	1046s	1080	ν (S-O) ν_3
	1140s	1172	
	619s	610	ν (S-O) ν_4
	640s	650	
	483m	480	ν (S-O) ν_2
	1631m		δ(H-O-H)
	3422m		ν (O-H)
	740m		$\rho_r(H_2O)$
	360w		ν (V-O)
$K_2[VO(SO_4)_2(H_2O)_3].H_2O$	973s	966	ν (V=O)
	1049s	1082	ν (S-O) ν_3
	1152s	1166	
	616s	613	ν (S-O) ν_4
	640s	648	
	479m	487	ν (S-O) ν_2
	1643m		δ(H-O-H)
	3420m		ν (O-H)
	750m		$\rho_r(H_2O)$
	340w		ν (V-O)


K [VO(O$_2$)$_2$ (H$_2$O)]
Transmittance(arbitrary scale)
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBER(cm^{-1})


K [VO(O$_2$)$_2$(H$_2$O)]
λ = 4880 Å
Raman Intensity
1000
900
800
700
600
500
WAVENUMBER (cm^{-1})


$Na_2[VO(SO_4)_2(H_2O)_3]\cdot H_2O$
Transmittance(arbitrary scale)
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER (cm^{-1})

Na$_2$[VO(SO$_4$)$_2$(H$_2$O)$_3$]·H$_2$O
λ = 4880 Å
Raman Intensity
1200
1100
1000
900
700
600
500
400
WAVENUMBER(cm^{-1})


$K_2[VO(SO_4)_2(H_2O)_3]\cdot H_2O$
Transmittance(arbitrary scale)
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER (cm^{-1})

which occur in the IR spectrum as medium intensity bands at 3120 cm^{-1} and 1620 cm^{-1}, respectively.

Having obtained enough indication, from the results of ESR, IR, and LR spectroscopic studies in respect of the yellow product, that the compound is an oxo-diperoxovanadate(V) complex, it was subjected to chemical analyses. The results of chemical analyses suggest the stoichiometry of $A:V:O_2^{2-}$ is 1:1:2. The molar conductances, based on the molecular weight calculated from the results of elemental analyses, were found to lie in the range 135 $\Omega^{-1}cm^2mol^{-1}$ clearly indicating that the compound is an 1:1 type of electrolyte.

Considering all the above results we are led to infer that the yellow intermediate reaction product is an aquo-oxo-diperoxovanadate(V) complex which can be formulated as $A[VO(O_2)_2(H_2O)]$.

It is believed that the origin of the oxo oxygen in the yellow intermediate compound is one of the O_2^{2-} group originally co-ordinated to the vanadium(V) centre. Presumably SO_2 insertion took place in the O-O bond of the peroxide group refered to above forming a sulphatodiperoxovanadate(V) complex, $\{[V(SO_4)(O_2)_2]^-\}$, which readily underwent hydrolysis in aqueous medium to produce the yellow oxodiperoxoaquovanadate(V), $[VO(O_2)_2(H_2O)]^-$, complex as isolated and H_2SO_4. The formation of oxo species from such reactions are extremely unusual but surely not unprecedented. It was observed[43] a few years ago that the TiOEP(SO_4) compound obtained from the reaction of TiOEP(O_2) with SO_2 underwent ready hydrolysis even in the presence of moisture giving Ti(O)OEP.

The pH of the solution was noted to be ca 6. It is pertinent to mention that in our earlier endeavour (Chapter 3) concerning our attempted synthesis of peroxo(sulphato)vanadate(V) complex, we observed that the reactions of vanadium(V) with an excess of H_2O_2 and SO_4^{2-} or SCN^- at pH ca 7 forms the complex oxodiperoxovanadate(V), but SO_4^{2-} did not get co-ordinated. Taking into consideration of the results described in Chapter 3, as well as the observations made in the present investigation we are compelled to state that co-ordination of SO_4^{2-} to a vanadium(V) centre in the presence of co-ordinated peroxide is a difficult task. However, more definitive reasons for this could not be discerned at the moment.

As mentioned earlier in this section that $A[V(O_2)_3].3H_2O$ (A = Na or K) with SO_2(g) first generates a yellow colour which ultimately turns to a permanent green-blue solution. The pH of the green-blue solution was found to be ca 2. The blue compound isolated from this solution is distinctly different from the yellow one, not only in terms of colour, but also in their physical properties, viz., the magnetic property, oxidation state of the metal centre and kinds of ligands attached to it. The blue compound was characterised as triaquobis(sulphato)oxovanadate(IV) complex $A_2[VO(SO_4)_2(H_2O)_3].H_2O$.

The molar conductances of the $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ complexes at ambient temperatures were found to lie between 235 and 262 $\Omega^{-1}cm^2mol^{-1}$, suggesting a 2:1 electrolytic nature of each of them, in conformity with the formulae assigned. The room temperature magnetic moment of the compounds were observed to fall between 1.51 and 1.53 μ_B lending credence to the contention that the vanadium in each of the compounds has an oxidation state of +4. The ESR spectra of the compounds in aqueous solution were recorded at room temperature as well as at 77°K. The spectra of the compounds show signals at $g_{av} = 1.992$, which indicates the occurrence of an oxo-vanadium(IV) species and also suggest that the compounds exist as monomers. The spectra were similar to that of vanadyl sulphate, $VO(SO_4).5H_2O$, suggesting that the co-ordination polyhedron around the vanadyl (VO^{2+}) centre in both the cases are probably similar.

The significant features of the IR spectra of $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ (A = Na or K) compounds involve absorptions of co-ordinated sulphate, co-ordinated water, and the V=O stretching. The IR and laser Raman spectra revealed that the band at <u>ca</u> 860 cm^{-1} due to the peroxo stretching in $A[VO(O_2)_2.H_2O]$ as well as the bands at 605 cm^{-1} and 520 cm^{-1} that were assigned to ν (V-O_2) disappeared completely. The sharp absorptions at 973 cm^{-1} must owe its origin to ν (V=O).

Sulphate ligand is an important spectroscopic probe, and is amenable to direct assessment of its mode of bonding to a metal centre by IR and LR spectroscopy. In the spectra of the present compounds, the appearance of medium intensity ν_1 and ν_2 modes of S-O stretchings at 970 and ca 485 cm^{-1}, respectively, and the splittings of ν_3 and ν_4 into two bands each (Table 5-5) as opposed to the absence of ν_1 and ν_2 and the presence of unsplit ν_3 and ν_4 modes in that of an ionic sulphate, provides strong evidence for lowering of symmetry of SO_4^{2-} from T_d to C_{3v}[44] and also its occurrence as a co-ordinated unidentate[44] ligand in the complex. It may be mentioned in passing that the co-ordination of SO_4^{2-} to the metal in an unidentate manner is an unusual feature in this case, because according to the reports we came across so far on reaction of SO_2 with co-ordinated peroxide invariably gave rise to a chelated $(C_{2v})SO_4^{2-}$ whenever the peroxide ligand had occurred as chelated ligand,[23,33,36] Nevertheless a perusal of familiar chemistry of vanadium(IV) reveals that SO_4^{2-} generally binds the VO^{2+} centre in an unidentate manner.[45] The LR spectra of $A[VO(SO_4)_2(H_2O)_3].H_2O$ (A = Na or K) complement the corresponding IR spectra by exhibiting S-O peaks at ca 970 and ca 480 cm^{-1} owing, respectively, to ν_1 and ν_2, and ca 1080, ca 1150, ca 610, due to ν_3, and also at ca 650 cm^{-1}, due to the ν_4 modes of SO_4^{2-} ligand co-ordinated in an unidentate fashion (C_{3v}). Another notable feature of the IR spectra of the $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ complexes is the observance of a band at ca 740 cm^{-1} which has been assigned to the rocking mode of co-ordinated water. This is particularly important because the formula of the complexes contain both co-ordinated as well as lattice water. Owing to the presence of lattice water the information obtainable from the ν (O-H) and δ(H-O-H) positions are not very significant in the present cases as far as the distinction between the two kinds of water molecule is concerned. Fortunately, appearance of the rocking mode of water as mentioned above supports the occurrence of co-ordinated water.

Results of pyrolysis studies on $K_2[VO(SO_4)_2(H_2O)_3].H_2O$, chosen as a representative, show that whereas one molecule of water per formula weight is lost at 110-120°C, loss of further water requires a much higher temperature lending support to the notion that one of the four water molecules occurs as lattice water.

Reaction of $A[V(O_2)_3].3H_2O$ (A = Na or K) with SO_2(g) in Presence of F^-

Following the study of the reaction between $A[V(O_2)_3].H_2O$ with SO_2(g), it was felt that it would be worthwhile to study the reaction in presence of some suitable ligand which might get co-ordinated to the vanadyl centre leading to the synthesis of ternary complexvanadates(IV). For this purpose we had to chose a ligand having a high affinity for the VO^{2+}, centre so that it could replace the solvent (H_2O) molecules co-ordinated to the metal. It is known that VO^{2+} entity binds very effectively to the most electronegative atoms, e.g., F^-, Cl^-, O etc., of which fluoro complexes are especially stable.[46] Also since VO^{2+} is a hard acid and F^- is a hard base, VO^{2+} should form a stable complex with F^-. Accordingly, the choice went in favour of F^-.

The reactions of $A[V(O_2)_3].3H_2O$ with $SO_2(g)$ conducted in the presence of alkali fluoride, AF, taken in a molar ratio between V:F as 1:2 (vide Experimental) afforded a novel blue coloured ternary complexvanadate(IV), $A_4[VO(SO_4)_2F_2(H_2O)].2H_2O$ (A = Na or K). Although the colour changes in the presence of F^- were found to be similar to those observed in the absence of it (as described in the preceding discussion), our attempts to isolate a yellow intermediate species did not lead to success. The blue coloured reaction product was isolated from the solution by facilitating precipitation with ethanol.

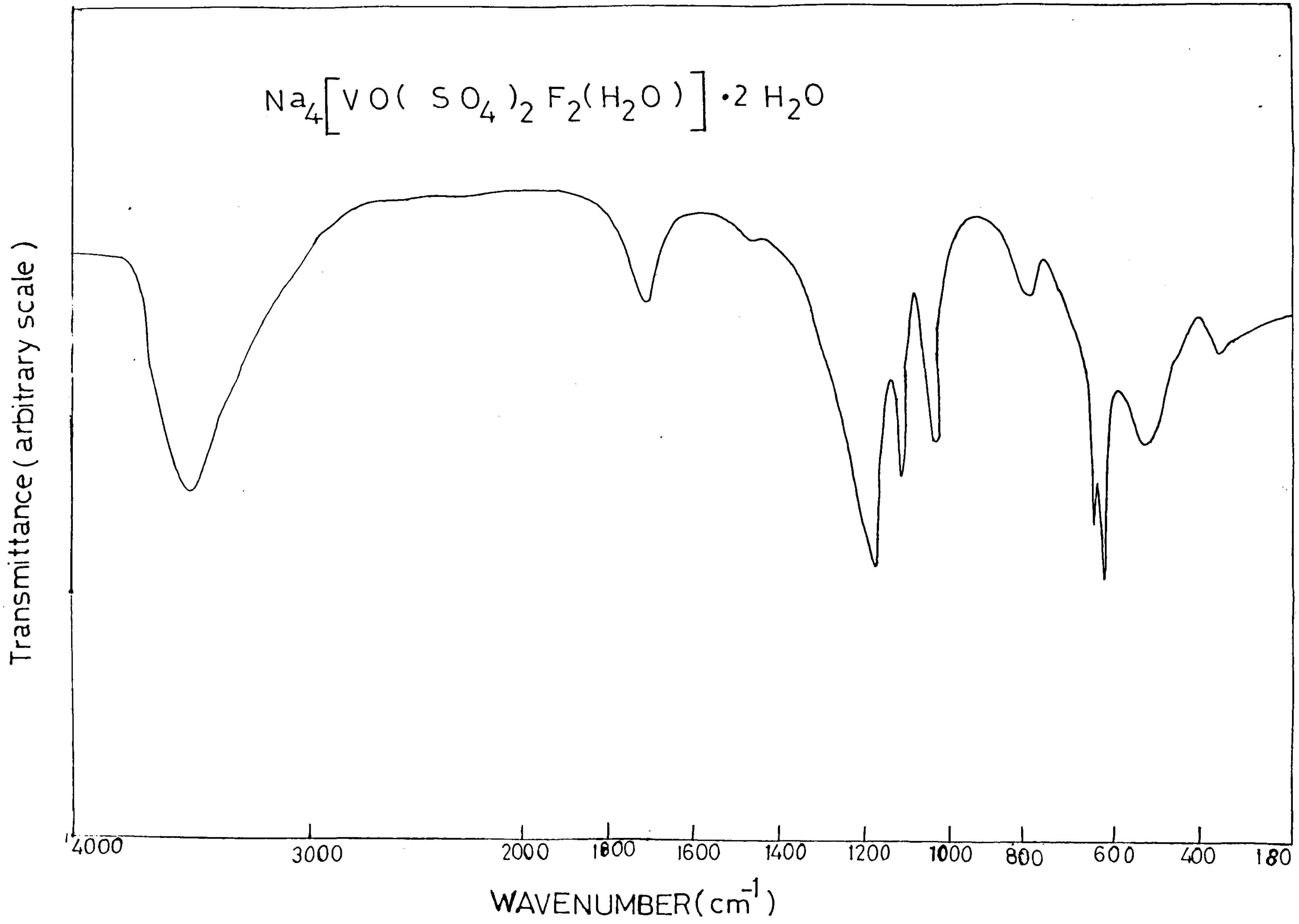
The compounds $A_4[VO(SO_4)_2F_2(H_2O)].2H_2O$ are blue microcrystalline products which are hygroscopic in nature. The compounds are soluble in water and permit conductivity measurements. The molar conductances of the complexes were found to be in the range 510-522 $\Omega^{-1}cm^2mol^{-1}$. The ESR spectra of $A_4[VOF_2(SO_4)_2(H_2O)].2H_2O$ compounds in aqueous solution were recorded at room temperatures as well as at liquid nitrogen (77°K) temperature. The ESR spectra were identical to that of $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ complexes with g_{av} = 1.996, characteristic of oxo-vanadium(IV) species. The spectra did not show any hyperfine coupling thereby precluding the possibility of any V-V interaction and also suggesting that the complex $[VOF_2(SO_4)_2(H_2O)]^{4-}$ species is monomeric in nature.

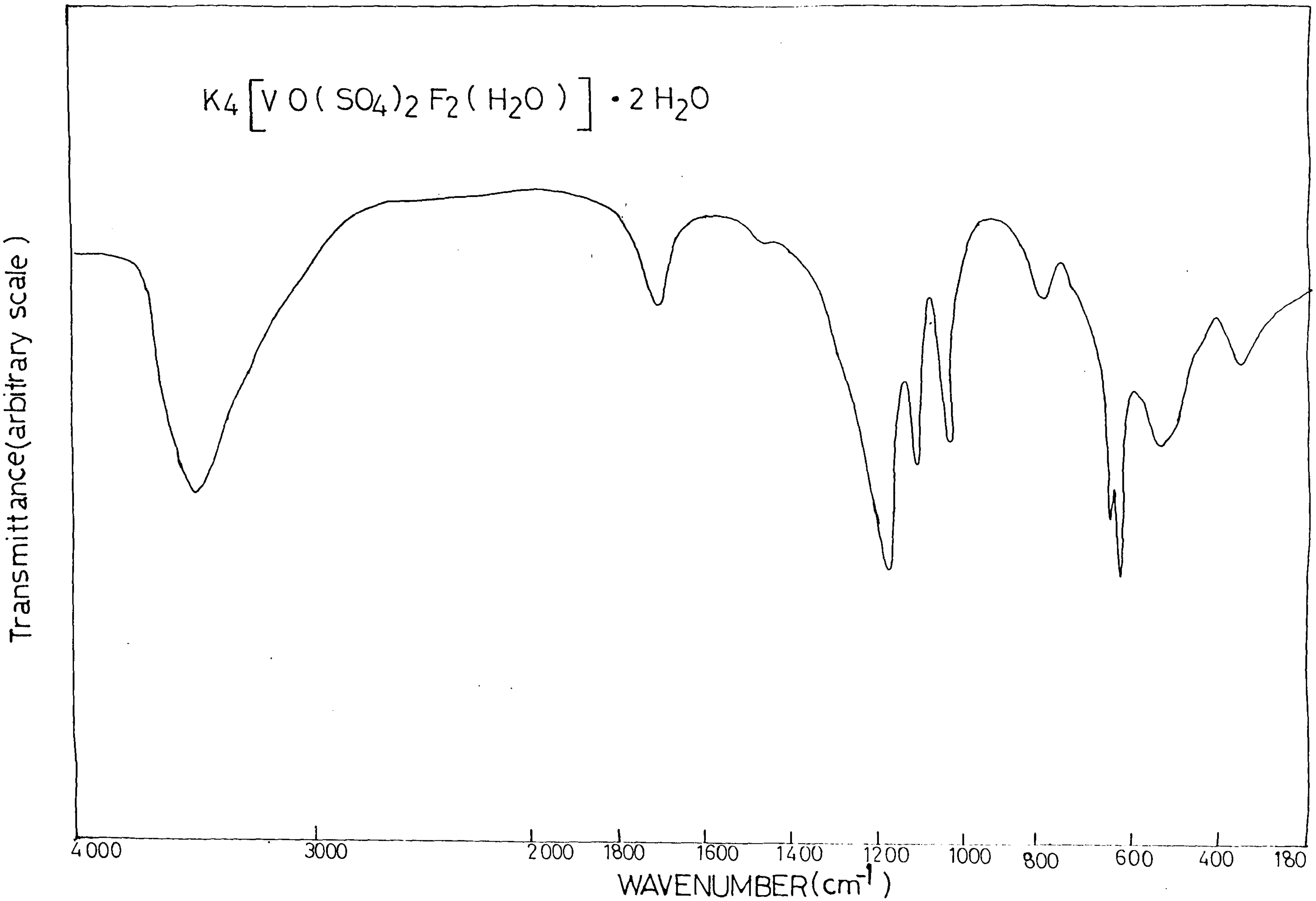
The IR and LR spectra of the compounds $A_4[VOF_2(SO_4)_2(H_2O)].2H_2O$ resembles that of $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ closely, which involve absorptions of co-ordinated sulphate, co-ordinated as well as lattice water, and the V=O stretching. In addition to these, the appearance of a medium intensity band at ca 520 cm^{-1} is quite significant. The absorption at ca 520 cm^{-1} is explained in terms of the occurrence of co-ordinated F^- ligands.

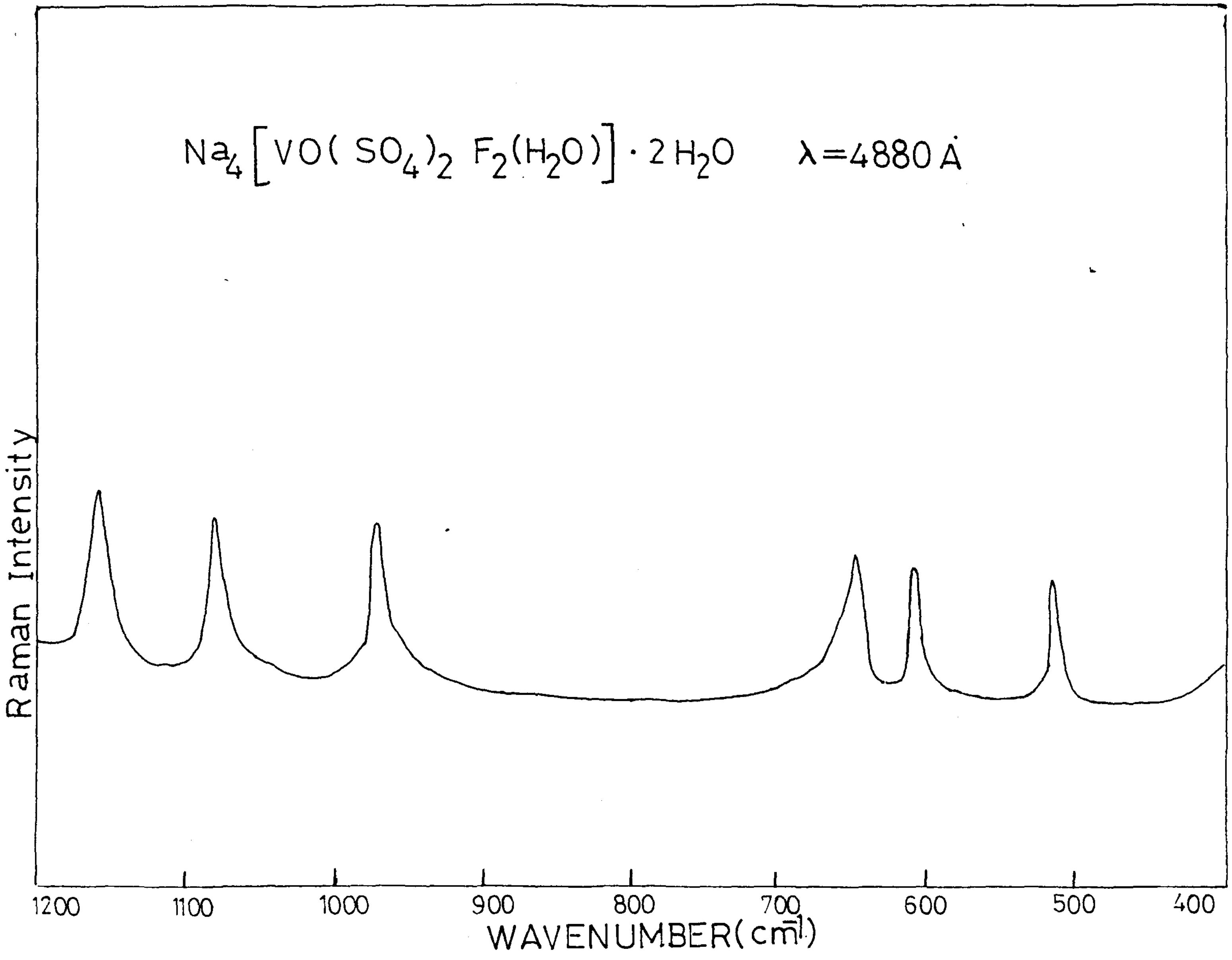
To sum up the new information derived from the various facets of studies described in this Chapter, it may be stated that a minimum of three peroxide ligands bonded to a vanadium(V) centre is required for the formation of a blue peroxovanadate(V) species. The complex species have been formulated as $[V(O_2)_3]^-$ which does not contain any oxo group bound to the metal centre. The complex species, as demonstrated, can be generated in solutions and the salts of the complex ion, viz. $A[V(O_2)_3]$ with A being Na or K can be synthesised under the experimental conditions given in this Chapter. The compounds are obtained as $A[V(O_2)_3]$ if the final products are dried over P_4O_{10} for a prolonged period, however, they are otherwise obtained as trihydrates, if they are dried over conc. H_2SO_4. The compounds are relatively more stable than the corresponding heteroligandperoxovanadates(V), namely, $A_2[V(O_2)_3X]$ ($X = Cl^-$ or F^-). The complex species $[V(O_2)_3]^-$

Table 5-6. Structurally Significant IR and Raman Bands of $A_4[VO(SO_4)_2F_2(H_2O)].2H_2O$ (A = Na or K)

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$Na_4[VO(SO_4)_2F_2(H_2O)].H_2O$	980s	972	ν (V=O)
	1060s	1080	ν (S-O) ν_3
	1140s	1165	
	620s	609	ν (S-O) ν_4
	640s	648	
	485m	510	ν (S-O) ν_2
	520m		ν (V-F)
	3420m		ν (O-H)
	1640m		δ (H-O-H)
	740m		ρ_r (H_2O)
	365w		ν (V-O)
$K_4[VO(SO_4)_2F_2(H_2O)].H_2O$	980s	967	ν (V=O)
	1050s	1073	ν (S-O) ν_3
	1120s	1171	
	610s	620	ν (S-O) ν_4
	620s	633	
	480m	469	ν (S-O) ν_2
	530m		ν (V-F)
	3419m		ν (O-H)
	1653m		δ (H-O-H)
	743m		ρ_r (H_2O)
	340w		ν (V-O)


$Na_4[VO(SO_4)_2F_2(H_2O)]\cdot 2H_2O$
Transmittance (arbitrary scale)
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400
180
WAVENUMBER(cm^{-1})


$K_4[VO(SO_4)_2F_2(H_2O)] \cdot 2H_2O$
Transmittance(arbitrary scale)
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400
180
WAVENUMBER(cm^{-1})


$Na_4[VO(SO_4)_2F_2(H_2O)]\cdot 2H_2O$
λ=4880 Å
Raman Intensity
1200
1100
1000
900
800
700
600
500
400
WAVENUMBER(cm⁻¹)

has been shown to retain its structural identity both in the solid state as well as in solution.

The results of our studies of reactions of the above mentioned highly peroxygenated vanadium(V) species with $SO_2(g)$ in an aqueous medium show a novel reaction sequence. While both the co-ordinated peroxide ligands as well as the metal centre i.e., vanadium(V) are prone to undergo ready electron transfer reactions with the chosen inorganic substrate (SO_2), the experimental results clearly exhibit that it is one of the edge bound peroxide ligand that participates in the electron transfer reaction in preference to vanadium(V). The reaction proceeds through distinct steps. To us it seems that first one of the three co-ordinated peroxide ligands undergoes a two-electron irreversible cleavage of the O-O bond leading to the formation of a diperoxomonosulphato-vanadate(V) intermediate, $\left\{[(O_2)_2V\text{-}O\text{-}SO_3]^-\right\}$, which readily undergoes hydrolysis to produce oxodiperoxoaquovanadate(V) complex, $[VO(O_2)_2H_2O]^-$ which has been isolated in the solid state as its potassium salt. Further reaction with SO_2, avoiding isolation of the yellow $[VO(O_2)_2H_2O]^-$ species, apparently involves electron-transfer reactions between peroxide ligands and SO_2, and also between vanadium(V) and SO_2 in a competetive manner since the reaction did not permit isolation of any more (other than the one already mentioned) vanadium(V) complex. The ultimate compound obtained is a blue oxosulphato vanadate(IV) complex, $[VO(SO_4)_2(H_2O)_3]^{2-}$. This was isolated as its alkali metal salts,

$A_2[VO(SO_4)_2(H_2O)_3].H_2O$, in which each of the two SO_4^{2-} ligands binds the metal centre in a monodentate fashion.

The reaction of $A[V(O_2)_3].3H_2O$ (A = Na or K) with $SO_2(g)$ in the presence of alkali fluoride, AF, afforded ternary fluorosulphatovanadate(IV) complexes of the type, $A_4[VO(SO_4)_2F_2(H_2O)].2H_2O$. This serves as a paradigm for the synthesis of ternary complexes of vanadyl, VO^{2+}, and may provide an easy access to such compounds for further studies.

The following are the notable points that emerged out of our studies on peroxovanadium chemistry the results of which have been described in Chapters 3, 4 and 5:

(i) The yellow oxodiperoxovanadate(V) complex, $[VO(O_2)_2]^-$, permits isolation in the solid state as $A[VO(O_2)_2]$ (A = alkali metal or NH_4).

(ii) Reactions of vanadium(V) with H_2O_2 and SCN^- or SO_4^{2-} afford yellow oxodiperoxovanadate(V) complexes containing only ionic SO_4^{2-}. Attempts to bring about co-ordination of SO_4^{2-} to a peroxovanadium(V) centre were unsuccessful.

(iii) The synthesis of heretofore unreported heteroligand peroxovanadate(V) complexes containing an amino acid as the heteroligand is possible under suitable experimental conditions. Glycine has been shown to form complexes of the following type: $A[VO(O_2)_2GlyH].H_2O$ (A = NH_4 or K).

(iv) A minimum of three peroxide groups being bonded to a vanadium(V) centre is required for the formation of a blue peroxovanadate(V) complex which does not contain any oxo group.

(v) The number of peroxo groups per vanadium centre increases with an increase in pH of the reaction solution.

(vi) In the reactions of peroxovanadates(V), containing more than two peroxide ligands with SO_2(g), it is one of the peroxo ligands, rather than the vanadium(V) centre, which is preferentially involved in an electron-transfer reaction.

(vii) An easy access to newer ternary complexes of vanadium(IV) may be possible from the reaction of triperoxovanadate(V) complexes with SO_2(g) in the presence of appropriate ligands.

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CHAPTER 6

CHAPTER 6

Direct Synthesis of Hexafluoroferrates(III), Working Out of Optimum Conditions for Hydrogen Peroxide Oxidation of Thiocyanate to Sulphate, And Reaction of Thiocyanate and Fluoride with Iron(III) and Hydrogen Peroxide as an Access to Fluoro(sulphato)-ferrates(III)[*]

The chemistry of fluoro and mixed-fluoro complexes of transition metals continues to attract much attention and keeps on providing new and exciting results.[1-7] Peculiarities of many such compounds in respect of their magnetic and structural behaviours probably make them relatively more interesting than their analogues containing other halides. Although much of the very recent activity in this area is devoted to studies related to kinetics[5] and magnetic properties[1,6,8,9] a great deal of effort is required for the search for direct synthetic procedures and for synthesis of novel fluoro and mixed-fluoro complex species. These are the pre-requisite for an heuristic approach in this field of chemistry. The synthesis and structural assessment of fluoronickelates(II),[10,11] fluoromanganates(III),[12,14] mixed-fluoromanganates(III),[4,13] fluoro and mixed-fluorocobaltates(II),[7,17] and fluoro and mixed-fluorocuprates(II) have been dealt with by other workers in the laboratory where the present work has been carried

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[*] The subject matter of this Chapter has been published:

Inorg.Chem., 1986, _25_, 3722;
Ind.J.Chem., 1985, _24A_, 447.

out. As a continuation of the endeavour[4,7,10-17] in this field, we considered it necessary to extend such studies to iron analogues As a case in point the difficulties involved in the synthesis of hexafluoroferrates(III), FeF_6^{3-}, have already been emphasised in the opening Chapter of the thesis. To the best of our knowledge, within the context of fluoroferrates(III), there exists no direct and simple method for the synthesis of hexafluoroferrates(III), FeF_6^{3-}, thus limiting their accessibility.

Moreover, mixed-ligand fluoro compounds of iron(III) do not seem to have any reported existence. Mixed-ligand fluoro compounds of transition metals in general are intrinsically important because of some of the extreme properties e.g. very highly antiferromagnetic character, exhibited by binary fluoro complexes are controlled through the formation of mixed-fluoro complexes. Such mixed-ligand complexes of transition metals enable a comparison of their properties with those of the corresponding binary fluoro complexes in addition to exhibiting some other interesting properties,[3,4,7,12-18] with some of them presumably having biochemical significance,[19,20] as well. Fluoro-sulphato compounds of manganese(III) [13] and cobalt(II)[7], for instance, have shown some unusual properties, distinctly different from those of the corresponding parent binary fluoro complexes, as evident from some of the recent reports, In view of the above we undertook investigations concerning direct synthesis of hexafluoroferrates(III) as well as developing synthetic routes to hitherto unknown fluoro-sulphatoferrates(III) followed by making an assessment of their structure and properties.

A planning of synthetic strategies and working out of appropriate experimental conditions are important pre-requisites for the synthesis and structural study of fluorometallates. Although various possible reaction pathways might be considered for the synthesis of fluoro(sulphato)ferrate(III) complexes, we have achieved success in synthesising such complexes by chemical oxidation of SCN^- to SO_4^{2-} by H_2O_2 in the presence of F^- ions and iron(III). It may be mentioned that a direct reaction of sulphate and fluoride with iron(III) in an acidic medium did not lead to the synthesis of desired complexes.

The oxidation of SCN^- to SO_4^{2-} by H_2O_2, under appropriate conditions was thought worth exploiting for the synthesis of sulphato compounds of metals. It was shown from the studies in solutions[21] that thiocyanate is oxidised to sulphate, which is also an example of electron-transfer reaction.[21,22] However, the optimum conditions, viz., appropriate pH of the reaction medium and the suitable molar ratio between SCN^- and H_2O_2 required for the quantitative conversion of SCN^- to SO_4^{2-} have not been known until date. In order to exploit this reaction in the context of syntheses of sulphato complexes the above mentioned informations are the pre-requisites. In view of the implied importance and synthetic utility of the reaction of SCN^- with H_2O_2 it also became necessary to ascertain the optimum conditions for the oxidation of SCN^- to SO_4^{2-} by H_2O_2.

The subject of the present Chapter is the direct synthesis of alkali-metal and ammonium hexafluoroferrates(III), A_3FeF_6 (A = Na, K or NH_4), and an account of the reaction of thiocyanate and hydrofluoric acid with iron(III) in the presence of hydrogen peroxide, with the latter leading to the first synthesis of fluoro(sulphato)ferrates(III). Also presented in this Chapter are the results of studies concerning the optimum condition for quantitative conversion of thiocyanate to sulphate and the scope of this reaction.

Experimental

The Chemicals used were all reagent grade (Sarabhai M. Chemicals, Glaxo, S.D's) products.

Synthesis of Alkali-Metal and Ammonium Hexafluoroferrates(III), A_3FeF_6 (A = Na, K or NH_4)

Anhydrous iron(III) chloride (1.0g, 6.2 mmol) was dissolved in water (5 cm^3) with gentle warming. Aqueous ammonia (specific gravity 0.9, 7 cm^3, excess) was added slowly with continuous stirring. The mixture was heated on a steam-bath for 15 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, alkali-metal or ammonium fluoride, AF (36.9 mmol) and 30% hydrogen peroxide (12 cm^3, 105.7 mmol) were placed in a polyethylene beaker provided with a polyethylene cover. An amount of 1.3 cm^3 (31.2 mmol) of 48% hydrofluoric acid was added dropwise with stirring to obtain a clear solution. The solution was stirred magnetically for a further period of ca 15 min, Addition of about 20 cm^3 of ethanol to the above solution precipitated very light yellowish white alkali-metal or ammonium hexafluoroferrate(III), A_3FeF_6. The compound was separated by filtration, washed three to four times with ethanol, and finally dried in vacuo over P_4O_{10}.

The yields of Na_3FeF_6, K_3FeF_6, and $(NH_4)_3FeF_6$ were 1.1g (75%), 1.4g (79%), and 1g (72%), respectively.

Reaction of Alkali-Thiocyanate, ASCN (A = NH_4 or K), with 30% Hydrogen Peroxide. Recommended Procedure for the Quantitative Conversion of SCN^- to SO_4^{2-}

Alkali thiocyanate, ASCN (A = NH_4 or K), was dissolved in 30% H_2O_2 with maintainance of molar ratio of ASCN to H_2O_2 as 1:8-10 followed by filtration. Corresponding alkali-hydroxide was added in portions to the filtrate with constant stirring until the pH of the solution was raised to 7-8. The solution was stirred magnetically for a further period of ca 10 min, and then an excess of ethanol was added to it until the white crystalline alkali sulphate, A_2SO_4, ceased to appear. The compound thus obtained was separated by filtration, washed 3-4 times with ethanol, and finally dried in vacuo over P_4O_{10}.

The reaction of 2.0g (26.3 mmol) of NH_4SCN with 27.0 cm^3 (237.6 mmol) of 30% H_2O_2 yielded 3.44g (99%) of $(NH_4)_2SO_4$, while the reaction of 2.0g (20.6 mmol) of KSCN with 23.4 cm^3 (206 mmol) of 30% H_2O_2 produced 3.52g (98%) of K_2SO_4.

Reactions of ASCN (A = NH_4 or K) with Iron(III) Hydroxide, Aqueous HF, and Hydrogen Peroxide

Iron(III) hydroxide was prepared from 1.0g of anhydrous iron(III) chloride in a similar way as described under the synthesis of A_3FeF_6.

The moist iron(III) hydroxide and solid potassium or ammonium thiocyanate, ASCN (12.4 mmol), were mixed thoroughly in a polyethylene beaker. To this was slowly added 13 cm^3 (114.6 mmol) of 30% hydrogen peroxide with occassional stirring. Stirring was continued until effervescence ceased to appear. An amount of 1.4 cm^3 (33.6 mmol) of 48% hydrofluoric acid was added dropwise to obtain a clear solution that was stirred magnetically for ca 15 min followed by the addition of 25 cm^3 of ethanol to afford a greyish white oily mass. The oily mass was separated by decantation and solidified by repeated treatment with ethanol and scratching for about 20 min. The product was isolated and dried in a manner similar to that described under the synthesis of A_3FeF_6.

The yield of $K_3[Fe(SO_4)F_4]$ was 1g (47%) and that of $(NH_4)_2[Fe(SO_4)F_3]$ was 0.7g (47%).

Elemental Analyses

Determination of iron, fluoride, sulphate, potassium, and sodium contents of the various compounds described in this Chapter have been made by the methods already described in Chapter 2.

The analytical data for A_3FeF_6 (A = NH_4, Na or K), $K_3[Fe(SO_4)F_4]$, and $(NH_4)_2[Fe(SO_4)F_3]$ are given in Table 6-1, while those of A_2SO_4 (A = NH_4 or K) as obtained from ASCN (A = NH_4 or K) oxidations are set out in Table 6-2.

Results and Discussion

It is owing to the lack of a suitable and easier method of synthesis of hexafluoroferrate(III) complexes that we thought it worthwhile to improvise a simple and direct method for the synthesis of the title complexes. It has now been possible for us to show that iron(III) hydroxide can be made to react with alkali-metal or ammonium fluoride, AF (A = Na, K or NH_4) and aqueous hydrofluoric acid in the presence of an excess of hydrogen peroxide to afford directly alkali-metal or ammonium hexafluoroferrates(III), A_3FeF_6, in yields higher than those obtained by the earlier method.[23] An excess of 30% hydrogen peroxide (vide Experimental) was necessary as this also provided

Table 6-1. Analytical Data of A_3FeF_6 (A = NH_4, Na or K), $K_3[Fe(SO_4)F_4]$, and $(NH_4)_2[Fe(SO_4)F_3]$

Compound	Found % (Calcd. %)			
	A	Fe	F	SO_4
$(NH_4)_3[FeF_6]$	18.91[a] (18.76)[a]	25.22 (24.93)	51.45 (50.89)	-
$Na_3[FeF_6]$	28.55 (28.89)	23.47 (23.38)	47.91 (47.73)	-
$K_3[FeF_6]$	40.48 (40.85)	19.87 (19.45)	40.1 (39.7)	-
$K_3[Fe(SO_4)F_4]$	33.58 (33.98)	16.51 (16.18)	33.22 (33.02)	28.21 (27.83)
$(NH_4)_2[Fe(SO_4)F_3]$	11.51[a] (11.44)	22.83 (22.79)	46.85 (46.53)	39.42 (39.20)

[a] Analysis for N

Table 6-2. Analytical Data and Molar Conductance Values of A_2SO_4 (A = NH_4 or K)

Compound	Molar conductance $\Omega^{-1}cm^2mol^{-1}$	Found % (Calcd %)	
		A	SO_4
$(NH_4)_2SO_4$	245	21.1[a] (21.2)[a]	72.5 (72.69)
K_2SO_4	250	44.7 (44.87)	55.2 (55.13)

[a] Analysis for N.

an appropriate medium for conducting the reactions. A similar volume maintained by using dilute hydrogen peroxide solutions was found to be detrimental to the synthesis. The role of alkali-metal or ammonium fluoride, AF, was to provide counter cations, A^+, as well as to enhance the F^- ion concentration of the reaction medium,while that of hydrofluoric acid was to dissolve iron(III) hydroxide and also to supply fluoride ions. Strategically more important is the key role played by H_2O_2 in the successful synthesis of hexafluoroferrates(III). It is believed that pentafluoroferrate(III) is first formed which co-ordinates with a peroxide (O_2^{2-}) ligand presumably to form an unstable peroxyfluoroferrate(III) intermediate. This unstable peroxy intermediate then reacts with F^- ions available in solution, rupturing the iron-peroxide bond with concomitant formation of a new metal-fluoride bond, ultimately leading to the formation of the FeF_6^{3-} complex species. At present this interpretation is admittedly speculative, however, the fact that similar reactions in the absence of hydrogen peroxide, even in the presence of relatively higher concentrations of fluoride ions, yield only pentafluoroferrates(III) definitely lends support to the contention. Moreover, recently while working on some peroxyfluorometallates,[24] it was observed that a peroxyfluorometallate complex could serve as a precursor for a binay fluorometallate species (cf. $Ti(O)F_5^{3-} + F^- \longrightarrow TiF_6^{2-}$), providing thereby a sort of a rationale for the present synthesis.

Because of the higher yields of products obtained by the new method, which is also easy to manipulate, this synthetic approach offers advantages over the method described in the literature.[23]

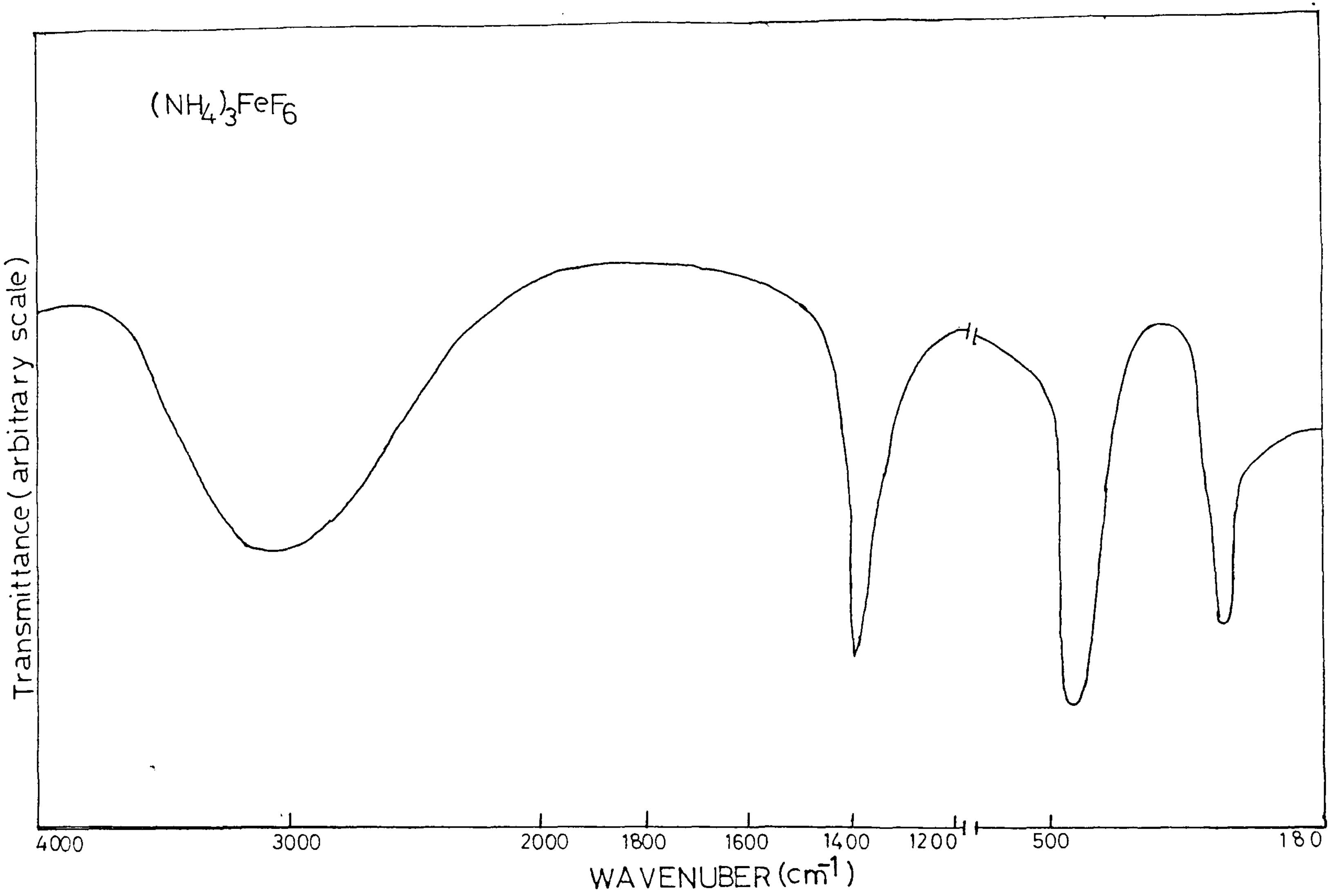
The alkali hexafluoroferrate(III), A_3FeF_6 compounds can be stored undecomposed for a prolonged period in sealed polyethylene envelopes, and their stability can be ascertained from the results of metal and fluoride estimations periodically. The results of elemental analyses are consistent with the formula of the compounds. Chemically estimated oxidation state, accomplished by iodometry, was found to lie between 2.9 and 3.1 in agreement with the occurrence of iron(III). They are high spin complexes with magnetic moments of 5.8 -5.9 μ_B and conforms well with values reported in the literature.[25] The IR spectra of the compounds exhibit a very strong, but somewhat broad band at 470-497 cm^{-1} assigned to ν (Fe-F) and a strong band around 290 cm^{-1} attributed to δ(F-Fe-F). These are in conformity with those observed earlier[26] on similar compounds.

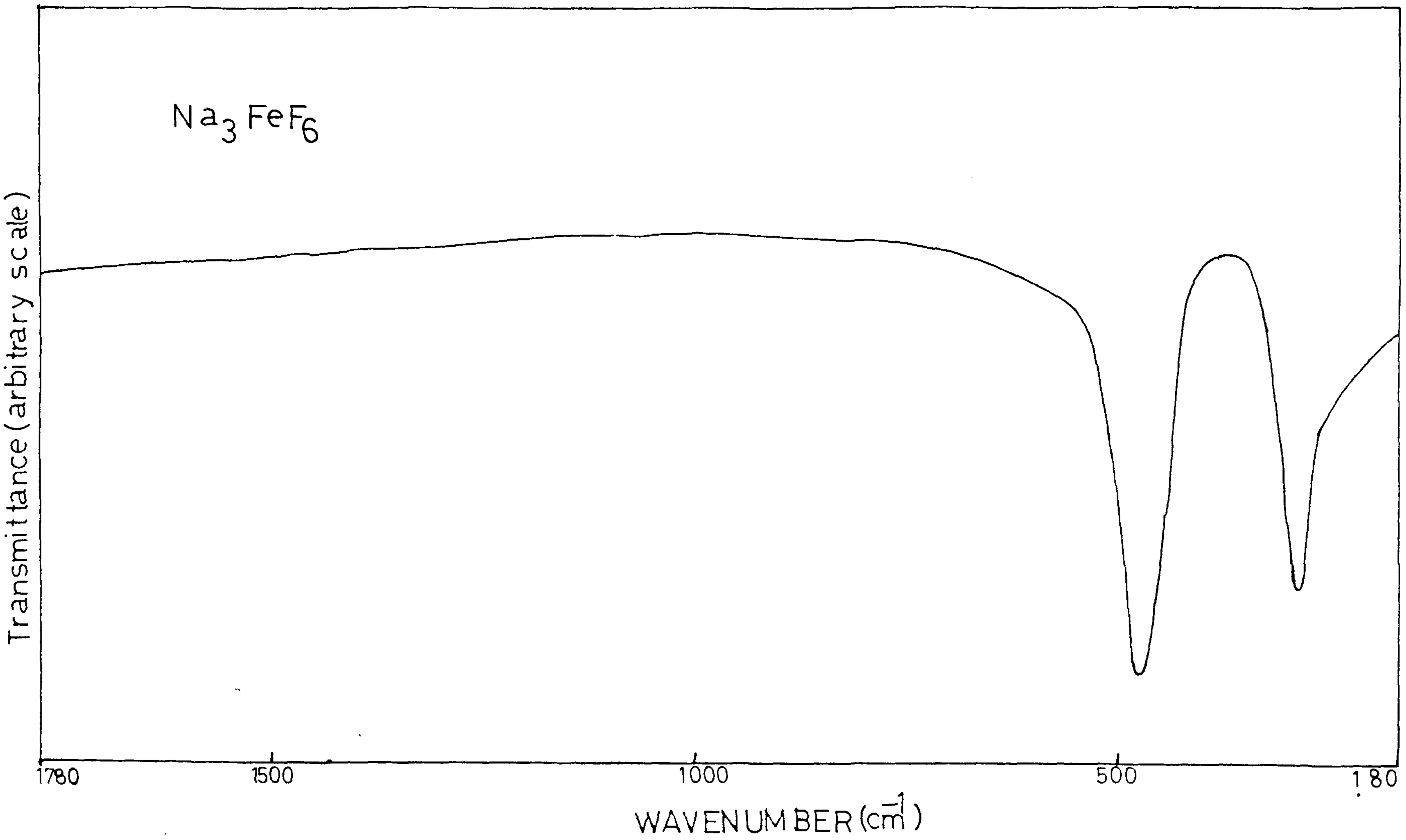
Reactions of ASCN (A = NH_4 or K) with 30% Hydrogen Peroxide

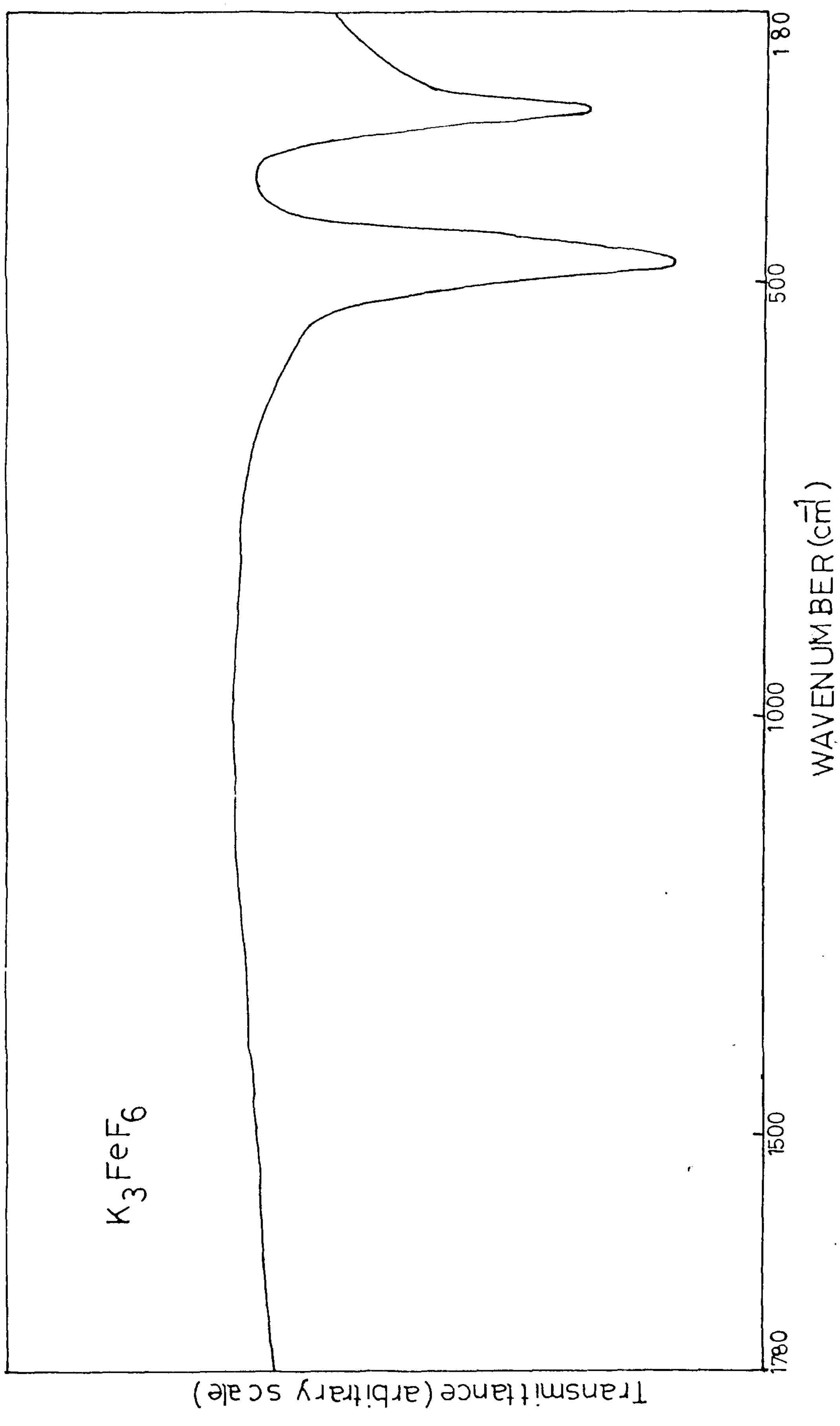
In the context of synthesis of fluorosulphatoferrates(III), we considered it necessary to evaluate the optimum conditions for the quantitative conversion of SCN^- to SO_4^{2-} by H_2O_2 such that the knowledge obtained thereof could be utilised for the purpose noted above. Previous workers reported[21] that SCN^- is oxidised to SO_4^{2-} by H_2O_2, unfortunately, however, the optimum conditions for the quantitative conversion were not available until date. In order to exploit this fascinating reaction it is essential to

Table 6-3. Structurally Significant IR and Raman Bands of A_3FeF_6 (A = NH_4, Na or K)

Compound	IR cm^{-1}	Assignment
$(NH_4)_3[FeF_6)$]	497s	ν (Fe-F)
	290m	δ (F-Fe-F)
	3160m	ν_3 N-H
	3045s	ν_1
	1400s	ν_2
$Na_3[FeF_6]$	480s	ν (Fe-F)
	292m	δ (F-Fe-F)
$K_3[FeF_6]$	470s	ν (Fe-F)
	290m	δ (F-Fe-F)


(NH$_4$)$_3$FeF$_6$
Transmittance (arbitrary scale)
4000
3000
2000
1800
1600
1400
1200
500
180
WAVENUBER (cm^{-1})


Na_3FeF_6
Transmittance (arbitrary scale)
1780
1500
1000
500
180
WAVENUMBER (cm^{-1})


K_3FeF_6
WAVENUMBER (cm^{-1})
1780
1500
1000
500
180
Transmittance (arbitrary scale)

obtain definite information concerning the optimum conditions for the quantitative formation of SO_4^{2-} through electron-transfer reaction between SCN^- and H_2O_2. The results of reactions of ASCN (A = NH_4 or K) and 30% H_2O_2 in the molar ratio 1: excess at different pH, adjusted by addition of the corresponding AOH, suggested the pH 7-8 to be very conducive to the quantitative conversion of SCN^- to SO_4^{2-}. The yield of A_2SO_4 was found to lie between 97 and 99%. The most suitable ratio of $SCN^-:H_2O_2$, for quantitative oxidation of SCN^- to SO_4^{2-} was found to be 1:8-10 (Table 6-4) although one would expect three moles of H_2O_2 to be required for the oxidation of one mole of SCN^- based on the change in oxidation state of sulphur. A lower ratio of $SCN^-:H_2O_2$ (1: $\leqslant$6) did not give rise to the quantitative isolation of A_2SO_4 owing to the possibility of sulphur being present as $S(CN)_2$[21] under this condition. A higher ratio of $SCN^-:H_2O_2$ (1: $>$10) was not considered desirable, as at high ratios decomposition of H_2O_2 to give oxygen is operative.[21] Further, the use of an excess of H_2O_2 is not advisable because of the possible contamination of A_2SO_4 by ammonia and nitrate, which form under this condition.[21]

It may be emphasised that since SCN^- is the conjugate base of a weak acid, it is expected that the species, to a large extent, might be present as SCN^- particularly at a neutral condition. Moreover, H_2O_2 behaves as a poor oxidant at lower pH, thus a lower yield of A_2SO_4 at pH $<$ 7 is not unexpected. At

Table 6-4.. Molar Ratio Between ASCN and H_2O_2[a] and Yield of A_2SO_4 (A = NH_4 or K)[b]

Molar ratio $NH_4SCN:H_2O_2$	Yield(%) of $(NH_4)_2SO_4$	Molar ratio $KSCN:H_2O_2$	Yield(%) of K_2SO_4
1 : 1	60	1 : 1	62
1 : 2	72	1 : 1.5	74.5
1 : 3	75	1 : 2	75
1 : 4	77	1 : 3	75
1 : 5	94	1 : 4	76
1 : 7	96	1 : 6	89
1 : 8	98	1 : 7	92
1 : 10	99	1 : 8	98
		1 : 10	98

[a] 30% H_2O_2 was used in each case. [b] pH of the medium was maintained at 7-8.

pH >8, the alkali-induced decomposition[27] of H_2O_2, and the slow reaction between HOCN (another oxidation product of SCN^-) and H_2O[21] could cause a lowering in the yield of A_2SO_4 at high pH.

The thiocyanate oxidation reaction was monitored by isolation of a small amount of the sample from the reaction solution and recording its IR spectrum. The complete disappearance of ν_{C-N}[28] and ν_{C-S}[28] at ca 2050 cm^{-1} and ca 750 cm^{-1}, respectively, and appearance of two sharp bands at ca 1110 cm^{-1} and ca 610 cm^{-1} owing to ν_3 and ν_4 modes, respectively,[29] of SO_4^{2-} ensure completion of the reaction.

The results of chemical analyses of the oxidation products and their molar conductances lying between 245 and 250 $\Omega^{-1}cm^2mol^{-1}$ are in complete agreement with the formulations as A_2SO_4 (A = NH_4 or K) and ensure purity of the products. The characteristic feature of the IR spectra are the absorptions at ca 1110s and ca 610s cm^{-1} assigned to the ν_3 and ν_4 modes, respectively, of ionic SO_4^{2-} (T_d symmetry). The three extra bands at 3160m, 3040s and 1400s cm^{-1} in $(NH_4)_2SO_4$ have been attributed to ν_3, ν_1, and ν_4 modes, respectively, of the NH_4^+ ion. Further, the absence of any absorptions in the regions typical for ν (C-N), ν (C-S), and δ (NCS) ensures the complete absence of unoxidised SCN^-.

Thus it is evident from the above results that a quantitative conversion of SCN^- to SO_4^{2-} can be achieved by the electron-transfer reaction between SCN^- and H_2O_2 at pH 7-8 with their molar ratio being maintained at 1:8-10.

Reactions of SCN^- and F^- with Iron(III) Hydroxide and Hydrogen Peroxide

There was some concern regarding the reaction of thiocyanate with iron(III), and consequent upon this, results of some very recent studies[30] have shown the possibility of oxidation of SCN^- to thrithiocyanate $(SCN)_3^-$, a rather unstable intermediate, by iron(III). Our principal concern was to investigate the main product of oxidation of thiocyanate in the presence of fluoride ions and iron(III) with a hope to get an access to mixed-ligand fluoro(sulphato)ferrates(III). This became necessary because our attempts to synthesise such mixed-ligand complexes from the reaction of sulphate and fluoride with iron(III) in an acidic medium had failed, unlike in the case of manganese(III)[13] and cobalt(II).[7] The products obtained therefrom were found to be only pentafluoroferrates(III), which did not contain any sulphate. Accordingly, chemical oxidation of SCN^- to SO_4^{2-} by H_2O_2 in the presence of F^- ions and iron(III) was undertaken. The knowledge obtained from a separate study as described earlier in this section concerning the oxidation of SCN^- to SO_4^{2-} by H_2O_2, was very useful in the present context. Hydrogen peroxide, besides being an oxidant capable of oxidising SCN^- to sulphate[21] also helps iron to retain its trivalent state.

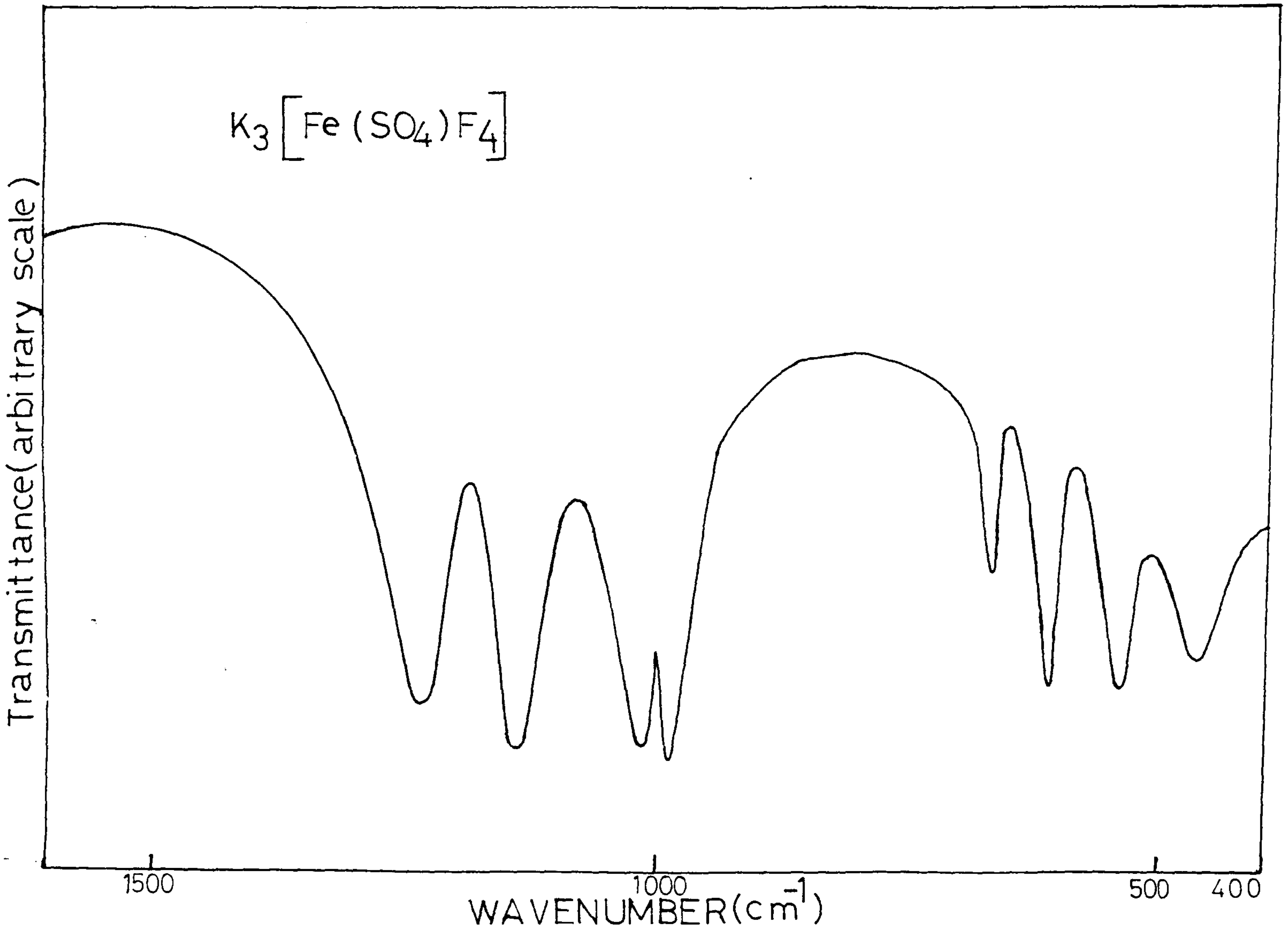
Initial studies of the reaction of SCN^- with iron(III) hydroxide, hydrofluoric acid and hydrogen peroxide were carried out by maintaining the optimum condition for SCN^- oxidation to SO_4^{2-} by H_2O_2 as evaluated by us. However, the slightly alkaline medium (pH$\sim$8) led to complication, owing to apparent side reactions leading to contamination of the reaction products, although the oxidation of SCN^- did take place. Subsequent experiments were therefore carried out in slightly acidic media. During the reaction of ASCN (A = NH_4 or K) and iron(III) hydroxide with aqueous HF and hydrogen peroxide, SCN^- was oxidised to SO_4^{2-} and metal hydroxide went into solution with the solution becoming practically colourless. The reactions ultimately led to the synthesis of the hitherto unreported compounds (vide Experimental) which analyse as $K_3[Fe(SO_4)F_4]$ and $(NH_4)_2[Fe(SO_4)F_3]$ as obtained from KSCN and NH_4SCN, respectively, providing an access to mixed-ligand fluoro(sulphato)ferrates(III). Presumably here again an intermediate peroxyfluoroferrate(III) species is first generated which then participates, through its co-ordinated peroxy group, in the oxidation of SCN^- finally to afford the heteroligand fluoroferrates(III),

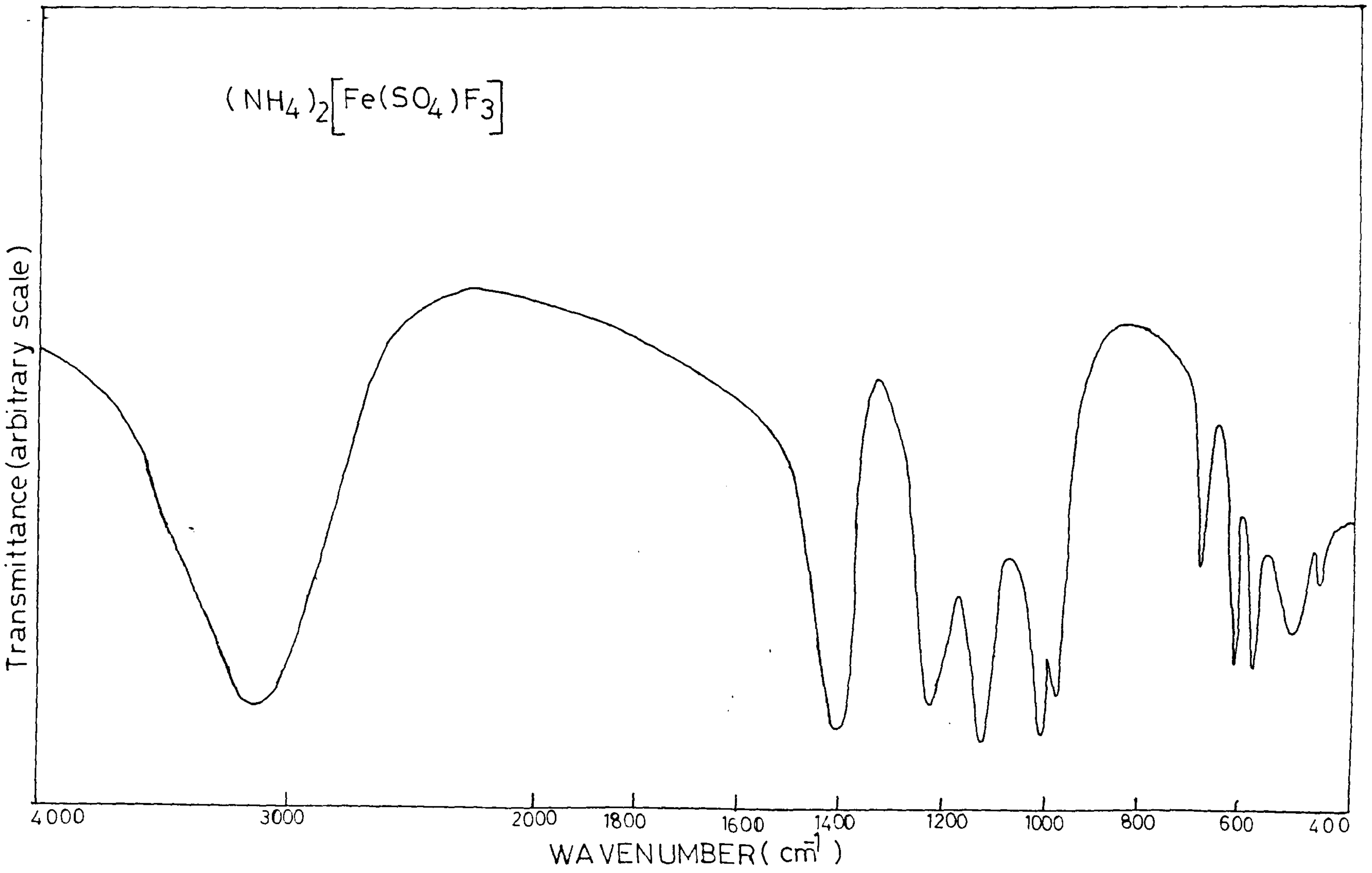
The $K_3[Fe(SO_4)F_4]$ and $(NH_4)_2[Fe(SO_4)F_3]$ complexes are stable and can be stored in sealed polyethylene sample containers. However, they attack glass in the presence of moisture. The compounds are insoluble in common organic solvents. Oxidation state of iron was estimated chemically by an iodometric method and magnetic moments were measured at room temperatures. While the chemically estimated oxidation state of iron was found to be 3, the magnetic moments of the compounds were found to be 5.7 μ_B suggesting the occurrence of high spin iron(III).

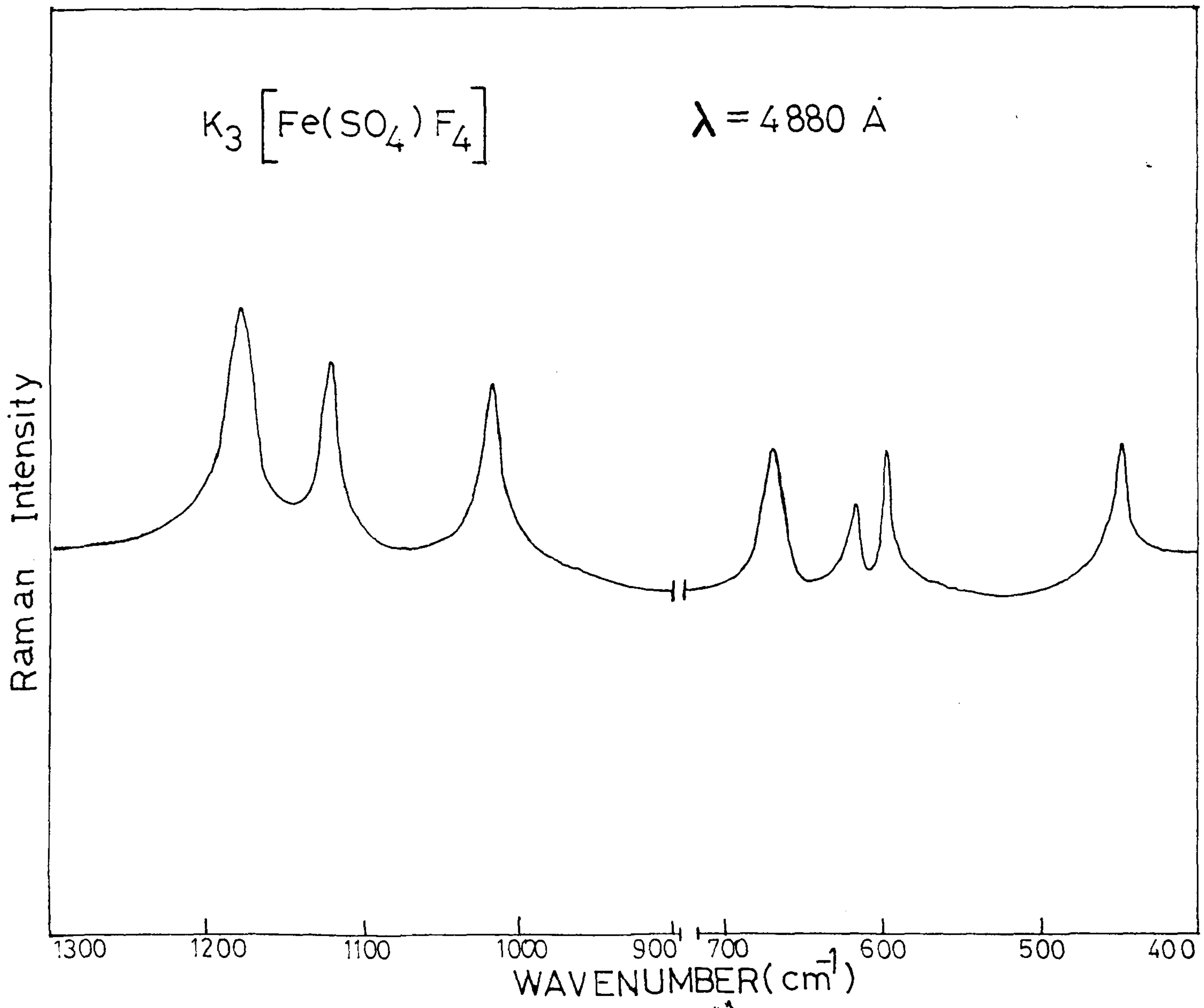
A study of the vibrational spectra of the reaction products revealed the complete absence of ν (C-N) at ca 2120 cm^{-1}, and the IR and laser Raman (lR) spectral patterns were very similar to other metal-sulphato complexes. When sulphate is co-ordinated its symmetry is lowered from T_d to C_{3v} or C_{2v}[31] depending on whether it binds the metal centre in a monodentate or a bidentate fashion.[31] In the case of C_{2v} symmetry of sulphate, its ν_3 and ν_4 modes are split into three bands each, while the ν_1 and ν_2 appear with medium intensity. Although both bridging and chelating sulphato ligands have a C_{2v} symmetry, they can generally be distinguished on the basis of their IR and Raman spectra since ν_3 vibrations for chelating bidentate sulphato complexes occur at higher energies than those of bridging sulphato complexes.[31] In the IR and LR spectra of the newly synthesised compounds each of the ν_3 and ν_4 vibrations were split into three bands with the ν_3 modes lying at ca 1225, ca 1130 and ca 1020 cm^{-1}. A comparison with other types of sulphato complexes[32] indicates that these vibrations fall at rather high energies for ν_3 modes and therefore suggests that SO_4^{2-} binds the iron(III) centre in a chelating bidentate manner. Another common feature of the fluoro(sulphato)-ferrates(III) is the band at ca 495 cm^{-1} which has been assigned

Table 6-5. Structurally Significant IR and Raman Bands of $K_3[Fe(SO_4)F_4]$ and $(NH_4)_2[Fe(SO_4)F_3]$

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment	
$K_3[Fe(SO_4)F_4]$	980m	970	ν_1	
	451m	450	ν_2	
	1225s	1220		
	1131s	1130	ν_3	ν (S-O)
	1020s	1020		
	669m	670		
	611s	610	ν_4	
	599s	600		
	490s		ν (Fe-F)	
$(NH_4)_2[Fe(SO_4)F_3]$	975m	980	ν_1	
	450m	450	ν_2	
	1223s	1220		
	1130s	1135	ν_3	ν (S-O)
	1010s	1010		
	670m	675		
	610s	615	ν_4	
	600s	600		
	495s		ν (Fe-F)	
	3160m		ν_3	
	3040s		ν_1	N-H
	1400s		ν_2	


$K_3[Fe(SO_4)F_4]$
Transmittance(arbitrary scale)
1500
1000
500
400
WAVENUMBER(cm^{-1})


$(NH_4)_2[Fe(SO_4)F_3]$
Transmittance (arbitrary scale)
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBER (cm^{-1})


$K_3[Fe(SO_4)F_4]$
$\lambda = 4880$ Å
Raman Intensity
1300
1200
1100
1000
900
700
600
500
400
WAVENUMBER(cm^{-1})

to the ν (Fe-F) mode arising from the presence of co-ordinated fluoride ligands. These results adduce support to the identity of the fluoro(sulphato)ferrates(III).

To conclude this Chapter the following points may be emphasised:

(i) Hexafluoroferrates(III) of the type A_3FeF_6 (A = Na, K or NH_4) can be directly synthesised in high yields, under appropriate experimental conditions, providing an easy access to such compounds.

(ii) Reactions of potassium or ammonium thiocyanate with iron(III) hydroxide, aqueous hydrofluoric acid, in the presence of H_2O_2 have resulted in the production of the hitherto unknown fluoro(sulphato)ferrates(III). These compounds provide excellent prospects and materials for further studies of their properties and for a comparison with those of the binary fluorometallates. In this way an insight into the fluoro-chemistry of iron may be gained.

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APPENDIX

APPENDIX

LIST OF PUBLICATIONS

1. Reactions of Vanadium(V) with Alkali Sulphate or Thiocyanate. Evidence for the Formation of Oxodiperoxovanadate(V) Complexes Containing Ionic Sulphate
   Mihir K. Chaudhuri and Nashreen S. Islam
   Transition Met. Chem. 1985, 10, 333.

2. Alkali Oxodiperoxovanadate(V) Complexes $[VO(O_2)_2]^-$. First Isolation in the Solid State, Characterisation and Structural Assessment
   Mihir K. Chaudhuri and Nashreen S. Islam
   J. Indian Chem. Soc., 1985, 62, 815.

3. First Synthesis and Structural Assessment of Alkali-Metal Triperoxovanadate(V), $A[V(O_2)_3]$
   Mihir K. Chaudhuri, S.K. Ghosh, and Nashreen S. Islam
   Inorg. Chem., 1985, 24, 2706.

4. Direct Synthesis of Hexafluoroferrates(III) and Reaction of Thiocyanate and Fluoride with Iron(III) and Hydrogen Peroxide as an Access to Fluoro(sulphato)ferrates(III)
   Mihir K. Chaudhuri and Nashreen S. Islam
   Inorg.Chem., 1986, 25, 3749.

5. Optimum Conditions for Hydrogen Peroxide Oxidation of Thiocyanate to Sulphate

   Mihir K. Chaudhuri and Nashreen S. Islam

   Ind. J. Chem., 1985, 24A, 447.

$0.5\,H_2O$. On heating the *trans* compound at 110 °C for 3 h the HCl was lost forming $[Co(en)_2Cl_2]Cl \cdot 0.5\,H_2O$. *Cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$(11) and *trans*-$[Cr(en)_2Cl_2]Cl$(12) were prepared by known methods and analysed to ascertain their composition. The purity of the *cis* and the *trans* forms of all cobalt(III)(14) and chromium(III)(15) complexes was checked by their electronic d-d spectra.

The *cis* complexes were resolved using d-α-bromocamphor-π-sulphonate (ammonium salt) and the enantiomer designated in the literature as the "l" form was isolated for the cobalt(III)(10) and chromium(III)(13) complexes.

Apparatus and procedure

A Varian 2300 (u.v.-vis.-n.i.r.) spectrophotometer was used for recording the spectra and a Rudolph Autopol Polarimeter for optical rotation measurements of solutions using a polarimeter tube of 20 cm path length.

An Abderhalden drying apparatus was used for heating the samples in small glass vials at constant temperature (boiling point of an appropriate refluxing solvent) to study the possible isomerisation and racemisation of the complexes.

Optical rotations of samples of the complexes were measured quickly after dissolving in water to form a solution of 0.032% (W/V) concentration; the measurements were made immediately on freshly prepared solutions at 589 nm. Since the specific rotation, [α], values are concentration dependent, all samples were measured at the same concentration. Spectra were recorded quickly using freshly prepared aqueous solutions.

Acknowledgement

The investigations were carried out in the School of Chemical Science of the University of Illinois, Urbana, Il., USA, during the tenure of one of the authors (D.B.) of a Visiting Professorship on a Senior Fullbright Program, in 1984. Thanks are due to the University of Illinois for providing all facilities for the work and to A.C.S. Petroleum Research Fund for financial support. Thanks are also due to the Council of International Exchange of Scholars, Washington D.C., USA, and the US Educational Foundation in India, New Delhi, for the assignment and award of travel grant to one of us (D.B.).

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(Received May 8th, 1985) TMC 1351

Reactions of Vanadium(V) with Alkali Sulphate or Thiocyanate. Evidence for the Formation of Oxodiperoxovanadate(V) Complexes Containing Ionic Sulphate

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Summary

Vanadium pentoxide (1 mol) reacts with alkali sulphate (2 mol) or alkali thiocyanate (2 mol) and an excess of hydrogen peroxide at pH 7–8, maintained by the addition of the corresponding alkali hydroxide, to produce yellow oxodiperoxovanadate(V) complexes containing sulphate. The compounds were characterised by elemental analyses, molar conductance measurements, and i.r. and laser Raman spectroscopic studies. The compounds are formulated as $M[VO(O_2)_2] \cdot M_2SO_4$ (M = alkali metal). The peroxide has been shown to be bonded to the vanadium(V) centre in a triangular bidentate (C_{2v}) manner.

Introduction

There has been a good deal of continued interest in the field of peroxovanadium chemistry(1–8). While many of the recent reports deal with solutions(2–7), the synthesis, isolation in the solid state, characterisation and structural assessment of peroxovanadium compounds have received much less attention. Within the context of the above subject there are several

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points which have not been attended to. One is the mode of binding of sulphate with vanadium(V) in the complex formed in the reaction with hydrogen peroxide in the presence of SO_4^{2-}, a reaction used in the spectro-photometric determination of vanadium. This report presents an interpretative account of the results of our studies involving the reactions of vanadium(V) and hydrogen peroxide in the presence of SO_4^{2-} or SCN^-, and shows that the yellow compound obtained is an oxodiperoxovanadate(V) complex containing ionic sulphate.

Experimental

Reagent grade chemicals were used. I.r. spectra were recorded on a Perkin-Elmer model 983 spectrophotometer. The laser Raman (l.R.) spectra were recorded on a SPEX Ramalog model 1403 spectrometer. The 4880 Å laser line from the Spectra-Physics model 165 argon laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube and a photon-counting processing system. The spectra were recorded at ambient temperatures by making freshly prepared solutions of the samples or pressed pellets of the compounds. Magnetic susceptibility measurements were made by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. Molar conductances were measured using a Philips PR 9500 conductivity bridge. The pH of the reaction solution was measured with a Systronics type 335 digital pH meter, and also with pH indicator (BDH) paper.

Reaction of V_2O_5 with H_2O_2 and M_2SO_4 (M = NH_4, Na or K). Synthesis of $M[VO(O_2)_2]$. M_2SO_4

In a typical reaction V_2O_5 and alkali sulphate, M_2SO_4, were intimately mixed in a 1 : 2 ratio , and the mixture dissolved in an excess of 30% H_2O_2 ($V_2O_5 : H_2O_2$ :: 1 : 32) with stirring. The solution was filtered to remove any traces of undissolved impurity, and the filtrate cooled in ice-water. Alkali hydroxide solution was added dropwise with constant stirring until the solution became permanent yellow and attained pH 7–8. The solution was stirred for a further period of *ca.* 10 min. An excess of EtOH was added to the above solution with occasional stirring until the yellow coloured microcystalline product, $M[VO(O_2)_2] \cdot M_2SO_4$, ceased to appear. The product was filtered, washed four times with EtOH, and finally dried *in vacuo* over P_4O_{10}.

Reaction of V_2O_5 with H_2O_2 and MSCN (M = NH_4 or K). Synthesis of $M[VO(O_2)_2] \cdot M_2SO_4$

In a representative procedure, a mixture of V_2O_5 and MSCN, in a 1 : 2 ratio, was dissolved in an excess of 30% H_2O_2 ($V_2O_5 : H_2O_2$ :: 1 : 42.5). The resultant solution was cooled in ice-water for *ca.* 15 min, followed by the addition of alkali hydroxide, MOH (M = NH_4 or K), drop by drop with continuous stirring until the solution became yellow with the pH lying between 7 and 8. The whole was cooled for *ca.* 30 min, and an excess of EtOH was added until precipitation was com-

Table 1. Reagents used to prepare, and yields of, $M[VO(O_2)_2] \cdot M_2SO_4$ (M = NH_4, Na or K).

Compound	Yield/g (%)	V_2O_5/g (mmol)	M_2SO_4 or MSCN/g (mmol)	30% H_2O_2/ cm^3 (mmol)
$NH_4[VO(O_2)_2] \cdot (NH_4)_2SO_4$	2.8	1.0	1.45	20
	(90)	(5.5)	(11)	(176.4)
$Na[VO(O_2)_2] \cdot Na_2SO_4$	2.7	1.0	1.56	20
	(82)	(5.5)	(11)	(176.4)
$K[VO(O_2)_2] \cdot K_2SO_4$	3.4	1.0	1.92	20
	(89)	(5.5)	(11)	(176.4)
$NH_4[VO(O_2)_2] \cdot (NH_4)_2SO_4$)	2.9	1.0	0.84	26.5
	(94)	(5.5)	(11)	(233.7)
$K[VO(O_2)_2] \cdot K_2SO_4$	3	1.0	1.1[b]	26.5
	(91)	(5.5)	(11)	(233.7)

Table 2. Analytical data, molar conductance values, and structurally important i.r. and laser Raman bands of $M[VO(O_2)_2] \cdot M_2SO_4$ (M = NH_4, Na or K).

Compound	Molar conductance ($\Omega^{-1}cm^2mol^{-1}$)	Found (Calcd.) % M or N	V	O_A[a]	SO_4	I.r. (cm^{-1})	Raman (cm^{-1})	Assignments
$NH_4[VO(O_2)_2] \cdot (NH_4)_2SO_4$	380	15.2	17.8	23.1	34.8	950s	950	$\nu(V{=}O)$
		(15.0)	(18.1)	(22.8)	(34.2)	875s	880	$\nu(-O-O-)$
						630s	625	$\nu(V-O_2)(\nu_3)$
						525m	520	$\nu(V-O_2)(\nu_2)$
						1125vs	1105	$\nu(S-O)(\nu_3)$
						615s	600	$\nu(S-O)(\nu_4)$
$Na[VO(O_2)_2] \cdot Na_2SO_4$	370	22.8	17.9	22.1	32.9	960s	950	$\nu(V{=}O)$
		(23.3)	(17.2)	(21.6)	(32.5)	870s	875	$\nu(-O-O-)$
						635s	620	$\nu(V-O_2)(\nu_3)$
						525m	525	$\nu(V-O_2)(\nu_2)$
						1120vs	1110	$\nu(S-O)(\nu_3)$
						610s	600	$\nu(S-O)(\nu_4)$
$K[VO(O_2)_2] \cdot K_2SO_4$	355	33.6	14.2	19.2	27.2	950s	960	$\nu(V{=}O)$
		(34.1)	(14.8)	(18.6)	(27.9)	870s	880	$\nu(-O-O-)$
						630s	620	$\nu(V-O_2)(\nu_3)$
						520m	520	$\nu(V-O_2)(\nu_2)$
						1120vs	1105	$\nu(S-O)(\nu_3)$
						610s	600	$\nu(S-O)(\nu_4)$

[a] Peroxo oxygen.

plete. The yellow microcrystalline product, $M[VO(O_2)_2] \cdot M_2SO_4$, was isolated as described above.

The amounts of reagents used and yields of the products are given in Table 1.

Elemental analysis

Vanadium, peroxide, sulphate, sodium, potassium and nitrogen were estimated by the methods described earlier(9, 10).

Physical data are summarised in Table 2.

Results and Discussion

It has been emphasised in the literature(11) that the reactions of vanadium(V) with hydrogen peroxide are quite complicated, and sensitive to pH. As a part of our programme involving the syntheses and structural evaluation of complex peroxovanadates(9), we were interested in the synthesis of peroxovanadate(V) compounds containing SO_4^{2-}, to characterise the peroxo-compound formed and to evaluate the nature of binding between sulphate and the vanadium(V) centre. Accordingly, vanadium pentoxide was allowed to react with hydrogen peroxide in the presence of alkali sulphate at a pH 7–8 maintained by the addition of the corresponding alkali hydroxide to give a yellow solution. Addition of an excess of ethanol, which facilitated precipitation, gave a yellow, microcrystalline product. The product was found to be stable for a prolonged period and completely soluble in water. The results of chemical analysis suggest the $M:V:O_2^{2-}:SO_4^{2-}$ as 3:1:2:1 stoichiometry. The molar conductances, based on the molecular weight calculated from the results of elemental analyses were found to lie in the 350–380 $\Omega^{-1}\,cm^2\,mol^{-1}$ range suggesting that the products may be formulated as $M_3[VO(O_2)_2(SO_4)]$, or, as well, as $M[VO(O_2)_2] \cdot M_2SO_4$. The compounds are all diamagnetic.

The i.r. spectra of the compounds resemble each other very closely, except for the additional cation modes in the NH_4^+ salt, suggesting that the compounds are structurally similar. The principal features of the spectra are the absorptions at *ca.* 950s, *ca.* 870s, and *ca.* 630s and *ca.* 525m cm^{-1} assigned to $\nu(V{=}O)$, $\nu(\text{-O-O-})$, and $\nu(V\text{-}O_2)$ modes(12, 13), respectively, (Table 2), and the absorptions at *ca.* 1120vs and *ca.* 615s attributed to the ν_3 and ν_4 modes of SO_4^{2-}(14, 15). Since the $\nu(\text{-O-O-})$ and the complementary $\nu(V\text{-}O_2)$ modes are observed in the positions stipulated for a triangularly bonded O_2^{2-} group, and the $\nu(S\text{-}O)$ (ν_3 and ν_4) modes of SO_4^{2-} fall in the regions typical of an ionic sulphate (T_d), it may be safely assumed that peroxide groups are bonded to the vanadium(V) in a triangular bidentate (C_{2v}) manner, and that the SO_4^{2-} is not coordinated to the metal. This was further augmented by the results of laser Raman spectroscopic studies. These showed $\nu(V{=}O)$ peak at *ca.* 950, $\nu(\text{-O-O-})$ peak at *ca.* 880 (ν_1) and $\nu(V\text{-}O_2)$ peaks at *ca.* 620 (ν_3) and at *ca.* 520 (ν_2) cm^{-1}. The ν_3 and ν_4 modes of $\nu(S\text{-}O)$, arising from the ionic sulphate, were observed at *ca.* 1105 and *ca.* 610 cm^{-1}, respectively. These results show that the compounds synthesised are oxodiperoxovanadate(V) complexes containing ionic sulphate and the compounds can be best formulated as $M[VO(O_2)_2] \cdot M_2SO_4$ ($M = NH_4$, Na or K).

In our attempts to explore the possibility of coordination of SO_4^{2-} to vanadium(V) in the presence of peroxide, the reaction of V_2O_5 and alkali thiocyanate, MSCN ($M = NH_4$ or K), was performed in the presence of an excess of hydrogen peroxide at pH 7–8 maintained by the addition of the corresponding MOH. The strategy was that SCN^- would be oxidised to $SO_4{}^{2-}$ (16, 17) *in situ* by H_2O_2, and remain coordinated to produce mixed ligand peroxo-sulphato-compounds. Here again yellow microcrystalline products were obtained, and the chemical analysis, i.r. and Raman spectroscopic studies showed that the compounds were the same, *viz.*, $M[VO(O_2)_2] \cdot M_2SO_4$, as those obtained from the reaction of V_2O_5 with H_2O_2 and M_2SO_4 at pH 7–8.

Thus, it is inferred from the results of the present work that the reactions of vanadium(V) with an excess of H_2O_2 and SO_4^{2-} or SCN^- at pH 7–8 forms the complex oxodiperoxovanadate(V), but that SO_4^{2-} does not coordinate.

Acknowledgements

We thank the Council of Scientific and Industrial Research, New Delhi, for awarding a Fellowship (to N.S.I.).

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(Received February 27th, 1985) TMC 1314

J. Indian Chem. Soc.,
Vol. LXII, November 1985, pp. 815-817

Alkali Oxodiperoxovanadate(V) Complexes $[VO(O_2)_2]^-$. First Isolation in the Solid State, Characterisation and Structural Assessment

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Alkali metal oxodiperoxovanadates(V), $A[VO(O_2)_2]$ ($A=NH_4$, Na or K), have been synthesised by the reaction of V_2O_5 with 30% hydrogen peroxide and the corresponding alkali hydroxide AOH, in the concentration ratio 1 : 41.8 : 5.3-6.6, followed by precipitation with ethanol. The compounds are yellow and diamagnetic, and their molar conductances in water at ambient temperature lie between 130 and 140 Ω^{-1} cm^2 mol^{-1}. The results of infrared and laser Raman spectroscopic studies suggest that the complex species $[VO(O_2)_2]^-$, contains a terminally bonded $V=O$ group, and that the peroxide (O_2^{2-}) ligand is bonded to the vanadium(V) centre in a triangular bidentate (C_{2v}) manner. The complex $[VO(O_2)_2]^-$ ion may be a pentacoordinated monomer, however, a hexacoordinated structure through a weak $—V=O....V=O....V=O....$ interaction can not he ruled out. As an example of its reactivity, the potassium salt of the complex ion $K[VO(O_2)_2]$, has been shown to undergo facile reaction with KF, and 2,2′-dipyridyl (dipy) to produce $K_2[VO(O_2)_2F]$, and $K[VO(O_2)_2\ dipy]$, respectively.

BECAUSE of the biochemical significance[1,2], and importance in the oxidation chemistry[3-6] for the activation and transfer of oxygen to organic substrates of peroxo transition metal compounds that studies on peroxo-vanadium chemistry has emerged as one of the active areas of current research[5,7-15]. The synthesis of well defined peroxovanadium compounds followed by the study of their different properties provide a means in understanding the chemistry of such compounds. It has been known that vanadium-hydrogen peroxide system gives different colour reactions under slightly varying pH of the reaction medium[10,16,17] and it is believed that the yellow colour of vanadium(V)-H_2O_2 solution owes its origin to the formation of a diperoxovanadate(V) anion[16,17], $[VO(O_2)_2]^-$. However, earlier attempts to obtain the complex in the solid state failed[17]. The triperoxovanadate(V) complex, $A[V(O_2)_3]$ (A=alkali metal), has been synthesised only very recently[18]. The present paper reports the first successful synthesis, characterisation and structural assessment of the yellow alkali oxodiperoxovanadates(V), $A[VO(O_2)_2]$ ($A=NH_4$, Na or K). Also reported are two reactions involving the potassium salt, $K[VO(O_2)_2]$, which highlight the scope for the use of these compounds in synthesis.

Experimental

The chemicals used were of reagent grade. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer. Raman spectral measurements were made on a SPEX Ramalog 1403 spectrometer. The 4800 Å laser line from the Spectra-Physics 165 argon laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube, followed by photon-count processing system. The sample was held either in a quartz capillary or in the form of a pressed pellet. The spectra were recorded at ambient temperatures. Molar conductance measurements were made using a Philips PR 9500 conductivity bridge. Magnetic susceptibility measurements were made by the Gouy method, using $Hg[Co(NCS)_4]$ as the calibrant. The pH was measured with a Systronics 335 digital pH meter.

Synthesis of alkali oxodiperoxovanadate(V), $A[VO(O_2)_2]$ ($A=NH_4$, Na or K) : Powdered V_2O_5 and 30% hydrogen peroxide were mixed in the concentration ratio of V_2O_5 : H_2O_2 as 1 : 41.8 followed by the addition of alkali hydroxide, AOH, with slow stirring until V_2O_5 dissolved to produce a clear yellow solution with its pH lying between 7 and 8. While aqueous ammonia was added in the form of its concentrated solution (specific gravity 0.9), sodium hydroxide or potassium hydroxide was added in the solid form. The resulting solution was cooled in an ice-water bath for ~30 min, and then an excess of pre-cooled ethanol was added to it until yellow coloured microcrystalline $A[VO(O_2)_2]$ compound ceased to appear. The compound was separated by centrifugation, washed four times with cold ethanol and finally dried *in vacuo* over diphosphorous pentoxide. The yield was 85-94%.

Reactions of potassium oxodiperoxovanadate(V), $K[VO(O_2)_2]$ with KF, and 2,2′-dipyridyl : To a concentrated aqueous solution of $K[VO(O_2)_2]$ was added an aqueous solution of KF, or an ethanolic solution of 2,2′-dipyridyl (dipy) with the concentration ratio between $K[VO(O_2)_2]$ and KF or dipy

TABLE 1—ANALYTICAL DATA, MOLAR CONDUCTANCE VALUES AND STRUCTURALLY SIGNIFICANT IR AND RAMAN BANDS OF THE COMPOUNDS

Compd.	Molar conductance Ω^{-1} cm^2 mol^{-1}	Analysis % : Found/(Calcd.)			Ir band cm^{-1}	Raman band cm^{-1}	Assignments
		A/N	V	O^a			
$NH_4[VO(O_2)_2]$	140	9.2^b	34.4	42.5	950 s	945	$\nu_{V=O}$
		(9.4)^b	(34.19)	(42.96)	885 s	880	$\nu_{O-O}(\nu_1)$
					605 s	610	$\nu_{V-O_2}(\nu_3)$
					525 s	530	$\nu_{V-O_2}(\nu_2)$
$Na[VO(O_2)_2]$	135	15.3	33.6	41.7	935 s	950	$\nu_{V=O}$
		(14.94)	(33.09)	(41.58)	870 s	880	$\nu_{O-O}(\nu_1)$
					605 s	600	$\nu_{V-O_2}(\nu_3)$
					530 s	530	$\nu_{V-O_2}(\nu_2)$
$K[VO(O_2)_2]$	130	22.7	30.3	37.2	960 s	945	$\nu_{V=O}$
		(23.0)	(29.96)	(37.64)	885 s	875	$\nu_{O-O}(\nu_1)$
					605 s	615	$\nu_{V-O_2}(\nu_3)$
					530 s	525	$\nu_{V-O_2}(\nu_2)$

^{a} Peroxo-oxygen. ^{b} Analysis for N.

maintained at 1 : 1. The resulting solution was stirred for ~15 min at the ice-bath temperature followed by the addition of cold ethanol until the precipitation of yellow microcrystalline product was complete. It was allowed to stand at the ice-bath temperature for ~30 min, and the product was isolated by centrifugation, purified by washing with ethanol and finally dried *in vacuo* over diphosphorous pentoxide. The product isolated from the reaction of $K[VO(O_2)_2]$ with KF was identified as $K_2[VO(O_2)_2F]$[19], while that obtained from the reaction of $K[VO(O_2)_2]$ with dipyridyl was found to be $K[VO(O_2)_2$ dipy]$.4H_2O$[14].

Elemental analyses : Vanadium, peroxide, nitrogen, sodium and potassium were estimated by the methods described earlier[20].

The results of elemental analyses, molar conductance values, infrared and Raman band positions along with their assignments are summarised in Table 1.

Results and Discussion

The yellow alkali metal oxodiperoxovanadates(V), $A[VO(O_2)_2]$ ($A=NH_4$, Na or K), are soluble in water at ambient temperatures, and they permit conductance measurements. The molar conductances of the newly synthesised compounds were found to lie in the range 130-140 Ω^{-1} cm^2 mol^{-1} (Table 1), suggesting 1 : 1 electrolytic nature of each of them in agreement with their formulae. The compounds are all diamagnetic, as evidenced from the results of magnetic susceptibility measurements, in conformity with the view that vanadium occurs in its +5 oxidation state (d^0) in each of them.

Alkali metal oxodiperoxovanadates(V) can be stored in sealed sample containers and their stability can be ascertained by the chemical determination of peroxide periodically. The peroxide estimation in such compounds must be considered as very important in order to determine the number of O_2^{2-} group coordinated to the metal centre. The peroxide content was determined by red-ox titrations[18,20,21] using standard Ce^{IV} solution, and also separately by standard potassium permanganate solution. The titration in each case was carried out in the presence of boric acid in order to prevent any loss of active oxygen, and the results obtained conspicuously suggested the occurrence of two peroxo (O_2^{2-}) groups per vanadium atom in each of the compounds.

The infrared and laser Raman spectra of the alkali metal oxodiperoxovanadates(V), $A[VO(O_2)_2]$ ($A=NH_4$, Na or K), are quite characteristic. Both ir and laser Raman spectra show bands at ~950, ~880, ~610, and ~530 cm^{-1} which have been assigned to $\nu_{V=O}$[22], ν_{O-O} (ν_1)[23,24], ν_{V-O_2} (ν_3)[23,24] and ν_{V-O_2} (ν_2)[23,24] modes, respectively. The O − O and metal − O_2 bands are important spectroscopic probes for molecular structure determination, and are amenable to infrared and Raman spectroscopic studies. The observed positions of ν_{O-O} and ν_{V-O_2} modes, and the number of such vibrations correspond to those which one would expect to observe for a triangularly bonded peroxide ligand[18,24], and accordingly it is argued that the peroxide ligands are bonded to the vanadium(V) centre in a triangular bidentate (C_{2v}) manner in each of the newly synthesised compounds. The distinction between ν_2 and ν_3 modes of ν_{V-O_2} was made on the basis of the fact that the ν_{V-O_2} band at ~530 cm^{-1} was comparatively more sharp and intense than that of the ν_{V-O_2} at ~610 cm^{-1}, and was polarised. The ν_1 mode is well separated from the ν_2 and ν_3 modes and the band at ~880 cm^{-1} is unambiguously assigned to the ν_1 (ν_{O-O}) mode of the coordinated peroxide (O_2^{2-}). The strong absorption at $\sim 950 \text{ cm}^{-1}$ owes its origin to the presence of a terminally bonded oxygen atom. It is on account of the large polarisability changes involved in the V=O bond that the $\nu_{V=O}$ appears as a strong band in the laser Raman spectra, and is quite characteristic for the newly synthesised compounds. In order to explore the possibility of any change in the structure of the complex anion $[VO(O_2)_2]^-$ in solution, laser Raman spectra of the freshly prepared solutions of alkali metal oxodiperoxovanadates(V) were recorded at ambient temperature. The solution spectra neither showed any new band nor any appreciable change in positions of the peaks observed in the corresponding solid state spectra. The only notable difference was that the solution laser Raman peaks, especially the $\nu_{V=O}$, ν_{O-O} (ν_1) and ν_{V-O_2} (ν_2) modes, were found to be relatively sharp. This, therefore, leads us to infer that the complex species $[VO(O_2)_2]^-$ most probably retains its structural identity both in the solid state as well as in solutions.

Acknowledgement

The authors thank the C.S.I.R., New Delhi, for the award of a fellowship to one of them (N.S.I.).

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Reprinted from Inorganic Chemistry, 1985, *24*, 2706

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First Synthesis and Structural Assessment of Alkali-Metal Triperoxovanadates(V), A[V(O_2)$_3$]

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Received December 28, 1984

It is probably owing to biochemical significance,[1,2] and importance in the oxidation chemistry,[3] of peroxo–transition-metal compounds that the study on peroxovanadium chemistry has emerged as one of the active areas of research.[4-10] The vanadium–hydrogen peroxide system is complicated owing to the formation of peroxovanadates of varied compositions and colors with varying acidity or alkalinity of the reaction media.[7,11,12] The blue tetraperoxovanadate(V) $K_3[V(O_2)_4]$ has been known,[13] presumably having a structure analogous to that of $K_3[Cr(O_2)_4]$.[14] However, the triperoxovanadates(V) $A[V(O_2)_3]$ (A = alkali metal) have not been synthesized and isolated in the solid state although the hetero triperoxovanadates(V) $A_2[V(O_2)_3X]$ (X = F or Cl) have been reported recently.[15] In view of this it was thought that the successful synthesis and isolation of the blue $[V(O_2)_3]^-$ complex would provide some fundamental information concerning the minimum number of O_2^{2-} ligands, per V^{5+} center, required for the formation of a blue peroxovanadate(V) species. The present paper reports the synthesis, isolation in the solid state, and characterization of the blue alkali-metal triperoxovanadates(V) $A[V(O_2)_3]$ (A = Na or K).

Experimental Section

The chemicals used were all reagent grade (B.D.H., E. Merck) products. Infrared spectra were recorded on a Perkin-elmer Model 983 spectrophotometer. The laser Raman spectra were recorded on a SPEX Ramalog Model 1403 spectrometer. The 6328-Å Laser line from a helium–neon laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube and a photon-counting processing system. The spectra were recorded at ambient temperatures by making freshly prepared solutions of the samples or pressed pellets of the compounds. Molar conductance measurements were made with a Philips PR 9500 conductivity bridge. Magnetic susceptibilities were measured by the Gouy method using $Hg[Co(NCS)_4]$ as the standard. The UV–vis spectra were recorded on a Beckman Model UV-26 spectrophotometer.

Synthesis of Alkali-Metal Triperoxovanadates(V), A[V(O_2)$_3$] (A = Na or K). Recommended Procedure. To finely powdered V_2O_5 was added an excess of 30% hydrogen peroxide, with slow stirring, in the molar ratio of V_2O_5:H_2O_2 as 1:42.5. Solid alkali-metal hydroxide, AOH, was slowly added to the above mixture under continuous stirring, until a blue color was developed (molar ratio V_2O_5:H_2O_2:AOH as 1:42.5:(10–12)). The blue solution was then cooled in an ice-water bath for ca. 30 min, followed by the addition of an excess of precooled ethyl alcohol until the blue microcrystalline $A[V(O_2)_3]$ ceased to appear. The blue compound was separated by centrifugation, washed four or five times with cold ethanol, and finally dried in vacuo over phosphorus pentoxide. The reaction was monitored by IR spectroscopy. The complete disappearance of the sharp band at ca. 950 cm^{-1} due to $\nu_{V=O}$, in the product isolated from a small amount of the blue solution, indicates completion of the reaction.

The yield of $Na[V(O_2)_3]$ was 0.8 g (86%) obtained from the reaction of 0.5 g (2.7 mmol) of V_2O_5 with 13 cm^3 (114.6 mmol) of 30% H_2O_2 and 1.1 g (27.5 mmol) of NaOH, while that of $K[V(O_2)_3]$ was 0.9 g (90%) obtained from 0.5 g of V_2O_5 with 13 cm^3 of 30% H_2O_2 and 1.8 g (32 mmol) of KOH.

Elemental Analyses. Vanadium was determined volumetrically by redox titration with potassium permanganate.[15,16] The estimation of total peroxide content, in each compound, was accomplished by redox titrations with a standard cerium(IV) solution[17] and also separately with a standard potassium permanganate solution.[18] In a representative titrimetric procedure for the estimation of total amount of coordinated peroxide, a weighed amount of the sample under investigation was added to 100 cm^3 of cold distilled water, acidified with 2 cm^3 of concentrated sulfuric acid, containing ca. 1.5 g of boric acid. The whole was gently stirred on a magnetic stirrer and titrated with a standard potassium permanganate solution[17] or with a standard Ce^{4+} solution.[18] Sodium and potassium were determined by the methods described in our earlier paper.[15]

The results of elemental analyses, molar conductance values, IR and laser Raman band positions and their assignments are summarized in Table I.

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Table I. Analytical Data, Molar Conductance Values, and IR and Raman Bands of $A[V(O_2)_3]$ (A = Na or K)

compd	molar conductance, Ω^{-1} cm^2 mol^{-1}	% found (% calcd) A	V	O_A[a]	IR, cm^{-1}	Raman, cm^{-1}	assignt
$Na[V(O_2)_3]$	135	13.8	30.4	55.8	855 (s)	850	ν_{-O-O-} (ν_1)
		(13.53)	(29.98)	(56.49)	610 (s)	600	ν_{V-O_2} (ν_3)
					525 (s)	530	ν_{V-O_2} (ν_2)
$K[V(O_2)_3]$	140	21.2	27.8	52.1	855 (s)	860	ν_{-O-O-} (ν_1)
		(21.02)	(27.38)	(51.6)	610 (s)	610	ν_{V-O_2} (ν_3)
					530 (s)	530	ν_{V-O_2} (ν_2)

[a] Peroxo oxygen.

Results and Discussion

Albeit there has been a continued interest in the peroxovanadium chemistry, most of the recent reports deal with the aspects of solution chemistry[3,5-10] while information on synthesis, isolation in the solid state, characterization, and structural assessment of peroxovanadate compounds is rather scanty. The synthesis of blue alkali-metal triperoxovanadates(V), $A[V(O_2)_3]$ (A = Na or K), has been achieved from the reaction of V_2O_5 with 30% H_2O_2 in the presence of a relatively large concentration of alkaline medium with the molar ratio of V_2O_5:H_2O_2:AOH being maintained at 1:42.5:(10–12). A high concentration of AOH is necessary and conducive to the formation and then isolation of $A[V(O_2)_3]$ compounds. Although the V^{5+}–H_2O_2 solution assumes a blue color at a relatively lower concentration of AOH, the IR spectrum of the product isolated from it shows a band at ca. 950 cm^{-1} owing to $\nu_{V=O}$ in addition to those expected for the coordinated O_2^{2-}. This suggests that the formation of the triperoxovanadate(V), $[V(O_2)_3]^-$, complex is not complete; thus, it is required to add a further amount of alkali-metal hydroxide after the first appearance of blue color, however, not beyond the stipulated limit (see the Experimental Section). It may be noted that the change of color of V^{5+}–H_2O_2 solution, with the increase in concentration of alkaline medium, from yellow to blue clearly indicates that the complex $[VO(O_2)_2]^-$ is first formed and then is ultimately converted to the $[V(O_2)_3]^-$ complex. The complete disappearance of the $\nu_{V=O}$ at ca. 950 cm^{-1} in the IR and laser Raman spectra of the compound ensures completion of the reaction. Thus $A[V(O_2)_3]$ compounds were obtained by the addition of ethanol, which facilitates precipitation. Attempts to synthesize $NH_4[V(O_2)_3]$ were futile. Although a transitory blue solution was obtained by the addition of NH_4OH solution (sp gr 0.9), the color was practically discharged, with brisk evolution of oxygen, during workup. It is worthwhile to mention that the tetraperoxovanadate(V), $[V(O_2)_4]^-$, complex, as opposed to the triperoxo species, is formed[12,19] only at temperatures below 0 °C presumably in the presence of a relatively higher amount of alkaline medium.

The blue triperoxovanadates(V) $A[V(O_2)_3]$ (A = Na or K) are diamagnetic in line with the occurrence of quinquevalent vanadium and, unlike the $A_2[V(O_2)_3X]$ (X = F or Cl)[15] and $A_3[V(O_2)_4]$[19] compounds, are stable in water. Whereas $A_2[V(O_2)_3X]$[15] and $A_3[V(O_2)_4]$[19] do not permit molar conductance measurements, the values for the $A[V(O_2)_3]$ compounds, at ambient temperatures, were found to lie in the range 130–140 Ω^{-1} cm^2 mol^{-1}, suggesting their 1:1 electrolytic nature, in complete agreement with the formulas. The estimation of peroxide content is emphasized to be very crucial in order to fix the number of O_2^{2-} groups bound to the V^{5+} center. The results of peroxide determination, accomplished by redox titrations[17,18] involving Ce^{4+} and potassium permanganate, conspicuously suggested the occurrence of three peroxide groups per V^{5+} center in each of the new compounds. The UV–vis spectra of the solutions recorded before isolation of the compound and of that obtained by redissolving the compound were similar and showed absorptions at 560 and 192 nm with the molar absorption coefficients being 84.3 and 1.04×10^4, respectively. This indicates that the complex species formed in solution and that isolated in the solid state are identical. The electronic spectral data for $[V(O_2)_4]^{3-}$ are not available in the literature, thus precluding comparison with those of $[V(O_2)_3]^-$.

The characteristic features of the IR and laser Raman (LR) spectra are the absorption at ca. 850 cm^{-1} owing to ν_{-O-O-}[20] and the two absorptions at ca. 600 and ca. 530 cm^{-1} due to ν_{V-O_2}[20] with all three originating from the coordinated peroxide groups. The typical pattern of the spectra suggests that each of the O_2^{2-} ligands is bonded to the V^{5+} center in a triangular bidentate manner. The –O–O– and metal–O_2 bonds are important spectroscopic probes for molecular structure assessment of peroxometal compounds and are amenable to direct IR and LR spectroscopy. Considering C_{2v} to be the local symmetry of a coordinated O_2^{2-} group, three vibrations, viz. ν_1 (ν_{-O-O-}), ν_2 (ν_{V-O_2}), and ν_3 (ν_{V-O_2}), are expected to be active in both IR and Raman spectra,[20] with the ν_1 and ν_2 modes being polarized in the latter and appearing comparatively more sharp and intense than ν_3 mode. Accordingly, the LR signals at ca. 850, ca. 530, and ca. 600 cm^{-1} have been assigned respectively to the ν_1, ν_2, and ν_3 modes of the coordinated O_2^{2-} ligands. The solution LR spectra of $A[V(O_2)_3]$ compounds resemble those of the corresponding solids, suggesting that the complex anion $[V(O_2)_3]^-$ possesses the same structure in the solid state as well as in solution. Further, the absence of any band at ca. 950 cm^{-1} due to $\nu_{V=O}$, especially in the LR spectra in which it would be very strong on account of the large polarizability changes involved in the V—O bond, renders it certain that the complex does not contain any V=O group.

It may be inferred that a minimum of three O_2^{2-} groups, coordinated to a V^{5+} center, is required for the formation of a blue color in the V^{5+}–H_2O_2 system. The complex $[V(O_2)_3]^-$ ion, unlike the $[V(O_2)_4]^{3-}$ species, retains its identity both in solution as well as in the solid state. The $[V(O_2)_3]^-$ ion may have a hexacoordinated monomeric structure with the O_2^{2-} groups being bonded to the V^{5+} center in a triangular bidentate manner.

Acknowledgment. The authors thank the Council of Scientific and Industrial Research, New Delhi, for awarding fellowships to S.K.G. and N.S.I.

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Direct Synthesis of Hexafluoroferrates(III) and Reaction of Thiocyanate and Fluoride with Iron(III) and Hydrogen Peroxide as an Access to Fluoro(sulfato)ferrates(III)

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Received March 11, 1986

The reaction of iron(III) hydroxide with alkali-metal or ammonium fluoride and 48% hydrofluoric acid in the presence of hydrogen peroxide, followed by the addition of ethanol, directly gives alkali-metal or ammonium hexafluoroferrates(III), A_3FeF_6 (A = Na, K, or NH_4), in very high yields. An investigation of the reaction of ammonium or potassium thiocyanate and 48% HF with iron(III) hydroxide in the presence of hydrogen peroxide has been carried out. Sulfate has been obtained as the oxidation product of SCN^-, without involving reduction of iron(III) and providing an access to fluoro(sulfato)ferrates(III) of the types $(NH_4)_2[Fe(SO_4)F_3]$ and $K_3[Fe(SO_4)F_4]$. Similar reactions with sulfates in lieu of thiocyanates, either in the presence of or in the absence of H_2O_2, do not afford fluoro(sulfato)ferrates(III), however. IR spectroscopy and laser Raman spectroscopy provide evidence for a chelated sulfate in each of the fluoro(sulfato)ferrates(III).

Introduction

The chemistry of fluoro and mixed-fluoro complexes of transition metals continues to attract much attention and to produce new and exciting results.[1-4] Although much of the very recent activity in this area is devoted to studies related to kinetics[3] and magnetic properties,[1,4] a great deal of effort is required for the search for direct synthetic procedures and for synthesis of novel fluoro and mixed-fluoro complex species. These are the prerequisites for an heuristic approach in this field of chemistry. Importance of such compounds as insulators and semiconductors have been emphasized in the literature,[5] and pentafluoroferrates(III) have shown very interesting magnetic properties.[1]

In some of our recent publications we have dealt with the synthesis and structural assessment of fluoronickelates(II),[6] fluoromanganates(III),[7,8] and mixed-fluoromanganates(III).[2,9] We have decided to extend our work to iron analogues. To the best of our knowledge, within the context of fluoroferrates(III), there exists no direct and simple method for the synthesis of hexafluoroferrates(III), FeF_6^{3-}, thus limiting their accessibility. Moreover, mixed-fluoroferrates(III), for instance fluoro(sulfato)ferrates(III), have no reported existence.

The subject of this paper is the direct synthesis of alkali-metal and ammonium hexafluoroferrates(III), A_3FeF_6 (A = Na, K, or NH_4), and an account of the reaction of thiocyanate and hydrofluoric acid with iron(III) in the presence of hydrogen peroxide, with the latter leading to the first synthesis of fluoro(sulfato)ferrates(III).

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer. The laser Raman (lR) spectra were recorded on a SPEX Ramalog Model 1403 spectrometer. The 4880-Å laser line from a Spectra-Physics Model 165 argon laser was used as the excitation source. The light scattered at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube followed by a photon-count processing system. The spectra were recorded at ambient temperatures by making pressed pellets of the compounds. Magnetic susceptibilities were measured by the Gouy method, using $Hg[Co(NCS)_4]$ as the calibrant.

Synthesis of Alkali-Metal and Ammonium Hexafluoroferrates(III), A_3FeF_6 (A = Na, K, or NH_4). Anhydrous iron(III) chloride (1.0 g, 6.2 mmol) was dissolved in water (5 cm^3) with gentle warming. Ammonium hydroxide solution (sp gr 0.9, 7 cm^3, excess) was added slowly with continuous stirring. The mixture was heated on a steam bath for 15 min,

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and the precipitate of iron(III) hydroxide was then filtered off and washed with water until free from chloride.

The moist iron(III) hydroxide, alkali-metal or ammonium fluoride, AF (36.9 mmol), and 30% hydrogen peroxide (12 cm^3, 105.7 mmol) were placed in a polyethylene beaker provided with a polyethylene cover. An amount of 1.3 cm^3 (31.2 mmol) of 48% hydrofluoric acid was added dropwise with stirring to obtain a clear solution. The solution was stirred magnetically for a further period of ca. 15 min. Addition of about 20 cm^3 of ethanol to the above solution precipitated very light yellowish white alkali-metal or ammonium hexafluoroferrate(III), A_3FeF_6. The compound was separated by filtration, washed three to four times with ethanol, and finally dried in vacuo over P_4O_{10}. The yields of Na_3FeF_6, K_3FeF_6, and $(NH_4)_3FeF_6$ were 1.1 g (75%), 1.4 g (79%), and 1 g (72%), respectively. Anal. Calcd for Na_3FeF_6: Na, 28.89; Fe, 23.38; F, 47.73. Found: Na, 28.55; Fe, 23.47; F, 47.91. Estimated oxidation state of Fe: 2.9. μ_{eff}: 5.8 μ_B. IR (cm^{-1}): 480 s (ν(Fe–F)), 292 m (δ(F–Fe–F)). Anal. Calcd for K_3FeF_6: K, 40.85; Fe, 19.45; F, 39.7. Found: K, 40.48; Fe, 19.87; F, 40.1. Estimated oxidation state of Fe: 3. μ_{eff}: 5.9 μ_B. IR (cm^{-1}): 475 s (ν(Fe–F)), 290 m (δ(F–Fe–F)). Anal. Calcd for $(NH_4)_3FeF_6$: N, 18.76; Fe, 24.93; F, 50.89. Found: N, 18.91; Fe, 25.22; F, 51.45. Estimated oxidation state of Fe: 3. μ_{eff}: 5.8 μ_B. IR (cm^{-1}): 497 s (ν(Fe–F), 290 m (δ(F–Fe–F), 3160 m, 3045 s, and 1400 s (ν_3, ν_1, and ν_2 modes of NH_4^+).

Reactions of ASCN (A = K or NH$_4$) with Iron(III) Hydroxide, Aqueous HF, and Hydrogen Peroxide. Iron(III) hydroxide was prepared from 1.0 g of anhydrous iron(III) chloride in a similar way as described above.

The moist iron(III) hydroxide and solid potassium or ammonium thiocyanate, ASCN (12.4 mmol), were mixed thoroughly in a polyethylene beaker. To this was slowly added 13 cm^3 (114.6 mmol) of 30% hydrogen peroxide with occassional stirring. Stirring was continued until effervescence ceased to appear. An amount of 1.4 cm^3 (33.6 mmol) of 48% hydrofluoric acid was added dropwise to obtain a clear solution that was stirred magnetically for ca. 15 min followed by the addition of 25 cm^3 of ethanol to afford a grayish white oily mass. The oily mass was separated by decantation and solidified by repeated treatment with ethanol and scratching for about 20 min. The product was isolated and dried in a manner similar to that described under the synthesis of A_3FeF_6. Elemental analyses were consistent with the formulations $K_3[Fe(SO_4)F_4]$ and $(NH_4)_2[Fe(SO_4)F_3]$ for the products of reactions with KSCN and NH_4SCN, respectively. The yield of $K_3[Fe(SO_4)F_4]$ was 1 g (47%), and that of $(NH_4)_2[Fe(SO_4)F_3]$ was 0.7 g (47%). Anal. Calcd for $K_3[Fe(SO_4)F_4]$: K, 33.98; Fe, 16.18; SO_4, 27.83; F, 33.02. Found: K, 33.58; Fe, 16.51; SO_4, 28.21; F, 33.22. Estimated oxidation state of Fe: 3. μ_{eff}: 5.7 μ_B. IR (cm^{-1}): 980 m (ν_1), 451 m (ν_2), 1225 s, 1131 s, 1020 s (ν_3), 669 m, 611 s, 599 s (ν_4), 490 s (ν(Fe–F)). Raman (cm^{-1}): 970 (ν_1), 450 (ν_2), 1220, 1130, 1020 (ν_3), 670, 610, 600 (ν_4) (ν_1–ν_4 are referring to SO_4^{2-} modes). Anal. Calcd for $(NH_4)_2[Fe(SO_4)F_3]$: N, 11.44; Fe, 22.79; SO_4, 39.2; F, 46.53. Found: N, 11.51; Fe, 22.83; SO_4, 39.42; F, 46.85. Estimated oxidation state of Fe: 3. μ_{eff}: 5.6 μ_B. IR (cm^{-1}): 975 m (ν_1), 450 m (ν_2), 1223 s, 1130 s, 1010 s (ν_3), 670 m, 610 s, 600 s (ν_4), 495 s (ν(Fe–F)), 3160 m, 3040 s, 1400 s (ν_3, ν_1, and ν_2 modes of NH_4^+). Raman (cm^{-1}): 980 (ν_1), 450 (ν_2), 1220, 1135, 1010 (ν_3), 675, 615, 600 (ν_4).

Results and Discussion

Direct Synthesis of Hexafluoroferrates(III), A_3FeF_6 (A = Na, K, or NH$_4$). The three principal types of binary fluoro complexes of iron(III), viz. FeF_6^{3-}, FeF_5^{2-}, and FeF_4^-, are documented in the literature, of which the pentafluoroferrate(III) species is most easily accessible.[10] In the context of the present work, it is evident that no direct route to hexafluoroferrate(III) seems to be available. The recommended method[11] requires first the synthesis of the FeF_5^{2-} complex, which on treatment with molten alkali-metal hydrogen fluoride, AHF_2, yields the corresponding hexafluoroferrate(III), A_3FeF_6. It has now been possible for us to show that iron(III) hydroxide can be made to react with alkali-metal or ammonium fluoride, AF (A = Na, K, or NH$_4$), and aqueous hydrofluoric acid in the presence of an excess of hydrogen peroxide to afford directly alkali-metal or ammonium hexafluoroferrates(III), A_3FeF_6, in yields higher than those obtained by the earlier method.[11] An excess of 30% hydrogen peroxide (vide Experimental Section) was necessary as this also provided an appropriate medium for conducting the reactions. A similar volume maintained by using dilute hydrogen peroxide solutions was found to be detrimental to the synthesis. The role of alkali-metal or ammonium fluoride, AF, was to provide countercations, A^+, as well as to enhance the F^- ion concentration of the reaction medium, while that of hydrofluoric acid was to dissolve iron(III) hydroxide and also, of course, to supply fluoride ions. Strategically more important is the key role played by H_2O_2 in the successful synthesis of hexafluoroferrates(III). It is believed that pentafluoroferrate(III) is first formed, which coordinates with a peroxide (O_2^{2-}) ligand, presumably to form an unstable peroxyfluoroferrate(III) intermediate. This unstable peroxy intermediate then reacts with F^- ions available in the solution, rupturing the iron–peroxide bond with concomitant formation of a new metal–fluoride bond, ultimately leading to the formation of the FeF_6^{3-} complex species. At present this interpretation is admittedly speculative; however, the fact that similar reactions in the absence of hydrogen peroxide, even in the presence of relatively higher concentrations of fluoride ions, yield only pentafluoroferrates(III) definitely lends support to the contention. Moreover, recently while working on some peroxyfluorometalates,[12] we observed that a peroxyfluorometalate complex could serve as a precursor for a binary fluorometalate species (cf. $Ti(O_2)F_5^{3-} + F^- \rightarrow TiF_6^{2-}$), providing thereby a sort of a rationale for the present synthesis. Because of the higher yields of products obtained by the new method, which is also easy to manipulate, this synthetic approach offers advantages over the method described in the literature.[11]

The results of elemental analyses are consistent with the formula of the compounds. The chemically estimated oxidation state, accomplished by iodometry, was found to lie between 2.9 and 3.1, in agreement with the occurrence of iron(III). They are high-spin complexes with magnetic moments of 5.8–5.9 μ_B and conform well with the values reported in the literature.[13] The IR spectra of the compounds exhibit a very strong but somewhat broad band at 470–497 cm^{-1}, assigned to ν(Fe–F),[14] and a strong band around 290 cm^{-1}, attributed to δ(F–Fe–F). These are in conformity with those observed earlier[14] on similar compounds.

Reactions of SCN$^-$ and F$^-$ with Iron(III) Hydroxide and Hydrogen Peroxide. There was some concern regarding the reaction of thiocyanate with iron(III), and consequently, results of some very recent studies[15] have shown the possibility of oxidation of SCN^- to trithiocyanate $(SCN)_3^-$, a rather unstable intermediate, by iron(III). Our principal concern was to investigate the main product of oxidation of thiocyanate in the presence of fluoride ions and iron(III) with a hope to get an access to mixed-ligand fluoro(sulfato)ferrates(III). This became necessary because our attempts to synthesize such mixed-ligand complexes from the reaction of sulfate and fluoride with iron(III) in an acidic medium had failed, unlike in the case of manganese(III).[9] The products obtained therefrom were found to be only pentafluoroferrates(III) that did not contain any sulfate. Accordingly, chemical oxidation of SCN^- to SO_4^{2-} in the presence of F^- ions and iron(III) was undertaken. Hydrogen peroxide was chosen as the oxidant because not only is it capable of oxidizing SCN^- to sulfate,[16,17] but also it helps iron to retain its trivalent state.

Initial studies of the reaction of SCN^- with iron(III) hydroxide, hydrofluoric acid, and hydrogen peroxide were carried out in a slightly alkaline medium but were found to be complicated owing to apparent side reactions leading to contamination of the reaction products, although the oxidation of thiocyanate did take place. Subsequent experiments were therefore carried out in acidic media. During the reaction of ASCN (A = K or NH$_4$) and iron(III) hydroxide with aqueous HF and hydrogen peroxide, SCN^- was oxidized to SO_4^{2-} and metal hydroxide went into solution with

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the solution becoming practically colorless. The reactions ultimately led to the synthesis of new compounds (vide Experimental Section) that analyze as $K_3[Fe(SO_4)F_4]$ and $(NH_4)_2[Fe(SO_4)F_3]$ as obtained from KSCN and NH_4SCN, respectively, providing an access to mixed-ligand fluoro(sulfato)ferrates(III). Presumably, here again an intermediate peroxyfluoroferrate(III) species is first generated, which then participates, through its coordinated peroxy group, in the oxidation of SCN^- finally to afford the heteroligand fluoroferrates(III).

A study of the vibrational spectra of the reaction products revealed the complete absence of ν(CN) at ca. 2120 cm^{-1}, and the IR and laser Raman (LR) spectral patterns were very similar to other metal sulfato complexes. When sulfate is coordinated, its symmetry is lowered from T_d to C_{3v} or C_{2v}[18] depending on whether it binds the metal center in a monodentate or a bidentate fashion.[18] In the case of C_{2v} symmetry of sulfate, its ν_3 and ν_4 modes are split into three bands each while the ν_1 and ν_2 modes appear with medium intensity. Although both bridging and chelating sulfato ligands have C_{2v} symmetry, they can generally be distinguished on the basis of their IR and Raman spectra since ν_3 vibrations for chelating bindate sulfato complexes occur at higher energies than those of bridging sulfato complexes.[18] In the IR and LR spectra of the newly synthesized compounds each of the ν_3 and ν_4 vibrations was split into three bands with the ν_3 modes lying at ca. 1225, ca. 1130, and ca. 1020 cm^{-1}. A comparison with other types of sulfato complexes[19] indicates that these vibrations fall at rather high energies for ν_3 modes and therefore suggests that SO_4^{2-} binds the iron(III) center in a chelating bidentate manner. Another common feature of fluoro(sulfato)ferrates(III) is the band at ca. 495 cm^{-1}, which has been assigned to the ν(Fe–F) mode arising from the presence of coordinated fluoride ligands.

For further characterization, the oxidation state of iron was estimated chemically by an iodometric method and magnetic moments were measured at room temperature. While the chemically estimated oxidation state of iron was found to be 3; the magnetic moments of the compounds were found to be ca. 5.7 μ_B, suggesting the occurrence of high-spin iron(III). These results adduce additional support to the identity of the fluoro(sulfato)ferrates(III).

Concluding Remarks. Under the appropriate experimental conditions hexafluoroferrates(III) of the type A_3FeF_6 (A = Na, K, or NH_4) can be directly synthesized in high yields, providing an easy access to such compounds. Reactions of potassium or ammonium thiocyanate with iron(III) hydroxide, aqueous hydrofluoric acid, and hydrogen peroxide have resulted in the production of hitherto unknown fluoro(sulfato)ferrates(III). These compounds provide excellent prospects as materials for further studies of their physical properties and for a comparison with those of the binary fluorometalates(III). In this way an insight into the fluorochemistry of iron may be gained.

Acknowledgment. The authors thank the Council of Scientific and Industrial Research, New Delhi, India, for the award of a research fellowship to N.S.I.

Registry No. Na_3FeF_6, 20955-11-7; K_3FeF_6, 13815-30-0; $(NH_4)_3FeF_6$, 13815-28-6; $K_3[Fe(SO_4)F_4]$, 103852-34-2; $(NH_4)_2[Fe(SO_4)F_3]$, 103852-35-3; KSCN, 333-20-0; NH_4SCN, 1762-95-4.

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Indian Journal of Chemistry
Vol. 24A, May 1985, p. 447

Optimum Conditions for Hydrogen Peroxide Oxidation of Thiocyanate to Sulphate

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Received 7 *November* 1984; *revised* 28 *January* 1985; *accepted* 19 *February* 1985

Ammonium or potassium thiocyanate is oxidised quantitatively (*yield* 97-99%) *to sulphate by* 30% H_2O_2 *at* pH 7-8 and SCN^- : H_2O_2 molar ratio of 1:8-10.

It is known that hydrogen peroxide oxidation of thiocyanate in solution to yield sulphate is an electron transfer reaction[1] but the optimum conditions like *p*H, molar ratio between SCN^- and H_2O_2 etc. required for the quantitative oxidation do not appear to have been reported so far. The optimum conditions for the quantitative conversion of SCN^- into SO_4^{2-} in the above reaction have now been worked out and are reported in this note.

All the chemicals used were of reagent grade quality.

Procedure for quantitative conversion of SCN^- *into* SO_4^{2-}

Ammonium or potassium thiocyanate (1 mol) was dissolved in 30% (v/v) H_2O_2 (8-10 mol) and filtered. To the filtrate was added the corresponding alkali hydroxide in portions, with constant stirring, until the *p*H of the solution was raised to 7-8. The solution was stirred for about 10 min and excess of ethanol added until the white crystalline sulphate ceased to appear. The compound was filtered, washed 3-4 times with ethanol, and dried *in vacuo* over phosphorous pentoxide.

The oxidation of NH_4SCN (2 g; 26.3 mmol) with 30% H_2O_2 (27 ml; 237.6 mmol) gave $(NH_4)_2SO_4$ in quantitative yield (3.44 g; 99%), while the reaction of KSCN (2 g; 20.6 mmol) with 30% H_2O_2 (23.4 ml; 206 mmol) gave K_2SO_4 in quantitative yield (3.52 g; 98%).

The thiocyanate oxidation reaction was monitored by IR spectroscopy. The complete disappearance of $\nu(C\equiv N)$ and $\nu(C-S)$ (ref. 2) around 2050 and 750 cm^{-1} respectively, and appearance of two sharp bands at 1110 and 610 cm^{-1} due to ν_3 and ν_4 modes respectively[3] of SO_4^{2-}, in a small amount of the sample isolated from the reaction solution, ensured completion of the reaction.

Sulphate was determined gravimetrically as barium sulphate. potassium and nitrogen were estimated by the methods described earlier[4]. The analytical results agreed very well with the values calculated for the corresponding sulphates. The purity of the compounds was checked by measuring their molar conductances (240-250 ohm^{-1} cm^2 mol^{-1}).

It was found that the oxidation of NH_4/K thiocyanates to sulphates was quantitative (sulphate yield 97-99%) in the *p*H range 7-8. The most suitable ratio of SCN^-: H_2O_2, for quantitative oxidation, was found to be 1:8-10, although stoichiometrically one mol of SCN^- would require 3 mol of H_2O_2. A molar ratio of 1: $\leq$ 6 (SCN^-:H_2O_2) did not give the sulphates in quantitative yields owing to the possibility of sulphur being present as $S(CN)_2$ under this condition[1]. A higher ratio of SCN^-:H_2O_2 (1: > 10) was not considered desirable for two reasons: (i) at high ratios H_2O_2 decomposes to give oxygen[1], and (ii) there is a possibility of contamination of sulphate by ammonia and nitrate, which are formed under this condition[1].

Since SCN^- is the conjugate base of a weak acid, it exists largely as SCN^- under neutral conditions (*p*H 7-8). Moreover, H_2O_2 behaves as a poor oxidant at lower *p*H; thus a low yield of sulphate at $pH < 7$ is not unexpected. At $pH > 8$, the alkali-induced decomposition[5] of H_2O_2 and the slow reaction between HOCN (another oxidation product of SCN^-) and H_2O (ref. 1) are responsible for lowering the yield of the sulphate.

The authors thank the CSIR, New Delhi, for awarding a fellowship to NSI.

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