EVIDENCE FOR THE OCCURRENCE OF MANGANESE(III) IN $[MnO_4]^-/SO_2$ REDOX REACTION AND SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF NEWER FLUORO COMPOUNDS OF MANGANESE(III) AND URANIUM(VI) $[UO_2^{2+}]$

ABSTRACT

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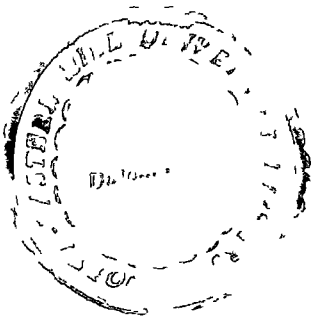

A THESIS SUBMITTED

IN FULFILMENT OF THE REQUIREMENT

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

TO

THE NORTH-EASTERN HILL UNIVERSITY

SHILLONG

INDIA

NOVEMBER 1993

Evidence for the Occurrence of Manganese(III) in $[MnO_4]^-/SO_2$ Redox Reaction

And

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Abstract

The chemistry of manganese(III) has drawn the attention of a number of research groups around the globe with each group having a specific interest. Somewhat similar is the situation with the chemistry of uranium, in which the interest of chemists never seems to diminish. In cognizance to the contemporary interest, a few selective problems related to the two chemistries were identified for the present Ph.D. research on which the studies were conducted. Thus the results of the investigation on the occurrence of manganese(III) in the $[MnO_4]^-/SO_2$ redox reaction as well as the synthesis and structural evaluation of newer fluoro and mixed-fluoro complexes of manganese(III) and uranium(VI) $[UO_2^{2+}]$ constitute the subject matter of the present thesis. The content of the thesis has been distributed over six Chapters. Attempts have been made to present each Chapter as a self-contained one including bibliography relevant to the text. For Chapters III-VI sections on brief introduction, experimental

description followed by results and discussion have been provided.

Chapter I presents a general introduction pertaining to the type of work undertaken. The relevant background information of the chemistry of the two metals viz., manganese and uranium has been discussed in this Chapter. In addition, the importance of and interest in the chosen aspects of chemistry of the two metals are highlighted. Special emphasis has also been put onto their fluoro chemistry. During this endeavour, a few intriguing problems have been identified to constitute the scope of the present work.

Chapter II describes the details of the methods used for the preparations of starting materials and elemental analyses as well as the particulars of instruments/equipment used for characterization and structural assessment of the newly synthesized compounds.

In Chapter III evidence has been provided for the occurrence of manganese in its tripositive level as an intermediate in the $[MnO_4]^-/SO_2$ redox reaction in an aqueous medium by experimentation involving *in situ* methods as well as by the isolation of manganese(III) products under similar conditions. Fluoride has been used as the intermediate stabilizer. While a combination of EPR and electron absorption spectroscopies was used to provide *in situ* evidence, the results of chemical analyses, chemical determination of oxidation level of manganese, magnetic susceptibility measurements and spectroscopic analyses were used

to ascertain the identity of the isolated products in support of the notion.

The $KMnO_4$ —— SO_2 redox reaction carried out with $Mn:F^-$ atom ratio of 1:4 indicated that the process involved three different stages: (i) formation of a brown product at pH 3-2.5, (ii) formation of a pink solid at pH 2.5-2 and (iii) finally dissolution of the pink product at pH < 2 accompanied by decolourisation of the reaction solution [*cf.* Mn(II)]. However, when an analogous reaction was conducted with $Mn:F^-$ concentration ratio of 1:10, the observations were nearly similar except that at pH 3-2.5 a brown solution instead of a brown product and at pH 2.5-2 a rose-pink product in lieu of a pink species were obtained. While the brown product, isolated from the reaction in which $Mn:F^-$ concentration was held at 1:4, did not adhere to any fixed stoichiometry, the oxidation level of the metal in the product was +3 [as ascertained by redox titrimetry]. The pink and the rose-pink products were identified to be $K_2[MnF_3(SO_4)]$ and $K_2[MnF_5].H_2O$, respectively.

The *in situ* EPR and electron absorption spectroscopic experiments were carried out in solution as a function of pH. While the ESR scan did not show any signal from the point of initiation of the reaction (*cf.* pH 5.5) till pH 2, the electron absorption spectra displayed a pattern characteristic of manganese(III) starting from pH 3.3 which persisted till pH 2. On

the contrary, for the reaction solutions at pH < 2 a typical six line EPR spectrum characteristic of divalent manganese was observed whereas the electronic absorption signals observed above pH 2 disappeared at pH ≤ 2.

The results therefore suggest that in the presence of F^- ion manganese(VII) is directly reduced to manganese(III) and thence to manganese(II).

Chapter IV of the thesis presents the results of studies on the effect of fluoride on the interaction of manganese(III) with some biochemically relevant ligands, viz., salicylic acid ($salH_2$), 1,2-bis(salicylideneiminato)ethane ($salenH_2$) and N,N'-(acetylacetonato)ethylenediamine ($acacenH_2$) in an aqueous medium. The investigation was monitored by isolation of a variety of binary as well as mixed-fluoromanganates(III) under different conditions.

The complexes $A_2[MnF_4(salH)]$ (A = K, Na or NH_4) were obtained from the reactions of MnO(OH) with alkali hydrofluoride, AHF_2, and salicylic acid at a molar stoichiometry of Mn:F:$salH_2$ of 1:4:6. The mixed-fluoro(salicylato)manganates(III) were green in colour, stable in the solid form and moderately soluble in methanol. The compounds have been characterized by a combination of elemental analyses, chemical determination of the oxidation state of manganese, solution electrical conductivity measurements, IR, LR and electron absorption spectroscopies and Scanning Electron

Microscopy. The room temperature (300 K) magnetic moment values of the complexes were found to lie in the range 4.5-4.6 BM. The values are somewhat lower than that expected for an ideal d^4 system. This has been attributed to weak antiferromagnetic exchange interactions between the contiguous manganese atoms through -Mn-F-Mn-F- chains in the crystal lattice. The notable features of the IR spectra of the complexes were the bands at *ca.* 1604, *ca.*1385 and *ca.*1230 cm^{-1} owing their origins to $\nu_{as}(COO^-)$, $\nu_s(COO^-)$ and δ(O-H) modes, respectively, of the coordinated salicylate ligand. The observed decrease and increase of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, respectively, as compared to free carboxylic acids, provide evidence for the salicylate being coordinated through its carboxyl oxygens in a monodentate fashion. Further, the lowering in frequency of δ(O-H) (*cf.* free alcohols) also provides an indication for the presence of a protonated hydroxyl functionality in the complexes with the OH group being coordinated to the metal centre through its oxygen lone pair electrons. Complimentary Raman signals at *ca.*1597, *ca.*1315 and *ca.*1237 cm^{-1} as well as the adopted synthetic methodology, wherein the natural pH of the reaction medium was 4, lend support to our contention. It is therefore logical to assume that salicylate is coordinated in a bidentate fashion through its protonated phenolic and deprotonated carboxyl groups. The presence of salicylate as $Hsal^-$ and the manner in which it is coordinated are very important

structural features of the complexes. This type of a situation is rather unusual though not unprecedented.

Also highlighted in this Chapter are the antagonistic effects of F^- on the formation of mixed-ligand fluoromanganates(III). Reactions conducted at similar concentrations of manganese and salicylic acid but higher concentrations of F^-, for instance at the molar stoichiometry of $Mn:salH_2:F$ as 1:6:12, afforded $A[MnF_4(H_2O)_2].H_2O$ (A = K, Na or NH_4). Incidentally, this enables us also to make the first report on the K and NH_4 salts of the diaquotetrafluoromanganates(III). However, the reactions carried out in the presence of a still larger excess of F^- (eg., $Mn:salH_2:F$ = 1:6:24) afforded the very well known binary pentafluoromanganates(III). Control reactions carried out in the absence of salicylic acid required lesser amount of F^- to produce $A[MnF_4(H_2O)_2]$ (A = K, Na or NH_4). But if similar reactions are conducted with comparable concentrations of F^- (*cf.* that of $A[MnF_4(H_2O)_2].H_2O$ the pentafluoromanganates(III) are obtained instead of the corresponding aquatetrafluoromanganates(III). It is thus evident from the above investigation that a large excess of F^- prevents the coordination of different co-ligands present in the reaction medium to manganese(III), thereby leading to the formation of binary fluoromanganates(III) only. This therefore implies that F^- is certainly a better ligand to stabilize and trap manganese(III).

Another objective of the study was to probe the effect of F^- on the interaction of manganese(III) with Schiff bases. Thus, the reactions of MnO(OH) with acacenH$_2$ or salenH$_2$ and aqueous HF led to the isolation of heretofore unreported tetrafluoromanganate(III), enH[MnF$_4$], instead of a mixed-fluoromanganate(III). The room temperature magnetic moment of the complex was recorded to be 4.2 BM. The relatively low value, as compared to that of 4.9 BM normally expected for ideal d^4 systems, is indicative of antiferromagnetic exchange interaction being operative in the system between the contiguous manganese atoms through the formation of -Mn-F-Mn-F- chains in the crystal lattice. This has been interpreted in terms of the effect of the specific counter ion (ie., enH^+) in bringing about a polymeric structure of the complex through enhanced hydrogen bonding. The observance of two strong bands at 578 and 625 cm^{-1} in the IR spectrum of the complex renders it reasonable to assume that the manganese(III) ion in the complex finds itself in a distorted octahedral environment probably with a D_{4h} symmetry (*cf.* MF_6^{n-}). Metatheses reactions of the complex enH[MnF$_4$] with Rb$_2$CO$_3$ and CsNO$_3$ afforded Rb[MnF$_4$(H$_2$O)] and Cs[MnF$_4$(H$_2$O)], respectively.

Chapter V of the thesis addresses to a simple synthesis of bis(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(acac)_2.2H_2O$, investigation of its nucleophilic substitution reactions with F^- as the nucleophile thereby gaining an access to the hitherto

unreported $[UO_2F_6]^{4-}$ and $[UO_2F_7]^{5-}$ and newer mixed-fluorouranates(VI) with organic co-ligands viz., amino acids, acetylacetonate and acetate.

$UO_3.4H_2O$ reacted with acetylacetone ($C_5H_8O_2$) to produce $UO_2(C_5H_7O_2)_2.2H_2O$ in a nearly quantitative yield. $UO_2(acac)_2.2H_2O$ underwent nucleophilic substitution reactions separately with NH_4F and aqueous HF. While the reaction of $UO_2(acac)_2.2H_2O$ with NH_4F in acetylacetone at pH 4 led to the first synthesis of $(NH_4)_4[UO_2F_6]$, the reaction of $UO_2(acac)_2$ generated *in situ*, with a controlled amount of aqueous HF at pH 3.5 afforded the molecular $[UO_2(acac)F(H_2O)_2].3H_2O$ complex. However, on lowering the pH value to *ca.*2 by the addition of aqueous HF only $[UO_2F_2].3H_2O$ was produced. The molecular $[UO_2(acac)F(H_2O)_2].3H_2O$ complex can therefore be considered to be an isolable intermediate in the process $UO_2(acac)_2.2H_2O$ to $[UO_2F_2].3H_2O$. The knowledge obtained from the above reactions as well as the reaction of $K_2U_2O_7$ with KF and acacH at pH 3.5 leading to $K_2[UO_2(acac)F_3]$ suggests that a pH of *ca.* 3.5 is conducive to the synthesis of the mixed-ligand fluoro(acetylacetonato) complexes of UO_2^{2+}.

The mixed-fluoro(acetato) complexes, $A[UO_2(CH_3COO)_2F].3H_2O$ (A = K, Na or NH_4), were obtained from the reactions of $A_2U_2O_7$ with glacial acetic acid and aqueous HF enabling us to provide the missing K and Na salts in addition to providing a general synthetic methodology for the salts of the $[UO_2(CH_3COO)_2F]^-$

complex ion. By adapting a synthetic methodology comparable to that of $[UO_2(acac)F(H_2O)_2].3H_2O$, a molecular mixed-ligand fluoro(acetato) complex $[UO_2(CH_3COO)F(H_2O)_2]$ was obtained from the reaction of $UO_3.4H_2O$ with glacial acetic acid and aqueous HF.

For the hetero-ligand fluorodioxouranates(VI) with amino acids, the co-ligands were drawn from glycine, L-alanine and L-cysteine. While the mixed-fluoro(glycine) complexes, $A_3[UO_2(GlyH)_2F_5].3H_2O$ (A = K or NH_4), were synthesized from the reactions of $UO_3.4H_2O$ with glycine and a combination of AF and HF, the fluoro(alanine) and fluoro(cysteinate) complexes, $K_3[UO_2(AlanH)_2F_5].2H_2O$ and $(NH_4)_5[UO_2(CysH)_2F_5].2H_2O$, were prepared by a method similar to that employed for the fluoro(glycine) complexes except that AHF_2 was used as the fluorinating agent. Each of the mixed-ligand fluoro(amino acid)-dioxouranates(VI), except $K_3[UO_2(GlyH)_2F_5].3H_2O$, was unstable in aqueous solution undergoing decomposition to form intractable products. Significantly, $K_3[UO_2(GlyH)_2F_5].3H_2O$ underwent hydrolysis in an aqueous medium to afford a well-defined but hitherto unknown binary fluoro complex, $K_5[UO_2F_7].2H_2O$, enabling us to make the first report on the heptafluorodioxouranate(VI) species.

The complexes have been characterized by a combination of chemical analyses, solution electrical conductance measurements, infrared (IR) and laser Raman (LR) spectroscopic studies and

Scanning Electron Microscopy. The common features of IR spectra of the complexes were the bands at *ca.*910 and *ca.*375 cm^{-1} assigned to ν(U=O) [trans-linked O=U=O] and ν(U-F) modes, respectively. In addition, bands due to the coordinated co-ligands were observed in the anticipated positions. The IR spectral features adduced support to the chelated bidentate character of the acetylacetonate and acetate ligands in the corresponding mixed-ligand fluoro complexes. Each of the three amino acid co-ligands acted in a unidentate manner being coordinated to UO_2^{2+} through the carboxylate oxygen atom in the respective complexes. While glycine and alanine occur in the zwitterionic form, cysteine is present as a uninegative ligand ($CysH^-$). The laser Raman (LR) spectra could be recorded only for $(NH_4)_4[UO_2F_6]$, $K_5[UO_2F_7].2H_2O$, $[UO_2F_2].3H_2O$, and $K_2[UO_2(acac)F_3]$, while an extensive fluoroscence foiled such attempts on the others. The Raman signals at *ca.*880 and *ca.*380 cm^{-1} complement the IR spectral results. The Scanning Electron Micrographs of the hitherto unreported binary fluoro complexes $(NH_4)_4[UO_2F_6]$ and $K_5[UO_2F_7].2H_2O$ attest to the homogeneity of the products as well as to their crystalline character.

Chapter VI, indeed the concluding Chapter, deals with the synthesis and structural evaluation of new mixed-fluoro complexes of UO_2^{2+} containing inorganic co-ligands as well as developing of two direct synthetic routes to the dioxotetrafluorouranate(VI), $[UO_2F_4]^{2-}$, complex species. The inorganic co-ligands have been

drawn from phosphate, nitrate and hydrazine.

While the reactions of $UO_3.4H_2O$ with H_3PO_4 and alkali hydrofluorides, AHF_2 (A = K, Na or NH_4), [pH *ca.*2] at a steam-bath temperature led to the isolation of new mixed-fluoro(phosphato) complexes of the type $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ (A = K, Na or NH_4), the mixed-fluoro(nitrato) complexes $A_2[UO_2(NO_3)_3F].3H_2O$ (A = K, Na or NH_4) were obtained from the reactions of $A_2U_2O_7$ with conc.HNO_3 and aqueous HF (48%) maintaining the $UO_2^{2+}:NO_3^-:F^-$ concentration ratio at 1:*ca.*11:*ca.*36. Synthesis of the mixed-fluoro(hydrazine) complex, $[UO_2(N_2H_4)_2F_2].2H_2O$, was rather straight forward. The reaction of $UO_3.4H_2O$ with AHF_2 (A = K or NH_4) and hydrazine hydrate at a natural pH of 8.5 helped hydrazine coordination to UO_2^{2+} in the presence of F^-, since in a basic medium the possibility of formation of hydrazonium ($N_2H_5^+$) ion did not exist.

The characterization of the compounds has been made by a combination of chemical analyses, solution electrical conductance measurements, electron absorption, IR and laser Raman (LR) spectroscopic studies. The occurrence of trans-linked O=U=O, coordinated fluoride and bidentate co-ligands are the common features of the complexes. The appearance of the ν_1 mode at *ca.*905 cm^{-1} and the splitting of the ν_3 mode into three intense bands at *ca.*1000, *ca.*1070 and *ca.*1120 cm^{-1} in the IR spectra of the fluoro(phosphato) complexes clearly indicate the presence of phosphate as PO_4^{3-} and occurring as a chelated ligand. In the IR

spectra of the mixed-fluoro(nitrato) complexes the observance of all the six fundamental modes of vibrations, ν_1 to ν_6 of coordinated nitrate, as well as a large separation of ν_1 and ν_4 modes (*ca.*215 cm^{-1}) makes it rational to suppose that the nitrate in each of the complexes, $A_2[UO_2(NO_3)_3F].3H_2O$ (A = K, Na or NH_4), is present as a bidentate ligand. The IR spectrum of $[UO_2(N_2H_4)_2F_2].2H_2O$ showed a medium intensity sharp band at 955 cm^{-1} which has been assigned to the ν(N-N) stretching vibration. This as well as the similarity of IR spectral features with those of the hydrazine and mixed-ligand hydrazine complexes of different metals enables us to state that the complex contains bidentate hydrazine ligands.

With the afore mentioned success, it has become possible to overcome the synthetic problems related to phosphato- and nitrato-uranyl complexes. The newly synthesized $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ were highly crystalline solids. This has been evidenced by the Scanning Electron Microscopy (SEM). Two different stereo-views of $Na_2[UO_2(PO_4)F(H_2O)_3].3H_2O$, chosen as a representative example, exposed the hexagonal crystal morphology and cylindrical shape of the complex. Though nitrato complexes of uranyl are generally believed to be very weak, the incorporation of fluoride gave additional stability to the uranyl-nitrato system.leading to the synthesis of $A_2[UO_2(NO_3)_3F].3H_2O$. The unaltered solution electrical

conductance values as well as electron absorption spectroscopic studies lend support to the contention.

The laser Raman (LR) spectra of aqueous solutions of the fluoro(phosphato) and fluoro(nitrato)uranates(VI) as well as the corresponding solid complexes, $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ and $A_2[UO_2(NO_3)_3F].3H_2O$, were recorded separately. While for the reaction solutions the symmetric stretching frequencies $\nu_s(U=O)$ [of O=U=O] were observed at *ca.*840 cm^{-1}, the band was found to occur at *ca.*900 cm^{-1} for the solids. This has been interpreted in terms of the decrease in the hydration number of the coordination shell of UO_2^{2+} of the solid complexes. Such an experiment could not be conducted for $[UO_2(N_2H_4)_2F_2].2H_2O$ owing to the precipitation of the compound instantaneously on addition of hydrazine.

Two improved synthetic methodologies developed for the dioxotetrafluorouranate(VI), $[UO_2F_4]^{2-}$, species have also been included in this Chapter. While one of the methodologies involved the interaction of a yellow product, obtained by treating a solution of uranyl nitrate with AOH (A = K, Na or NH_4), with aqueous HF (48%) and A_2CO_3, the other was based upon a nucleophilic substitution reaction. In the latter reaction $UO_2(O_2).2H_2O$ was allowed to react with 48% HF in the presence of alkali fluoride, AF (A = K, Na or NH_4), leading to the isolation of $A_2[UO_2F_4].3H_2O$ (A = K, Na or NH_4). The compounds have been

characterized by the techniques mentioned already in the contexts of other complexes.

A large portion of the work described in various Chapters of the thesis has been published in parts:

Chapter III

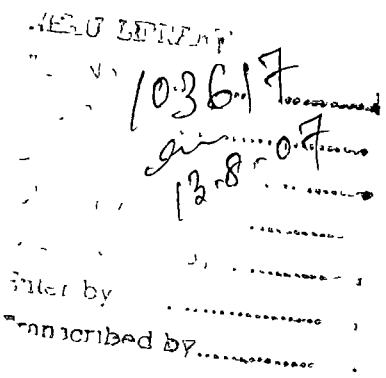
J.Chem.Soc.,Dalton Trans., 1993 (in press) [Paper No. 3/03328G/DAP].

Chapter V

Proc.Indian Acad.Sci., 1992, 104, 479.

J.Fluorine Chem., 1992, 56, 305.

Polyhedron, 1993, 12, 227.



Chapter VI

Polyhedron (in press) [Paper No. 905478].

A manuscript based upon the results incorporated in Chapter IV is now under preparation for communication.

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Dr. Mihir K.Chaudhuri, Dr.rer.nat.(FRG), FASc., FNA,
Professor of Chemistry
Department of Chemistry

Professor Darlando T. Khathing
Department of Physics

We certify that the thesis entitled "EVIDENCE FOR THE OCCURRENCE OF MANGANESE(III) IN $[MnO_4]^-/SO_2$ REDOX REACTION AND SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF NEWER FLUORO COMPOUNDS OF MANGANESE(III) AND URANIUM(VI) $[UO_2^{2+}]$" submitted by Mr. P.Srinivas for the degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under our supervision. He has been duly registered and the thesis 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

Darlando T Khathing

Signatures of Supervisors

Place: Shillong
Date: 30 November 1993.

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This is to certify that Shri P.Srinivas has satisfactorily completed the following Pre-Ph.D. courses as prescribed by the University:

1. *Selected Topics in Physical Chemistry*
   (Course No. Chem. 642)
2. *Bioinorganic Chemistry*
   (Course No. Chem. 608)
3. *Medicinal Chemistry*
   (School Level)
4. *Basic Course in German Language*
   (University Level)

Professor and Head
Department of Chemistry

CONTENTS

ACKNOWLEDGEMENT

I take this opportunity to express heartfelt gratitude to my mentors Professor Mihir K.Chaudhuri, Department of Chemistry, and Professor Darlando T.Khathing, Department of Physics, who by their joint supervision, valuable guidance, tireless efforts, and constant encouragement enabled me to succeed in this endeavour.

I remain greatly indebted to Dr.V.R.Rao and Dr.P.C.Paul for their untiring cooperation in course of my Ph.D. work.

I also take this opportunity to thank and acknowledge my other colleagues and friends for their active cooperation and selfless help over all these years. To name a few: Dr.M. Bhattacharjee, Mr.S.K.Chettri, Mr.G.C.Mandal, Dr.B.Dey, Dr.M. Sudarshan, Mr.F.Mathew, Mr.J.Joseph, Mr.S.Deb, Dr.A.K.Deb, Mr.S. Chaudhury, Dr.C.R.Bhattacharjee, Mr.P.K.Tarafder, Mr.C.K.Jana, Mrs.Susan C.Philip, Dr.M.N.Bhattacharjee, Dr.R.N.D.Purkayastha, Dr.S.N.Mazumdar, Mr.A.DebRoy, Mr.B.S.Purkayastha, Dr.T.S.Basu Baul and Mr.J.C. Lohani.

Thanks are due to the Heads, Departments of Chemistry and Physics, Dean, School of Physical Sciences, Head, RSIC-NEHU and the University authorities in general for allowing me a free and extensive usage of all the available research facilities. I wish to place on record my sincere thanks to the faculty members, Departments of Chemistry and Physics.

I also wish to thank the non-teaching staff members of the Departments of Chemistry and Physics as well as the technical staff of RSIC-NEHU for their assistance.

Financial assistance from the Department of Atomic Energy, Government of India, and The Council of Scientific and Industrial Research, New Delhi is gratefully acknowledged.

Last, but not the least, I wish to express my deep sense of gratitude to my parents and brother for their patience and support extended to me throughout this period.

P. Srinivas

Date:30 November 1993 (P.Srinivas)

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to ascertain the identity of the isolated products in support of the notion.

The $KMnO_4$ —— SO_2 redox reaction carried out with $Mn:F^-$ atom ratio of 1:4 indicated that the process involved three different stages: (i) formation of a brown product at pH 3-2.5, (ii) formation of a pink solid at pH 2.5-2 and (iii) finally dissolution of the pink product at pH < 2 accompanied by decolourisation of the reaction solution [*cf.* Mn(II)]. However, when an analogous reaction was conducted with $Mn:F^-$ concentration ratio of 1:10, the observations were nearly similar except that at pH 3-2.5 a brown solution instead of a brown product and at pH 2.5-2 a rose-pink product in lieu of a pink species were obtained. While the brown product, isolated from the reaction in which $Mn:F^-$ concentration was held at 1:4, did not adhere to any fixed stoichiometry, the oxidation level of the metal in the product was +3 [as ascertained by redox titrimetry]. The pink and the rose-pink products were identified to be $K_2[MnF_3(SO_4)]$ and $K_2[MnF_5].H_2O$, respectively.

The *in situ* EPR and electron absorption spectroscopic experiments were carried out in solution as a function of pH. While the ESR scan did not show any signal from the point of initiation of the reaction (*cf.* pH 5.5) till pH 2, the electron absorption spectra displayed a pattern characteristic of manganese(III) starting from pH 3.3 which persisted till pH 2. On

the contrary, for the reaction solutions at pH < 2 a typical six line EPR spectrum characteristic of divalent manganese was observed whereas the electronic absorption signals observed above pH 2 disappeared at pH ≤ 2.

The results therefore suggest that in the presence of F^- ion manganese(VII) is directly reduced to manganese(III) and thence to manganese(II).

Chapter IV of the thesis presents the results of studies on the effect of fluoride on the interaction of manganese(III) with some biochemically relevant ligands, viz., salicylic acid ($salH_2$), 1,2-bis(salicylideneiminato)ethane ($salenH_2$) and N,N'-(acetylacetonato)ethylenediamine ($acacenH_2$) in an aqueous medium. The investigation was monitored by isolation of a variety of binary as well as mixed-fluoromanganates(III) under different conditions.

The complexes $A_2[MnF_4(salH)]$ (A = K, Na or NH_4) were obtained from the reactions of MnO(OH) with alkali hydrofluoride, AHF_2, and salicylic acid at a molar stoichiometry of Mn:F:$salH_2$ of 1:4:6. The mixed-fluoro(salicylato)manganates(III) were green in colour, stable in the solid form and moderately soluble in methanol. The compounds have been characterized by a combination of elemental analyses, chemical determination of the oxidation state of manganese, solution electrical conductivity measurements, IR, LR and electron absorption spectroscopies and Scanning Electron

Microscopy. The room temperature (300 K) magnetic moment values of the complexes were found to lie in the range 4.5-4.6 BM. The values are somewhat lower than that expected for an ideal d^4 system. This has been attributed to weak antiferromagnetic exchange interactions between the contiguous manganese atoms through -Mn-F-Mn-F- chains in the crystal lattice. The notable features of the IR spectra of the complexes were the bands at *ca.* 1604, *ca.*1385 and *ca.*1230 cm^{-1} owing their origins to $\nu_{as}(COO^-)$, $\nu_s(COO^-)$ and δ(O-H) modes, respectively, of the coordinated salicylate ligand. The observed decrease and increase of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, respectively, as compared to free carboxylic acids, provide evidence for the salicylate being coordinated through its carboxyl oxygens in a monodentate fashion. Further, the lowering in frequency of δ(O-H) (*cf.* free alcohols) also provides an indication for the presence of a protonated hydroxyl functionality in the complexes with the OH group being coordinated to the metal centre through its oxygen lone pair electrons. Complimentary Raman signals at *ca.*1597, *ca.*1315 and *ca.*1237 cm^{-1} as well as the adopted synthetic methodology, wherein the natural pH of the reaction medium was 4, lend support to our contention. It is therefore logical to assume that salicylate is coordinated in a bidentate fashion through its protonated phenolic and deprotonated carboxyl groups. The presence of salicylate as $Hsal^-$ and the manner in which it is coordinated are very important

structural features of the complexes. This type of a situation is rather unusual though not unprecedented.

Also highlighted in this Chapter are the antagonistic effects of F^- on the formation of mixed-ligand fluoromanganates(III). Reactions conducted at similar concentrations of manganese and salicylic acid but higher concentrations of F^-, for instance at the molar stoichiometry of $Mn:salH_2:F$ as 1:6:12, afforded $A[MnF_4(H_2O)_2].H_2O$ (A = K, Na or NH_4). Incidentally, this enables us also to make the first report on the K and NH_4 salts of the diaquotetrafluoromanganates(III). However, the reactions carried out in the presence of a still larger excess of F^- (eg., $Mn:salH_2:F$ = 1:6:24) afforded the very well known binary pentafluoromanganates(III). Control reactions carried out in the absence of salicylic acid required lesser amount of F^- to produce $A[MnF_4(H_2O)_2]$ (A = K, Na or NH_4). But if similar reactions are conducted with comparable concentrations of F^- (*cf.* that of $A[MnF_4(H_2O)_2].H_2O$ the pentafluoromanganates(III) are obtained instead of the corresponding aquatetrafluoromanganates(III). It is thus evident from the above investigation that a large excess of F^- prevents the coordination of different co-ligands present in the reaction medium to manganese(III), thereby leading to the formation of binary fluoromanganates(III) only. This therefore implies that F^- is certainly a better ligand to stabilize and trap manganese(III).

Another objective of the study was to probe the effect of F^- on the interaction of manganese(III) with Schiff bases. Thus, the reactions of MnO(OH) with acacenH$_2$ or salenH$_2$ and aqueous HF led to the isolation of heretofore unreported tetrafluoromanganate(III), enH[MnF$_4$], instead of a mixed-fluoromanganate(III). The room temperature magnetic moment of the complex was recorded to be 4.2 BM. The relatively low value, as compared to that of 4.9 BM normally expected for ideal d^4 systems, is indicative of antiferromagnetic exchange interaction being operative in the system between the contiguous manganese atoms through the formation of -Mn-F-Mn-F- chains in the crystal lattice. This has been interpreted in terms of the effect of the specific counter ion (ie., enH^+) in bringing about a polymeric structure of the complex through enhanced hydrogen bonding. The observance of two strong bands at 578 and 625 cm^{-1} in the IR spectrum of the complex renders it reasonable to assume that the manganese(III) ion in the complex finds itself in a distorted octahedral environment probably with a D_{4h} symmetry (*cf.* MF_6^{n-}). Metatheses reactions of the complex enH[MnF$_4$] with Rb$_2$CO$_3$ and CsNO$_3$ afforded Rb[MnF$_4$(H$_2$O)] and Cs[MnF$_4$(H$_2$O)], respectively.

Chapter V of the thesis addresses to a simple synthesis of bis(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(acac)_2.2H_2O$, investigation of its nucleophilic substitution reactions with F^- as the nucleophile thereby gaining an access to the hitherto

unreported $[UO_2F_6]^{4-}$ and $[UO_2F_7]^{5-}$ and newer mixed-fluorouranates(VI) with organic co-ligands viz., amino acids, acetylacetonate and acetate.

$UO_3.4H_2O$ reacted with acetylacetone ($C_5H_8O_2$) to produce $UO_2(C_5H_7O_2)_2.2H_2O$ in a nearly quantitative yield. $UO_2(acac)_2.2H_2O$ underwent nucleophilic substitution reactions separately with NH_4F and aqueous HF. While the reaction of $UO_2(acac)_2.2H_2O$ with NH_4F in acetylacetone at pH 4 led to the first synthesis of $(NH_4)_4[UO_2F_6]$, the reaction of $UO_2(acac)_2$ generated *in situ*, with a controlled amount of aqueous HF at pH 3.5 afforded the molecular $[UO_2(acac)F(H_2O)_2].3H_2O$ complex. However, on lowering the pH value to *ca.*2 by the addition of aqueous HF only $[UO_2F_2].3H_2O$ was produced. The molecular $[UO_2(acac)F(H_2O)_2].3H_2O$ complex can therefore be considered to be an isolable intermediate in the process $UO_2(acac)_2.2H_2O$ to $[UO_2F_2].3H_2O$. The knowledge obtained from the above reactions as well as the reaction of $K_2U_2O_7$ with KF and acacH at pH 3.5 leading to $K_2[UO_2(acac)F_3]$ suggests that a pH of *ca.* 3.5 is conducive to the synthesis of the mixed-ligand fluoro(acetylacetonato) complexes of UO_2^{2+}.

The mixed-fluoro(acetato) complexes, $A[UO_2(CH_3COO)_2F].3H_2O$ (A = K, Na or NH_4), were obtained from the reactions of $A_2U_2O_7$ with glacial acetic acid and aqueous HF enabling us to provide the missing K and Na salts in addition to providing a general synthetic methodology for the salts of the $[UO_2(CH_3COO)_2F]^-$

complex ion. By adapting a synthetic methodology comparable to that of $[UO_2(acac)F(H_2O)_2].3H_2O$, a molecular mixed-ligand fluoro(acetato) complex $[UO_2(CH_3COO)F(H_2O)_2]$ was obtained from the reaction of $UO_3.4H_2O$ with glacial acetic acid and aqueous HF.

For the hetero-ligand fluorodioxouranates(VI) with amino acids, the co-ligands were drawn from glycine, L-alanine and L-cysteine. While the mixed-fluoro(glycine) complexes, $A_3[UO_2(GlyH)_2F_5].3H_2O$ (A = K or NH_4), were synthesized from the reactions of $UO_3.4H_2O$ with glycine and a combination of AF and HF, the fluoro(alanine) and fluoro(cysteinate) complexes, $K_3[UO_2(AlanH)_2F_5].2H_2O$ and $(NH_4)_5[UO_2(CysH)_2F_5].2H_2O$, were prepared by a method similar to that employed for the fluoro(glycine) complexes except that AHF_2 was used as the fluorinating agent. Each of the mixed-ligand fluoro(amino acid)-dioxouranates(VI), except $K_3[UO_2(GlyH)_2F_5].3H_2O$, was unstable in aqueous solution undergoing decomposition to form intractable products. Significantly, $K_3[UO_2(GlyH)_2F_5].3H_2O$ underwent hydrolysis in an aqueous medium to afford a well-defined but hitherto unknown binary fluoro complex, $K_5[UO_2F_7].2H_2O$, enabling us to make the first report on the heptafluorodioxouranate(VI) species.

The complexes have been characterized by a combination of chemical analyses, solution electrical conductance measurements, infrared (IR) and laser Raman (LR) spectroscopic studies and

Scanning Electron Microscopy. The common features of IR spectra of the complexes were the bands at *ca.*910 and *ca.*375 cm^{-1} assigned to ν(U=O) [trans-linked O=U=O] and ν(U-F) modes, respectively. In addition, bands due to the coordinated co-ligands were observed in the anticipated positions. The IR spectral features adduced support to the chelated bidentate character of the acetylacetonate and acetate ligands in the corresponding mixed-ligand fluoro complexes. Each of the three amino acid co-ligands acted in a unidentate manner being coordinated to UO_2^{2+} through the carboxylate oxygen atom in the respective complexes. While glycine and alanine occur in the zwitterionic form, cysteine is present as a uninegative ligand ($CysH^-$). The laser Raman (LR) spectra could be recorded only for $(NH_4)_4[UO_2F_6]$, $K_5[UO_2F_7].2H_2O$, $[UO_2F_2].3H_2O$, and $K_2[UO_2(acac)F_3]$, while an extensive fluoroscence foiled such attempts on the others. The Raman signals at *ca.*880 and *ca.*380 cm^{-1} complement the IR spectral results. The Scanning Electron Micrographs of the hitherto unreported binary fluoro complexes $(NH_4)_4[UO_2F_6]$ and $K_5[UO_2F_7].2H_2O$ attest to the homogeneity of the products as well as to their crystalline character.

Chapter VI, indeed the concluding Chapter, deals with the synthesis and structural evaluation of new mixed-fluoro complexes of UO_2^{2+} containing inorganic co-ligands as well as developing of two direct synthetic routes to the dioxotetrafluorouranate(VI), $[UO_2F_4]^{2-}$, complex species. The inorganic co-ligands have been

drawn from phosphate, nitrate and hydrazine.

While the reactions of $UO_3.4H_2O$ with H_3PO_4 and alkali hydrofluorides, AHF_2 (A = K, Na or NH_4), [pH *ca.*2] at a steam-bath temperature led to the isolation of new mixed-fluoro(phosphato) complexes of the type $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ (A = K, Na or NH_4), the mixed-fluoro(nitrato) complexes $A_2[UO_2(NO_3)_3F].3H_2O$ (A = K, Na or NH_4) were obtained from the reactions of $A_2U_2O_7$ with conc.HNO_3 and aqueous HF (48%) maintaining the $UO_2^{2+}:NO_3^-:F^-$ concentration ratio at 1:*ca.*11:*ca.*36. Synthesis of the mixed-fluoro(hydrazine) complex, $[UO_2(N_2H_4)_2F_2].2H_2O$, was rather straight forward. The reaction of $UO_3.4H_2O$ with AHF_2 (A = K or NH_4) and hydrazine hydrate at a natural pH of 8.5 helped hydrazine coordination to UO_2^{2+} in the presence of F^-, since in a basic medium the possibility of formation of hydrazonium ($N_2H_5^+$) ion did not exist.

The characterization of the compounds has been made by a combination of chemical analyses, solution electrical conductance measurements, electron absorption, IR and laser Raman (LR) spectroscopic studies. The occurrence of trans-linked O=U=O, coordinated fluoride and bidentate co-ligands are the common features of the complexes. The appearance of the ν_1 mode at *ca.*905 cm^{-1} and the splitting of the ν_3 mode into three intense bands at *ca.*1000, *ca.*1070 and *ca.*1120 cm^{-1} in the IR spectra of the fluoro(phosphato) complexes clearly indicate the presence of phosphate as PO_4^{3-} and occurring as a chelated ligand. In the IR

spectra of the mixed-fluoro(nitrato) complexes the observance of all the six fundamental modes of vibrations, ν_1 to ν_6 of coordinated nitrate, as well as a large separation of ν_1 and ν_4 modes (*ca.*215 cm^{-1}) makes it rational to suppose that the nitrate in each of the complexes, $A_2[UO_2(NO_3)_3F].3H_2O$ (A = K, Na or NH_4), is present as a bidentate ligand. The IR spectrum of $[UO_2(N_2H_4)_2F_2].2H_2O$ showed a medium intensity sharp band at 955 cm^{-1} which has been assigned to the ν(N-N) stretching vibration. This as well as the similarity of IR spectral features with those of the hydrazine and mixed-ligand hydrazine complexes of different metals enables us to state that the complex contains bidentate hydrazine ligands.

With the afore mentioned success, it has become possible to overcome the synthetic problems related to phosphato- and nitrato-uranyl complexes. The newly synthesized $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ were highly crystalline solids. This has been evidenced by the Scanning Electron Microscopy (SEM). Two different stereo-views of $Na_2[UO_2(PO_4)F(H_2O)_3].3H_2O$, chosen as a representative example, exposed the hexagonal crystal morphology and cylindrical shape of the complex. Though nitrato complexes of uranyl are generally believed to be very weak, the incorporation of fluoride gave additional stability to the uranyl-nitrato system.leading to the synthesis of $A_2[UO_2(NO_3)_3F].3H_2O$. The unaltered solution electrical

conductance values as well as electron absorption spectroscopic studies lend support to the contention.

The laser Raman (LR) spectra of aqueous solutions of the fluoro(phosphato) and fluoro(nitrato)uranates(VI) as well as the corresponding solid complexes, $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ and $A_2[UO_2(NO_3)_3F].3H_2O$, were recorded separately. While for the reaction solutions the symmetric stretching frequencies $\nu_s(U=O)$ [of O=U=O] were observed at *ca.*840 cm^{-1}, the band was found to occur at *ca.*900 cm^{-1} for the solids. This has been interpreted in terms of the decrease in the hydration number of the coordination shell of UO_2^{2+} of the solid complexes. Such an experiment could not be conducted for $[UO_2(N_2H_4)_2F_2].2H_2O$ owing to the precipitation of the compound instantaneously on addition of hydrazine.

Two improved synthetic methodologies developed for the dioxotetrafluorouranate(VI), $[UO_2F_4]^{2-}$, species have also been included in this Chapter. While one of the methodologies involved the interaction of a yellow product, obtained by treating a solution of uranyl nitrate with AOH (A = K, Na or NH_4), with aqueous HF (48%) and A_2CO_3, the other was based upon a nucleophilic substitution reaction. In the latter reaction $UO_2(O_2).2H_2O$ was allowed to react with 48% HF in the presence of alkali fluoride, AF (A = K, Na or NH_4), leading to the isolation of $A_2[UO_2F_4].3H_2O$ (A = K, Na or NH_4). The compounds have been

characterized by the techniques mentioned already in the contexts of other complexes.

A large portion of the work described in various Chapters of the thesis has been published in parts:

Chapter III

J.Chem.Soc.,Dalton Trans., 1993 (in press) [Paper No. 3/03328G/DAP].

Chapter V

Proc.Indian Acad.Sci., 1992, 104, 479.

J.Fluorine Chem., 1992, 56, 305.

Polyhedron, 1993, 12, 227.

Chapter VI

Polyhedron (in press) [Paper No. 905478].

A manuscript based upon the results incorporated in Chapter IV is now under preparation for communication.

CHAPTER I

INTRODUCTION

In trying to write the introduction of the thesis, an attempt has been made to portray the chosen topics of research viz., some selected aspects of manganese(III) and uranium(VI) chemistry, a rather exciting theme of investigation. In this endeavour, it was considered appropriate to begin with the background information pertaining the chemistry of the two metals.

Manganese, having a ground state electronic configuration $[Ar][3d^5][4s^2]$ and belonging to the first row transition metal series is known to display the largest spectrum of oxidation

states ranging from -3 to +7. Like for any other metal, manganese chemistry is generally classified into two sub-groups — the lower oxidation state or organometallic chemistry and the higher oxidation state or coordination chemistry. While the lower oxidation states are generally found[1] in compounds with Mn-C bonds, carbonyl and nitrosyl derivatives, and the intermediate oxidation levels are available as different types of binary and complex compounds, the higher oxidation states (+5, +6 and +7) are largely represented in the chemistry of oxo-ligand manganates.[2a]

The relatively more studied oxidation levels of the metal are +2, +3 and +4 of which the tripositive level is the unstable one, while the chemistry of the +4 level involves compounds in which the coordination partners of the metal are O-donor ligands.[2b] The manganese(III) system is oxidizing and unstable[3] with respect to disproportionation.

$$2\ Mn(III) \longrightarrow Mn(IV) + Mn(II)$$

$$Mn(IV) \longrightarrow MnO_2 + 4H^+$$

It can be generally stabilized[4,5] by (i) increase of acidity, (ii) increase of Mn(II) concentration and (iii) by complex formation. Since manganese(II) is known to form very weak complexes, the last mentioned method has been generally employed for stabilization of trivalent state of the metal. Hence it is not

surprising that the simple ion of Mn(III) does not appear to be stable, so that the stable compounds of Mn(III) are mostly complex.[4] The complex formation[4,6] with anions which is pH dependent usually results in a lowering of the redox potential for the Mn(III)/Mn(II) couple, thereby enhancing the stability of Mn(III). Accordingly, suitable complexing agents for stabilizing manganese(III) in aqueous solutions has been one of the prerequisites for further studies.

Manganese(III) is generally stabilized[7a] in solution as well as the solid by a variety of ligands like F^-, SO_4^{2-}, $C_2O_4^{2-}$, PO_4^{3-}, $P_2O_7^{4-}$, EDTA, polyhydroxy ligands namely triethanolamine, glucarate ion, glycolate ion, catechol and substituted catechols. However, the complexes of manganese(III) with fluoride[8-12] are the relatively more stable ones in line with the enhanced basic character of F^-. In addition to imparting stability, coordination of a fluoride ligand to Mn(III) also brings about notable changes in magnetic and structural behaviour of the complexes. It is well documented in the literature[8,13,14] that binary fluoro complexes of manganese(III) have magnetic moments lower than that expected for a normal Mn(III) case owing to strong antiferromagnetic exchange interaction between the contiguous manganese atoms in the polymeric structure of the complexes, whereas manganese(III) complexes with other ligands such as oxalate, sulphate etc. show normal behaviour.[15] It was therefore anticipated that mixed-ligand

fluoromanganates(III) may show somewhat different magnetic behaviour from that of the binary manganese(III) compounds. Besides, Mn(III) having the $3d^4$ outer electronic configuration is expected to effect the structures of most of its compounds through a variety of electronic effects like for instance, ligand field splitting and most prominently Jahn-Teller distortions.[16] The majority of the complexes of manganese(III) are high spin with the magnetic moments of the octahedral complexes exhibiting spin only value, giving an indication of the fact that spin-orbit coupling is negligible in these complexes.[17]

Interestingly, when a solution contains a metal ion and two different ligands, there is always a finite possibility of a mixed-ligand complex formation. In view of the potential donating ability of many counter anions and solvents, there are a very few cases when this possibility is out of question.[18] Various kinds of mixed-ligand complexes of metals have been studied and in many cases their importance in chemical[19,20] and bio-systems[21,22] have been emphasized. In the area of mixed-ligand metal compounds, three main types of ternary complexes may be distinguished: (a) complexes containing two different unidentate ligands (b) complexes containing one or more of unidentate and one or more of bi- or multidentate ligands as required by the coordination number of the metal center and (c) complexes containing two or more of bi- or multidentate ligands. A survey of the literature

reveals that work on manganese chemistry has been mainly centred around complexes of type (a)[23-30] and type (c),[31-51] whereas there are relatively fewer reports on type (b)[52-60] complexes excluding those from our group[8-11,61,62] which had fluoride as the unidentate ligand.

Significantly, fluorometallates are important in their own right as well. There has been a constant activity in research involving fluoro containing compounds.[8-11,61-95] For instance, it is important to note that the first chemical synthesis of elemental fluorine was achieved as late as 1986.[73] Quite exciting to note is that fluorometallates appear to be also very suitable candidates for metal chemical vapor deposition processes (MCVD).[91,92] This provides another point of thrust to the study of fluoro metal chemistry. Besides, fluorometallates have also found use in various fields of science and technology[96] viz., laser technology, micro electronics, production of pure metals by thermal reduction, fluoride glass[93,94] for ultra low loss optical fibres,[95] etc. The three main factors which makes the chemistry of fluorine so different from other members of the halogen family[74] are:

(i) low dissociation energy of fluorine molecule [$D(F_2)$ = 37.7 Kcal/mole].

(ii) relatively high strength of bonds formed between fluorine and metals or non-metals.

(iii)the relatively small size of the fluorine atom and fluoride ion giving rise to the most electronegative as well as the most ionic ligands.

These properties thereby render it suitable for stabilizing higher oxidation states of metals besides making the crystal structures of metal fluorides[16] comparatively simpler, governed mainly by geometric and electrostatic principles. Despite its similarity to the biologically ubiquitious chloride ions, fluoride is blamed for several harmful processes including cancer. X-ray crystallographic studies have shown that a fluoride inhibited enzyme cytochrome C peroxidase has fluoride as ligand to the iron of the haem site.[97] This fluoride then attracts N-H bonds on neighbouring histidine and arginine groups, thereby disabling the enzyme through the hydrogen bonds.

Thus though fluoro metal chemistry is one of the oldest branches of research in inorganic chemistry, a great deal of effort is still required for the search for direct and easy to manipulate synthetic procedures for novel fluoro and mixed-fluoro complexes.

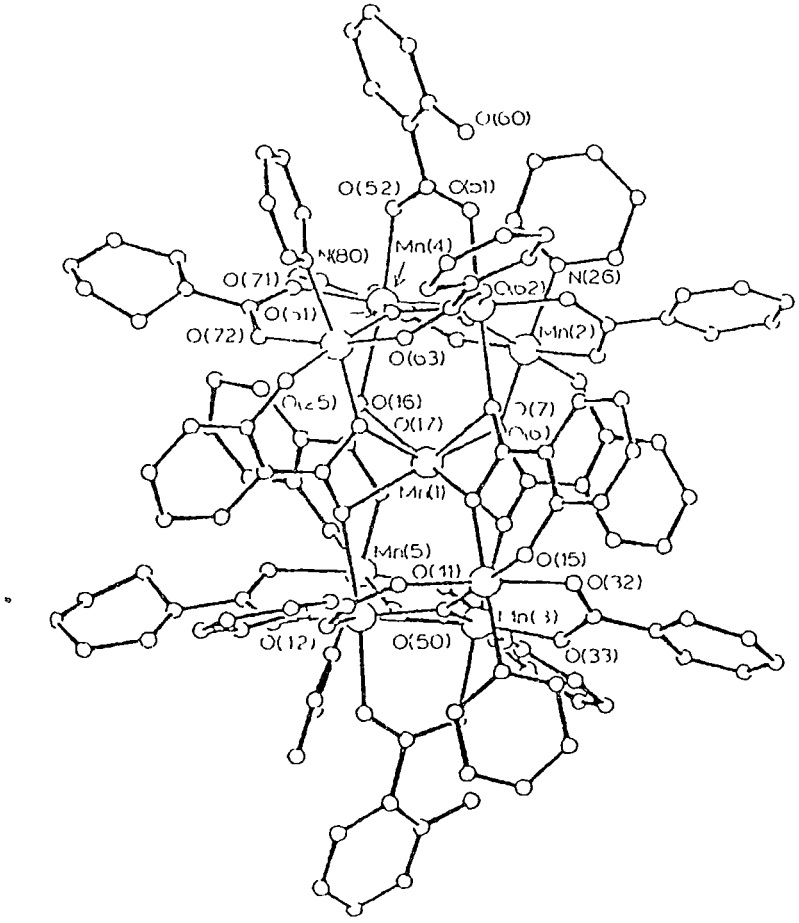
There has been a continued interest in the chemistry of manganese both for the inorganic as well as the bio-chemists. From the biochemical point of view the studies have been largely concentrated towards developing structural models describing metallocentres of manganese containing enzymes. It is by now quite

well established that superoxide dismutase,[98,99] acid phosphatases[100] and pseudo catalases[101] contain manganese in their catalytic centre. An enzyme that has received relatively lesser attention is the manganese peroxidase[102,103] that is thought to use a diffusible manganese-hydroxy acid complex to decompose lignin. The chief among the systems of interest is the oxygen evolving complex (OEC)[104-110] which is believed to be present in the molecular apparatus photosystem-II (PS-II)[108] and capable of oxidizing coordinated water molecules to oxygen.

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

It is well known that Mn, Ca^{2+} and Cl^- are essential for the activity of PS-II, whereas F^- ions act as effective inhibitors.[111] This can be understood in terms of fluoride preventing the multi nuclear complex formation which is in fact responsible for the activity of PS-II. A variety of N or O or mixed nitrogen/oxygen (NO) donor ligands like pyridine (pyr), N,N'-bis(salicylaldehydo)-1,2-propylenediamine (salpn), 1,2-bis(salicylideneiminato)ethane (salen), ethanol (EtOH), acetate (OAc), bromo subtituted catechol (Br_4Cat), salicylic acid ($salH_2$), $OPPh_3$, picolinic acid (picH), acetonitrile (MeCN), etc. have been used for the formation of a variety of di- or multi-nuclear manganese complexes. Notable examples are $(NH_4)_2[Mn(malonate)_2(CH_3OH)_2][Mn(malonate)_2]_n$,[60] $Mn_2(salpn)_2(OH)_2.4C_5H_5N$,[111] $K_2[Mn_2(Br_4Cat)_4(OPPh_3)_2]$,[111] $[Mn(EtOH)_4][Mn_2(sal)_4(pyr)_2]$,[112] $[Mn_8O_4(OAc)_{12}(pic)_2]$,[114]

$[Mn_9(OOCPh)_8(salH)_2(sal)_4(pyr)_4]$,[113] $[Mn_4O_2(COOPh)(pic)_2(MeCN)_2]$,[114] etc. Many of these complexes are important from bio-modelling point of view. Until date structurally characterized species of an impressive range of nuclearities include Mn_6,[115-119] Mn_7,[120,121] Mn_8,[122] Mn_9,[113,122,123] Mn_{10},[124] Mn_{11}[125] and Mn_{12}.[126-128] One of the most well characterized species is the Mn_9 complex[113] whose structure is as shown below.



Structure of $[Mn_9(OOCPh)_8(salH)_2(sal)_4(pyr)_4]$

Apart from their role in biochemical processes, many manganese(III) compounds play a significant role in catalytic processes. Manganese(III) compounds of acetylacetonate[129] and tris chelates of napthoquinone oximes[130] are used as catalysts for vinyl polymerizations and olefin epoxidation, respectively. Manganese(III) phosphates[131] and arsenates[131] have also been studied owing to their possible use as non-linear optical materials, ionic exchangers, host compounds for intercalation reactions, etc. In general, manganese(III) compounds with a range of oxygen ligands are almost invariably good oxidizing agents and are as such used in organic hydrocarbon chemistry, especially the acetate, sulphate and diphosphonate.[2c,132-134] Like the acetate, $Mn(acac)_3$[7b] also acts as an oxidant (alkenes to lactones),[135] coupling phenol and in the presence of donors such as DMSO initiates the free radical polymerization of acrylonitrile.

Thus the chemistry of manganese(III) is an area of contemporary interest and a few research groups world over have focussed their attention over this area of chemistry.

The group at NEHU, Shillong, where the present Ph.D research was carried out has also been working on manganese(III) chemistry for more than a decade. The principal interest of our group has been the stabilization of manganese(III) in aqueous medium with the help of suitable complexing agents especially fluoride, thereby leading to the synthesis of stable fluoromanganates(III).

Notable examples are $[MnF_5]^{2-}$,[8] $[MnF_3(SO_4)]^{2-}$,[9] $[MnF_4]^-$,[136] $[MnF_3(C_2O_4)]^{2-}$,[10] $[MnF_4(EDTA)]^-$, $[MnF_4(GlyH)_2]^-$, $[MnF_2(HPO_4)_2]^{3-}$, $[MnF_3(H_2O)(bpy)]$, $[MnF_3(H_2O)(phen)]$ and $[MnF_3(urea)_2]$.[12] Some of these complexes have exhibited unusual magnetic properties. The strong antiferromagnetism observed in $[MnF_5]^{2-}$ was variably controlled in some of the complexes like $[MnF_3(SO_4)]^{2-}$, $[MnF_3(C_2O_4)]^{2-}$ and $[MnF_3(urea)_2]$, while the rest behaved as usual d^4 systems. Moreover, there was a remarkable increase in stability of $[MnF_3(C_2O_4)]^{2-}$ as compared to $[Mn(C_2O_4)_3]^{3-}$ and the effect of F^- on the manganese(III) based chemical actinometer was also studied. Thus it is apparent that manganese(III)-fluoro and mixed-fluoro chemistry is capable of yielding a variety of valuable newer information. In view of the foregoing discussion, it is also evident that though a good amount of work has been carried out on manganese(III) chemistry, fluoro chemistry of manganese(III) has received far less attention.

Incidentally, fluoride is also known to form very stable complexes with uranyl ion, which could as well be appreciated in terms of the Pearson's SHAB principle[137] according to which UO_2^{2+} being a hard acid is expected to form stable complexes with F^- which is a hard base.

Uranium, a member of the actinide series and having the $[Rn]5f^36d^17s^2$ ground state electronic configuration is known to exist primarily in four oxidation states ranging from +3 to +6

with their f^n configuration being f^3 to f^0, respectively. The most stable oxidation state of uranium is U(VI), the reduction of which in an aqueous medium generally leads to U(IV),[138a] the intermediate U(V) however, being prone to disproportionation.[139] The lowest among the four commonly encountered oxidation levels ie., U(III)[140] is a strong reducing agent which is slowly oxidized by water with evolution of hydrogen. The principal chemistry of uranium in its hexavalent state both in solution as well as the solid is as uranyl ion, UO_2^{2+}. In aqueous solutions, UO_2^{2+} forms hydrates[138b] which act as fairly strong acids giving off protons around pH 3. The main hydrolysed species of UO_2^{2+} at 25^oC are $[UO_2(OH)]^+$, $[(UO_2)_2(OH)_2]^{2+}$ and $[(UO_2)_3(OH)_5]^+$ and at higher temperatures the monomer is the most stable. Including oxygens of the uranyl group, the coordination number of the metal atom is generally eight,[138b] the lowest number observed being six. In the case of eight coordination, the six donor atoms of the ligands form a hexagon[138b] around the equators of the linear uranyl group. In those cases where chelating[138b] ligands participate, the hexagon is generally planar, whereas it is puckered when non-chelating ligands[138b] are coordinated. In fact for non-chelating ligands the lower coordination numbers are more common. In general, seven coordination[141] is very usual for dioxoactinide(VI) complexes in which the rigid O=M=O group provides the axis for the pentagonal bipyramidal geometry. The complex ion $[UO_2(CH_3COO)_3]^-$

presents a typical example of the planar six coordination in the equatorial plane of the O-U-O ion.[143]

Aqueous uranyl ion is known to form complexes with a variety of inorganic and organic ligands over a wide pH range. The ligands that stabilize this ion include fluoride, peroxide (O_2^{2-}), β-diketonates, sulphate (SO_4^{2-}), carbonate (CO_3^{2-}), phosphates, carboxylates, nitrates, etc. Amongst these, fluoride, as mentioned earlier in this section, forms the relatively more stable complexes, most probably owing to a large gain of entropy.[138d] In striking contrast, the complexes formed by the heavier halides are very weak. The fluorides of the uranyl ion are highly soluble in water and these solutions[138d] are well protected against hydrolysis by the strong complex formation.

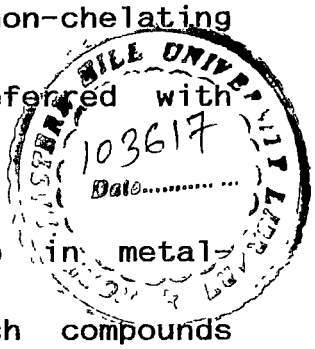
Interestingly, the compounds of UO_2^{2+} have got a range of applications as well. Some of the complexes[144,145] of UO_2^{2+} are important from the point of view that they may have applications in solar energy conversion systems due to their inherent spectral properties and they may also be of potential use in the photogeneration of oxygen which is of great importance in the photocleavage of water. Uranyl compounds are also known to catalyse the oxidation of many organic acids in the presence of light.[145] One of the characteristic features of uranyl compounds is fluoroscence and uranyl oxalate[7c,146,147] is a classic example of an actinometer. Besides, uranyl salts usually show

luminiscence[148] both in solid and solution, but the luminiscence life-time in solution is less than that in the solid. Complexation of F^- to UO_2^{2+} has been shown to increase the luminiscence life time in solution and the phenomenon was then applied to the determination of small amounts of uranium.[148] In addition to these, uranyl compounds are also used as oxidants. For eg. $[UO_2(O_2)].4H_2O$[149] has been used for the oxidation of olefins to epoxides and oxidative cleavage products. Further, UO_2HPO_4[150] is known to behave as a solid ionic conductor. Yet another manifestation of applications of uranyl compounds is the use of alkali metal uranyl ferrocyanides[152] as promising selective sorbents for Rb and Cs, thereby qualifying them for the isolation and concentration of these elements from acid solution. The interest in the fluoro chemistry of uranium stems from the special importance which fluoro compounds of uranium have in atomic energy programs. For instance UF_6,[7a,152] the most volatile uranium compound is used in gas diffusion plants for the separation of uranium isotopes, as a powerful fluorinating agent and as a selective oxidant for chlorofluorocarbons as in the cleavage of ethers.[152] Further, substitution of fluorine[153] in the ligand shell of uranyl 1,3 diketonates increases its volatility and the ease with which they can be eluted.

The number of known complexes of UO_2^{2+} is very large and virtually every kind of O, N and even S donors have been found in

such complexes. A variety of binary uranyl fluoro complexes obtained from aqueous solution are well documented in the literature. Notable among them are the ones with UO_2^{2+}:F stoichiometry of 1:2, 1:2.5, 1:3, 1:3.5, 1:4, 1:4.5 and 1:5 with their formulae being $[UO_2F_2]$,[154-158] $[(UO_2)_2F_5]^-$,[154,159] $[UO_2F_3]^-$,[154,159] $[UO_2F_4]^{2-}$,[160] $[(UO_2)_2F_7]^{3-}$,[161] $[(UO_2)_2F_9]^{5-}$,[154] and $[UO_2F_5]^{3-}$,[154] respectively. It has been shown that by simply varying the conditions it is possible to prepare different uranyl fluoro compounds with a given alkali metal cation. Addition of KF to a solution of $UO_2(NO_3)_2$ yields a precipitate of $K_3[UO_2F_5]$,[154] which on recrystallization from a solution containing 13% KHF_2 produces $K_5[(UO_2)_2F_9]$, while recrystallization of $K_3[UO_2F_5]$ or $K_5[(UO_2)_2F_9]$ from uranyl nitrate solution affords $K_3[(UO_2)_2F_7]$. Uranyl fluoride, UO_2F_2, has been generally prepared by the action of hydrogen fluoride on uranyl acetate[156] at 250^oC or uranyl phosphate hydrate[157] at 350- 500^oC and by treating uranyl chloride[158] with liquid anhydrous hydrogen fluoride at room temperature. Yet another method developed recently by Chakravorti and Chowdhury[155] required the preparation of $[UO_2(O_2)].2H_2O$ which on conversion to $H[UO_2F_3].H_2O$ afforded anhydrous UO_2F_2 by dehydration and dehydrofluoridation under heating at *ca.*150^oC. Varying proportions of $CsF:UO_2F_2$[154] afforded the complexes $Cs[UO_2F_3].H_2O$, $Cs[UO_2F_3]$, $Cs_2[UO_2F_4]$ and $Cs_3[UO_2F_5]$ from dilute aqueous hydrofluoric acid. Relevant to note here is that compounds

having UO_2^{2+}:F stoichiometry greater than five had no reported existence in the literature till 1991. These materials therefore provide synthetic challenges, especially for complexes having UO_2^{2+}:F stoichiometry either six or seven as with non-chelating ligands[138b] the lower coordination numbers is more preferred with dioxouranium(VI) ions.



Based upon the experience gathered by the group in metal-acetylacetonate chemistry[80,162-164] and the use of such compounds as inorganic synthons for fluorometallates[80,162-163] viz. $[NiF_4]^{2-}$, $[ZnF_4]^{2-}$,$[MnF_5]^{2-}$,$[CrF_5(H_2O]^{2-}$ and $[VOF_4]^{2-}$, it was anticipated that one of the possible ways for accessing the desired fluorodioxouranates(VI) could be by using $UO_2(acac)_2.2H_2O$ as a synthetic precursor. Thus it became necessary for us to synthesize the bis(acetylacetonato)dioxouranium(VI) dihydrate complex in this context.

It may be mentioned in passing that metal acetylacetonates in general, constitute a very privileged class of inorganic compounds. They find wide utility as catalysts in various organic processes,[165] as NMR shift reagents,[166] as antioxidants,[167] etc. Besides, they can be used as precursors for thermal and photochemical production of homogeneous and heterogeneous catalysts.[168] In addition, metal acetylacetonates have been used very recently as suitable probes for metal organic chemical vapour deposition (MOCVD) techniques[169] leading to the desired kind of

metal oxides useful for the preparation of high Tc superconducting films. In view of the recent applications of metal acetylacetonates as well as the earlier recognized ones, there has been a resurgence in the acetylacetonate chemistry and accordingly this has drawn the attention of chemists and material scientists.

As discussed earlier in this Chapter in the context of manganese chemistry, mixed-ligand complexes of metals are generally observed to be comparatively more stable than the corresponding binary complexes. This has been supported by elementary electrostatic considerations, steric effect and back coordination.[170] A variety of mixed-ligand uranyl complexes are well documented in the literature but most of them are complexes containing two or more bi- or multidentate[171-186] ligands. Interestingly, there are relatively fewer reports on complexes containing a combination[187-191] of mono and bi-or multidentate ligands, in particular mixed-ligand fluorouranates(VI).[192-201] For the mixed-ligand fluoro complexes of UO_2^{2+} the coligands were largely drawn from sulphate,[192] oxalate,[193] carbonate,[194] acetate,[124e] acetylacetonate,[195] propionate,[196] malonate,[197] peroxide,[198] urea,[199] DMSO[200] and chloride or bromide.[201] Notable examples are $[UO_2F_2(C_2O_4)_2]^{4-}$, $[UO_2F_2(C_2O_4)]^{2-}$, $[UO_2F_3(SO_4)]^{3-}$, $[UO_2F_2(acac)(H_2O)_2]^{-}$, $[UO_2F(acac)_2(H_2O)_2]^{-}$, $[UO_2F_2(propionate)_2]^{2-}$, $[UO_2F_2(malonate)_2]^{4-}$, $[UO_2(O_2)_2F_2]^{2-}$, $[UO_2F_2(DMSO)_n]$ and $[UO_2F_2(urea)_2]$.

Scope of the work

In cognizance to the relevant background presented in the non-exhaustive overview given above on manganese and uranium chemistry, we sought to address the following problems of fluoro and heteroligand fluoro chemistry of the two chosen metals.

(i) The reduction of permanganate in a variety of acid solutions viz. H_2SO_3, HCl and H_3AsO_4 were studied and in each case the product was conjectured to be an unstable complex of manganese(III).[202] Perhaps the best known chemical test for the two reagents ——— potassium permanganate, $KMnO_4$ and SO_2 ——— is the decolorization of an aqueous $KMnO_4$ solution by SO_2. Significantly, there has been no convincing evidence for the occurrence of manganese(III) in the process. Thus, a definitive evidence for the occurrence of manganese(III) in the Mn(VII) - Mn(II) redox process was essential in order to gain knowledge about this fundamentally important reaction.

(ii) Much of the recent studies on manganese(III) are directed towards biochemical modelling for understanding the exact role of manganese centres in a variety of enzymes especially those involved in the oxidation of peroxide to dioxygen in dimanganese catalases[203,204] and oxidation of water to dioxygen in the oxygen evolving centre (OEC) of Photosystem-II (PS-II).[104-110] Majority of the ligands used

for such studies are oxygen or mixed nitrogen,oxygen (N,O) donor ligands. Significant to note here is that while Cl^- ions are known to be essential for the activity of PS-II, F^- ions act as effective inhibitors most probably by preventing multinuclear complex formation. In view of the alleged deleterious effect of F^- in the formation of di- or multi-nuclear manganese complexes, it became imperative to investigate the interaction of F^- with manganese(III), for instance, in the presence of biochemically relevant ligands by way of isolation and characterization of the complexes from such reactions.

(iii) Owing to the inherent problems in the literature methods[164] for the synthesis of $[UO_2(acac)_2].2H_2O$, especially the extra preparation and purification steps required for obtaining the starting material, an improved synthetic methodology was sought. Remarkable is the conspicuous absence of the $[UO_2F_6]^{4-}$ and $[UO_2F_7]^{5-}$ complex species, which therefore calls for immediate attention on to binary fluorouranate(VI) chemistry.

(iv) Equally important is also a systematic synthetic investigation on mixed-fluorouranates(VI) with a variety of inorganic and organic coligands aiming at developing viable methodologies to provide a ready access to this facet of a relatively less explored area of uranyl chemistry. While the

organic coligands may be drawn from amino acids, acetylacetonate and carboxylates, the inorganic coligands may include phosphate, nitrate and hydrazine.

It is hoped that investigation on a selection of problems identified above should not only contribute to our present knowledge on the chemistry of manganese and uranium but also provide newer materials for further studies.

The subject matter of the thesis has been divided into six Chapters. The present Chapter gives a non-exhaustive background information on the relevant aspects of the chemistry of the two chosen metals viz. manganese and uranium and identifies some of the problems considered imperative to investigate, thereby presenting the scope of the work. Chapter II narrates the details of the methods used for the preparation of starting materials and elemental analyses as well as the particulars of instruments/equipment used for structural characterization. While Chapter III provides evidence for manganese-III in the $KMnO_4$ — SO_2 redox reaction using fluoride as the intermediate stabilizer, Chapter IV presents the results of the studies on the interaction of manganese(III) with some biochemically relevant ligands in the presence of F^- leading to several binary and mixed-fluoro manganates(III). The first syntheses of $[UO_2F_6]^{4-}$ and $[UO_2F_7]^{5-}$ as well as mixed-fluoro uranates(VI) with organic coligands viz. amino acids, acetylacetonate and acetate constitute the theme of

Chapter V. Chapter VI, indeed the concluding Chapter, describes newer mixed-fluorouranates(VI) with inorganic coligands viz. phosphate, nitrate and hydrazine as well as improved synthetic routes to $[UO_2F_4]^{2-}$. An attempt has been made to present each Chapter as a self-contained one with a brief introduction, sections on experimental and results and discussion followed by relevant bibliography. In this endeavour, some repetition in the bibliography is duly apologised.

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CHAPTER II

METHODS OF PREPARATION OF STARTING MATERIALS, ELEMENTAL ANALYSES AND PARTICULARS OF INSTRUMENTS/EQUIPMENT USED FOR CHARACTERIZATION AND STRUCTURAL ASSESSMENT OF THE COMPOUNDS

Detailed procedures adopted for the preparation of different starting materials as well as for quantitative determination of various constituents and the relevant particulars of the instruments/equipment used for the characterization and structural assessment of the newly synthesized compounds are described in this Chapter.

All the chemicals used were of reagent grade quality.

Preparation of alkali hydrogen fluorides,[1] AHF_2 (A = K, Na or NH_4)

An amount of 36.2 mmol of powdered alkali carbonate A_2CO_3 was dissolved in 40% hydrofluoric acid maintaining the ratio of M:HF as 1:4. To the clear solution thus obtained, pyridine was added slowly until the precipitation was complete. The white crystalline compound thus obtained was separated by decantation, washed free from hydrofluoric acid by pyridine, and then with acetone and finally dried *in vacuo*.

Preparation of $MnO(OH)$[2]

In a typical preparation, a solution of 2.2g (11.84 mmol) of $MnSO_4.H_2O$ in 350 cm^3 of water was treated with 34 cm^3 of a 3% H_2O_2 (30 mmol) solution. An amount of 50 cm^3 of a 0.2M ammonia solution (10 mmol) was added under constant stirring. The mixture was boiled for *ca.* 5 min. and then filtered. The dark brown compound formed in this process was washed with about 1.5 lit. of hot water on the filter and then used for the subsequent reactions.

Preparation of $UO_3.4H_2O$

Uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, (5.0g, 9.96 mmol) was dissolved in water (100 cm^3), to which was added pyridine (10 cm^3) whereupon a yellow precipitate appeared. This was separated

by decantation, washed three or four times with water, twice with acetone and finally dried on a steam-bath to obtain yellow uranium trioxide, $UO_3.4H_2O$ (yield: 2.8g, [78.4%]).

Elemental Analyses

Manganese[3]

Manganese was determined by complexometric titration with EDTA using Eriochrome Black T as an indicator.

In this procedure, an accurately weighed amount of the compound was decomposed by the addition of 20-25 cm^3 of 0.1M NaOH solution and the mixture was heated for *ca.*10-15 min. on a steam-bath for complete decomposition. The resulting hydrated oxide of manganese was quantitatively separated by filtration and washed three or four times with cold water. The brown-black precipitate was dissolved in dilute hydrochloric acid followed by the addition of 0.5g of hydoxyl ammonium chloride to prevent oxidation. The solution was diluted to 100 cm^3, warmed slightly and then neutralised by the addition of 0.1M NaOH solution. 3 cm^3 of triethanolamine was added to keep manganese in solution, when it was subsequently made alkaline by the addition of 2 cm^3 of a buffer solution (pH = 10) and then several drops of Erio T indicator was added. The resulting mixture was titrated with

standard 0.05M EDTA solution at about 40°C until the colour permanently changed from red to blue.

$$1\ cm^3\ 0.05M\ EDTA = 2.747\ mg\ of\ Mn$$

Uranium[4]

Uranium was estimated gravimetrically as uranyl oxinate.

An accurately weighed amount of the compound was dissolved in a minimum volume of dilute (6M) nitric acid followed by the addition of dilute ammonia until a yellow precipitate was obtained. The precipitate was filtered off on a Whatman 541 filter paper, washed three or four times with water and finally dissolved in a minimum volume of 1% acetic acid solution. To the resulting solution 5g of ammonium acetate was added, which was then heated to boiling followed by the addition of 4% oxine solution dropwise, until an orange precipitate appeared. The whole was then heated on a water-bath for *ca.* 15 min. and then filtered through a sintered glass crucible (G-4). The precipitate was washed three or four times with hot water, then by cold water and finally dried to constant weight at 110°C. The precipitate was weighed as uranyl oxinate, $[UO_2(C_9H_6ON)_2.C_9H_7ON]$.

Fluoride[5]

An accurately weighed amount of a fluoromanganate(III) or a fluorouranate(VI) compound was dissolved in water. The

fluoromanganate(III) compound was decomposed with 20-25 cm^3 of 0.1M NaOH solution, and the fluorouranate(VI) compound was decomposed by the addition of 20-25 cm^3 of 25% aqueous ammonia. The mixture was heated over steam-bath for *ca.* 15 min. to ensure complete decomposition. The hydrated manganese oxide and ammonium diuranate formed due to the addition of NaOH and aqueous ammonia, respectively, was separated out by filtration and washed several times with water. The filtrate and washings were collected for fluoride estimation. To the combined washings and filtrate, two or three 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 (6M) was added to it until the colour just changed to yellow followed by the addition of 0.1M NaOH solution until the colour just changed to blue. The mixture was then treated with 1 cm^3 of conc. HCl and 5g of $Pb(NO_3)_2$ and then heated on a steam-bath. After all the lead nitrate had dissolved, 5g 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 precipitate lead chloride fluoride, PbClF, was filtered through a sintered glass crucible (G-4) and weighed as PbClF after drying at 140-150^oC to constant weight. In the volumetric estimation, the precipitate PbClF was quantitatively collected by filtration through a Whatman 542

filter paper, washed once with cold water, then three or four 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 a steam-bath for 5 min. A known excess of 0.1M $AgNO_3$ solution was added to it followed by digestion on a steam-bath for *ca.* 30 min. and then cooled to room temperature in the absence of light. The precipitated silver chloride was filtered through a sintered glass crucible (G-4) and washed thoroughly with cold water. The unreacted silver nitrate in the filtrate and washings was titrated with 0.1M KSCN solution using 1 cm^3 of ferric ion indicator solution 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 $AgNO_3$ consumed.

$$1\ cm^3\ 1M\ AgNO_3 = 0.019g\ of\ F$$

Sulphate[6]

A known amount of trifluoromonosulphatomanganate(III) was decomposed by the addition of 20-25 cm^3 of 0.1M NaOH solution. The mixture was heated over a steam-bath for *ca.* 15 min. to ensure complete decomposition. The hydrated manganese oxide thus formed

was separated out by filtration and washed several times with water. The filtrate and washings were retained for sulphate estimation. The solution was concentrated by boiling and neutralised with 6M nitric acid. The solution so obtained was acidified by the addition of 0.5 cm^3 of conc.HCl and heated to boiling. A warm solution (10 cm^3) of 5% Barium chloride in water was added dropwise with stirring and the resultant precipitate was allowed to settle for *ca.* 5 min. The supernatant liquid was tested for complete precipitation by adding a few drops of barium chloride solution. 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 on a steam-bath for 1h in order to achieve complete precipitation of $BaSO_4$.

The precipitated barium sulphate was filtered through a previously weighed sintered glass crucible (G-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^oC followed by cooling in a dessicator. The heating process was continued until a constant weight was attained.

The sulphate content of the compound was finally weighed as $BaSO_4$.

Phosphate[7]

An accurately weighed amount of fluorophosphatouranate(VI) was treated with 25 cm^3 of water and was then dissolved completly by the addition of *ca.* 1 cm^3 of 6M nitric acid. A 25% solution of aqueous ammonia (sp.gr.0.91) was added to the solution slowly with stirring, and the mixture heated over a steam-bath for *ca.* 30 min. The precipitated ammonium diuranate was separated by filtration and washed three or four times with cold water. The combined filtrate and washings was neutralised by the addition of 6M HNO_3 followed by the addition 3 cm^3 of conc.HCl and a few drops of methyl red indicator. An amount of 25 cm^3 of magnesia mixture was added to the solution followed by a slow addition of concentrated aqueous ammonia (sp.gr.0.91) with vigorous stirring, until the indicator turned yellow. Stirring was continued for a further period of 5 min. and finally an excess of 5 cm^3 of concentrated aqueous ammonia (sp.gr. 0.91) was added slowly. The resulting mixture was allowed to stand in cold for 4h, whereupon the white precipitate of ammonium magnesium phosphate hexahydrate settled down. The precipitate was separated quantitatively by filtration, using a sintered glass crucible (G-4) and washed with distilled ethanol three or four times and finally with small portions of ether. The precipitate was dried under *vacuo.* for *ca.* 20 min. and finally weighed as $MgNH_4PO_4.6H_2O$.

Carbon, Hydrogen and Nitrogen

The carbon, hydrogen and nitrogen contents were estimated by micro-analytical methods. The results of the analyses were obtained from the Micro Analytical Laboratory, Department of Chemistry, North-Eastern Hill University, Shillong.

Sodium

The sodium content was determined by flame photometry. A solution containing sodium ions was acidified with hydrochloric acid. The acidified solution thus obtained was used for flame photometry.

Rubidium and Caesium[8]

The rubidium and caesium contents in the respective salts of tetrafluoromanganates(III) were estimated gravimetrically as their perchlorates. The precipitate was obtained by following the standard procedure and weighed as $AClO_4$ (A = Rb or Cs).

Determination of Elements by Atomic Absorption Spectrophotometry

The Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer (AAS) was used for the quantitative determination of potassium, manganese and uranium. In each estimation, a solution of a known amount of the compound

containing the element under determination was used for the AAS experiment.

Chemical Determination of Oxidation State of Manganese

The oxidation state of manganese was determined iodometrically by treating a freshly prepared ice-cold potassium iodide solution, acidified with dilute sulphuric acid, with the compound, followed by titration of the liberated iodine against a standard sodium thiosulphate solution. The iodometry experiment was done under an ice-cold condition.

Particulars of Instruments/Equipment Used

pH Measurement

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

Solution Electrical Conductance

Solution Electrical conductance measurements were made by using a Systronics Type 304 digital direct reading conductivity meter and also a Wayne kerr Automatic Precision Bridge B 905 conductometer.

Magnetic Susceptibility

Magnetic susceptibilities of the complexes were measured by the Gouy method using $Hg[Co(NCS)_4]$ as the standard for calibration.

Infrared Spectra

Infrared spectra were recorded in KBr on Perkin-Elmer models 297 and 983 spectrophotometers.

laser Raman Spectra

laser Raman (LR) Spectra were obtained on a SPEX Ramalog Model 1403 spectrometer. The 4880 Å laser line from Spectra Physics Model 165-09 Argon laser and the 6471 Å laser line from coherent mode Innova 90K Krypton ion laser were used as the excitation sources. The scattered light at 90^{o} was detected with the help of a cooled RCA 31034 photomultiplier tube followed by photon-count processing system. The sample was held either in the form of a pellet in KBr or in solution. The recording was done at ambient temperature.

Electron Absorption Spectra

Electron Absorption Spectral measurements of freshly prepared solutions were made on a Cary Model 2390 and Hitachi Model 330

UV-Vis-NIR Spectrophotometers fitted with a thermostated cell holder.

Reflectance Spectra

Reflectance Spectra were recorded against MgO using a Carl Zeiss Jena VSU 2-P instrument.

ESR Spectra

The ESR Spectra of the reaction solutions were recorded as a function of pH using a Varian E 109 X-Band ESR Spectrometer fitted with 100 K_c field modulator.

Mass Spectra[9]

The mass spectra were recorded on a Varian MAT CH-5 spectrometer. A direct insertion probe was used to introduce the sample directly into the ion source without any prior heating. The sample was held under *vacuo*. (inside the mass spectrometer) for *ca*. 1h in the direct inlet probe before electron impact was initiated. The operating conditions were: electron energy, 70 eV (1 eV = 1.6×10^{-19} J); source temperature, $100^{o}C$; resolution, 10,000; accelerating voltage, 8 KV. The mass spectrometric observations were made with the ionising beam held constant to obtain reproducible ion intensities.

Scanning Electron Microscopy (SEM)

All the SEM experiments were carried out on a JEOL SEM, JSM-35 CF Model Scanning Electron Microscope. A suspension of the sample in about half a test tube of the solvent in which it was either insoluble or sparingly soluble was ultrasonicated in an ECONO-CLEAN Ultrasonicator for *ca.* 30 min. Then a drop of the resultant solution was added onto the surface of the brass stub (30 mm dia. x 20 mm high) and allowed to evaporate at room temperature. This was then coated with gold in a fine coat ion sputter JFC-1100. Observations were made on the Scanning Electron Microscope JSM 35 CF operated at 15 KV. Tilt control was fixed at 0^{o} for setting the specimen stage in a horizontal position. WD selector was turned fully clockwise to set the working distance (WD) to 39 mm.

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CHAPTER III

EVIDENCE FOR THE OCCURRENCE OF MANGANESE(III) INTERMEDIATE IN THE PERMANGANATE/SULFUR DIOXIDE ($[MnO_4]^-/SO_2$) REDOX REACTION*

The reduction of manganese(VII) of potassium permanganate, $KMnO_4$, to manganese(II) by SO_2(g) or SO_2(solution) [$SO_2.xH_2O$] in

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*The work described herein has been accepted for publication in *J.Chem.Soc.,Dalton Trans.*, 1993 (in press) [Paper No. 3/03328G/DAP]

an aqueous medium is a very well known text book phenomenon.[1] This reaction has been a very useful test for either of the reagents. Because of the sensitivity of the reaction, this knowledge is expected to be important also for ascertaining environmental pollution resulting from $SO_2(g)$ including acid rain problems.

Since the metal is capable of exhibiting a range of oxidation states from +7 to +2 in aqueous medium, involvement of one or more of the intermediate oxidation levels cannot be ruled out. As a matter of fact, the occurrence of manganese(III) in the Mn(VII) - Mn(II) redox reaction in a variety of acid solutions like H_2SO_3, H_3AsO_4 and HCl was conjectured by DeThomas and Purdy.[2] But in each case the instability of the manganese(III) products precluded a convincing evidence.

The chemistry of the tripositive oxidation level of manganese is of topical importance[3] and the recent years have witnessed an upsurge in the field for a variety of reasons. Notable are its biochemical relevance in diverse redox functions, like water splitting by photosynthetic enzymes,[4] H_2O_2 disproportionation in microorganisms,[5] reduction of ribo to deoxyribonucleotides in corneyform bacteria[6] and oxidation of coordinated water to oxygen.[7] Our reseach group has been involved in the study of manganese(III) chemistry[8-10] and one of our major concerns has

been to improvise ways to stabilize it in aqueous medium. Some of our recent successes[8-10] in fluoride assisted stabilization of this oxidation level of the metal, intrigued us to look for a convincing evidence for the involvement of manganese(III) in the Mn(VII) - Mn(II) redox process. Thus, we were primarily concerned with the following question: Does the MnO_4^-/SO_2 reaction leading to Mn(II) involve the formation of manganese(III) intermediate ?

Based on a number of empirical observations, it has been our argument that fluoride is a very efficient stabilizer for manganese(III)[8-10] in both aqueous solution and the solid state. It is with this perception that we proposed to demonstrate the possible involvement of manganese(III) in the Mn(VII)-SO_2(g) reaction.

A detailed account of the results of the work undertaken in this direction has been incorporated in this Chapter.

Experimental

Chemicals used were all reagent grade products (E.Merck (India) Ltd., B.D.H, I.D.P.L, S.d-Fine Chem.). The details of the instruments/equipment used for the characterization of the products as well as for *in situ* experiments are given in Chapter II.

Reaction of $SO_2(g)$ *with* $KMnO_4$ *in aqueous solution in the presence of fluoride* (F^-).

(i) *Isolation and Characterization of Reaction Intermediates*

(a) *Reaction Intermediate* $K_2[MnF_3(SO_4)]$

An amount of 1.0g (6.33 mmol) of $KMnO_4$ was thoroughly mixed with 0.98g (12.55 mmol) of KHF_2, maintaining the ratio of Mn:F as 1:4. The mixture was then dissolved in 30 cm^3 of water and $SO_2(g)$ was bubbled through the solution with constant stirring until a brown solid precipitated out. The flow of $SO_2(g)$ was continued whereupon the product redissolved to give a clear solution from which a crystalline pink solid precipitated out on further bubbling of $SO_2(g)$. The pH of the reaction solution was measured to be 2 - 2.5 and the flow of $SO_2(g)$ was stopped at this stage. The product obtained as above was filtered, washed with ethanol two or three times, and finally dried *in vacuo* over conc.H_2SO_4. The product was analysed as $K_2[MnF_3(SO_4)]$.

(b) *Reaction Intermediate* $K_2[MnF_5].H_2O$

$KMnO_4$ (1.0g, 6.33 mmol) and KHF_2 (2.47g, 31.64 mmol) were dissolved in 30 cm^3 of water maintaining the ratio of Mn:F as 1:10. $SO_2(g)$ was bubbled through the solution with stirring until a rose-pink solid precipitated out. At this stage, the pH of the reaction solution was found to be 2 - 2.5. The rose-pink product as obtained in the present case was isolated by

filtration followed by washing twice with ethanol and finally drying *in vacuo* over conc.H_2SO_4.The product was identified to be $K_2[MnF_5].H_2O$.

The analytical and characterization data of the products are summarized in Tables 3.1 and 3.2, repectively.

(ii) *In situ methods for detection of reaction intermediates*

(a) *EPR experiments*

The solution EPR experiments were conducted at room temperature. A solution of a mixture of $KMnO_4$ and KHF_2 in the molar ratio 1:2 ($Mn:F^-$ = 1:4) was prepared. The solution strength was maintained at 10^{-3}M with respect to $KMnO_4$.

A regulated flow of $SO_2(g)$ was maintained by using a mechanical regulator and a micro-jet. The pH of the reaction solution was recorded with a direct reading digital pH meter. The solution registered a pH of *ca.*5.5 prior to the initiation of bubbling of SO_2 gas. The reactant gas was then slowly bubbled through the solution into which the electrodes of the pH meter were already dipped so that the pH could be recorded simultaneously with the progress of flow of the gas. The SO_2 gas flow was stopped at every interval of lowering of pH by 0.2 followed by drawing a small volume of the solution and recording its EPR.

Table 3.1: Analytical Data and Magnetic Moment Values of the Products $K_2[MnF_3(SO_4)]$ and $K_2[MnF_5].H_2O$

Product	u_B (BM)	Element	Found (%)	Calcd. (%)
$K_2[MnF_3(SO_4)]$	4.1	Mn	19.3	19.2
		F	20.3	19.92
		SO_4^{2-}	33.63	33.56
		K	27.54	27.32
$K_2[MnF_5].H_2O$	3.2	Mn	22.42	22.3
		F	37.96	38.6
		K	31.54	31.75

Table 3.2: IR and Reflectance Spectral Data of the Products $K_2[MnF_3(SO_4)]$ and $K_2[MnF_5].H_2O$ with their Assignments

Product	IR (cm^{-1})	Assignment	Reflectance (nm)	Assignment
$K_2[MnF_3(SO_4)]$	1230s, 1145s, 1030s	ν_3(S-O)	730	$^5B_{1g} \longrightarrow {}^5A_{1g}$
	975s	ν_1(S-O)	550	$^5B_{1g} \longrightarrow {}^5B_{2g}$
	680s, 635s, 605s	ν_4(S-O)	462	$^5B_{1g} \longrightarrow {}^5E_g$
	525s	ν(Mn-F)		
$K_2[MnF_5].H_2O$	615m	ν(Mn-F)ν_3	833	$^5B_{1g} \longrightarrow {}^5A_{1g}$
	565s	ν(Mn-F)ν_4	540	$^5B_{1g} \longrightarrow {}^5B_{2g}$
	1635m	δ(H-O-H)	476	$^5B_{1g} \longrightarrow {}^5E_g$
	3468s	ν(O-H)		

(b) *Electron Absorption Spectra*

An exercise similar as above was done except that electron absorption spectra, instead of EPR spectra, were recorded at different pH values. The spectra were recorded at ambient temperature.

Elemental Analyses and *Chemical Determination of Oxidation State of Manganese*

Quantitative determinations of manganese, fluoride, sulphate and potassium as well as the chemical determination of oxidation state of manganese were made by the methods/procedure decribed in Chapter II.

Results and Discussion

One of the methods commonly employed for the preparation of manganese(III) complexes has been by the reduction of Mn(VII) (*cf.* MnO_4^-). It is generally believed[11] that this occurs by a rapid reduction of some of the Mn(VII) to Mn(II) (aq.) followed by its reaction with MnO_4^- leading to the formation of manganese(III). Alternatively, the reduction of Mn(VII) to Mn(II) through manganese(III) also cannot be ruled out. It was hence perceived that in the presence of F^- manganese(III) could be trapped before manganese(II) in the $KMnO_4$-SO_2 redox reaction, if the latter route

were operative. Our approach therefore has been to detect the reaction intermediate in the MnO_4^-/SO_2 redox reaction involving *in situ* methods as well as by isolation of the products formed under an analogous condition. The former was warranted especially to verify whether or not the formation of manganese(II) preceded that of manganese(III) in the chosen reaction. This became all the more necessary since a rapid reduction of $[MnO_4]^-$ to Mn^{+2} (aq.) followed by the reaction of aquated manganese(II) with MnO_4^- leading to manganese(III) could be an alternative possibility.

Reactions and Isolation of Manganese(III) Intermediates

It was conjectured that Mn(III) could be trapped in an aqueous medium using fluoride as the stabilising ligand. Thus, reactions of $KMnO_4$ with SO_2(g) were conducted separately with Mn:F being maintained at 1:4 and 1:10. Permanganate interacted with the reductant as evidenced by the liberation of heat. With the progress of bubbling of SO_2(g), there was a lowering of pH of the reaction solution. The experiment conducted with Mn:F atom ratio 1:4, exhibited three different stages of reactions. First, formation of a brown product at pH 3-2.5 with the mother liquor becoming nearly colourless; second, disappearance of the brown product with concommitant precipitation of a pink compound at pH 2.5-2; and the third, dissolution of the pink product at pH $<$ 2 accompanied by decolourisation of the reaction solution.

In the subsequent reaction runs, the reactions were arrested at the stages of formation of a brown product (stage 1) and a pink compound formation (stage 2). The product isolated from the final stage (stage 3) contained manganese(II), SO_4^{2-} and F^- without occurring in a fixed stoichiometry.

A similar reaction conducted at Mn:F^- concentration 1:10 appeared to be comparatively more facile. No brown product was formed, rather at pH 3-2.5 a brown colour of the solution was observed which immediatly turned pink at pH 2.5-2 and precipitated a rose-pink compound rendering the mother liquor colourless. Here again, if the reaction was not halted by discontinuing the SO_2(g) flow, the rose-pink product formed at pH 2.5-2 (stage 2) dissolved at pH < 2 producing a colourless solution (*cf.*Mn(II)). The white product isolated from the solution provided similar results as those obtained from the final stage of the previous (*cf.*Mn:F as 1:4) reaction. The product was a mixture containing manganese(II), SO_4^{2-}, F^- and K^+, as ascertained from chemical and physical studies. In order to comment on the course of the MnO_4^-/SO_2 redox process, one of the essential requirements was to isolate the products and ascertain the oxidation level of the metal in them.

Identity of the intermediates

Brown product.——— This contained fluoride and sulphate in addition to manganese occurring in its tripositive state. However,

the products obtained from the repeated reaction runs did not conform with a fixed stoichiometry among K, Mn(III), SO_4^{2-}, and F^- precluding any definite formulation. Interestingly, the analytical results indicated the occurrence of F^-:Mn(III) as 1:≥2, and the IR spectrum (Fig.3.1) suggested the presence of coordinated sulphate.

Pink product. ——— The compound obtained from the reaction of $KMnO_4$ with SO_2(g) at Mn:F :: 1:4, showed the presence of K^+, F^-, SO_4^{2-} and Mn(III) in the ratio 2:3:1:1. Replicate experimental runs led to concurrent results, including the chemically determined oxidation state of manganese. The chemical determination of oxidation state of the metal was of paramount importance in this investigation especially because of anamolous magnetic behaviour of trivalent manganese[8-10,12] complexes. The room temperature (290 K) magnetic moment of the compound was found to be 4.1 BM and this somewhat low value has been attributed to weak antiferromagnetic exchange interaction often encountered in fluoro and mixed-fluoro manganates(III).[8-10,12]

The IR spectrum (Fig.3.2) displayed characteristic bands at 1230s, 1145s, 1030s, 975s, 680s, 635s, 605s and 525s, which have been assigned to the absorptions originating from ν_3(S-O), ν_1(S-O) and ν_4(S-O) modes of coordinated sulphate and ν(Mn-F) from coordinated fluoride. The splitting of ν_3 and ν_4 modes of sulphate into three bands each indicates the presence of C_{2v} symmetry of

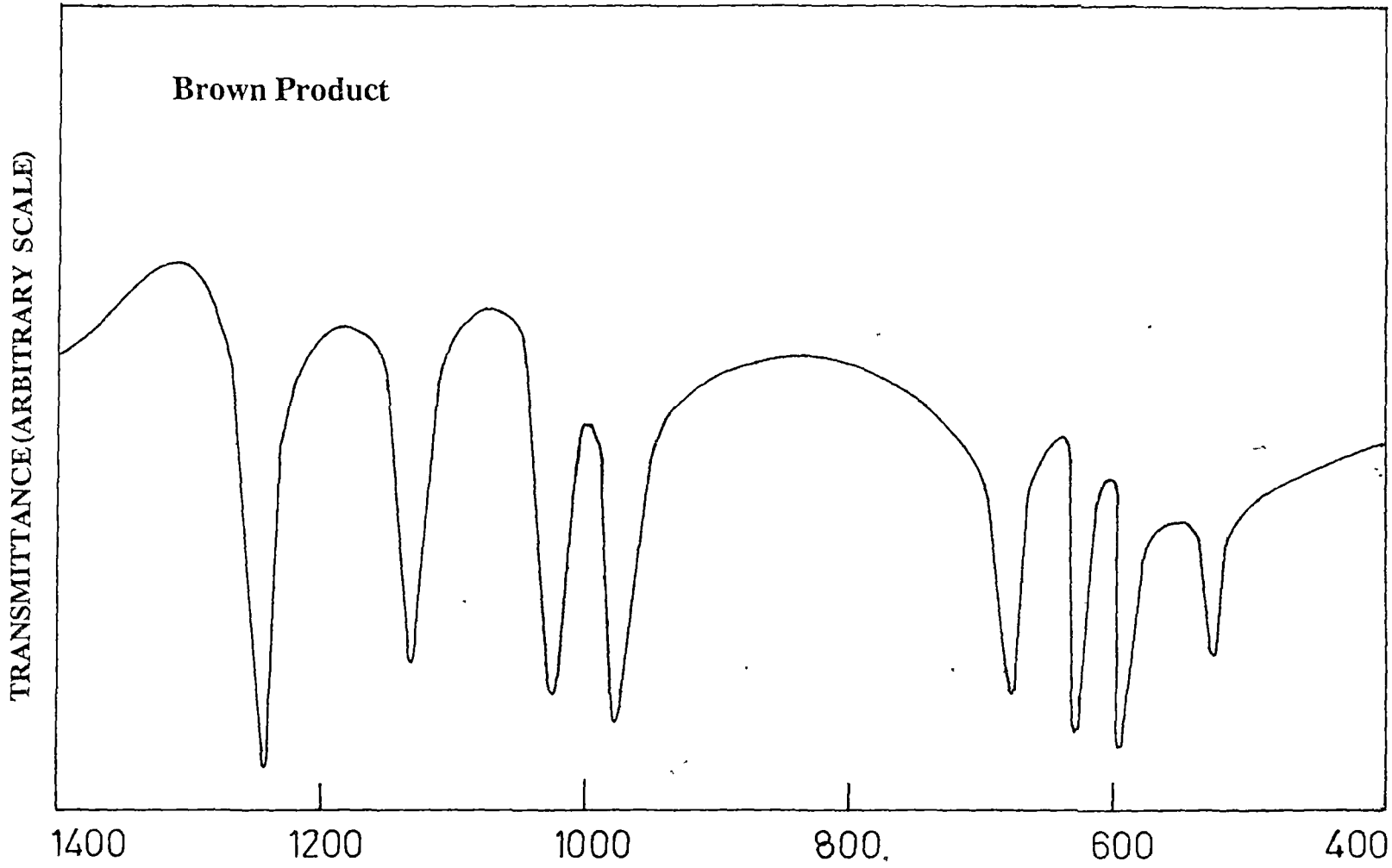

FIG. 3.1: IR SPECTRUM

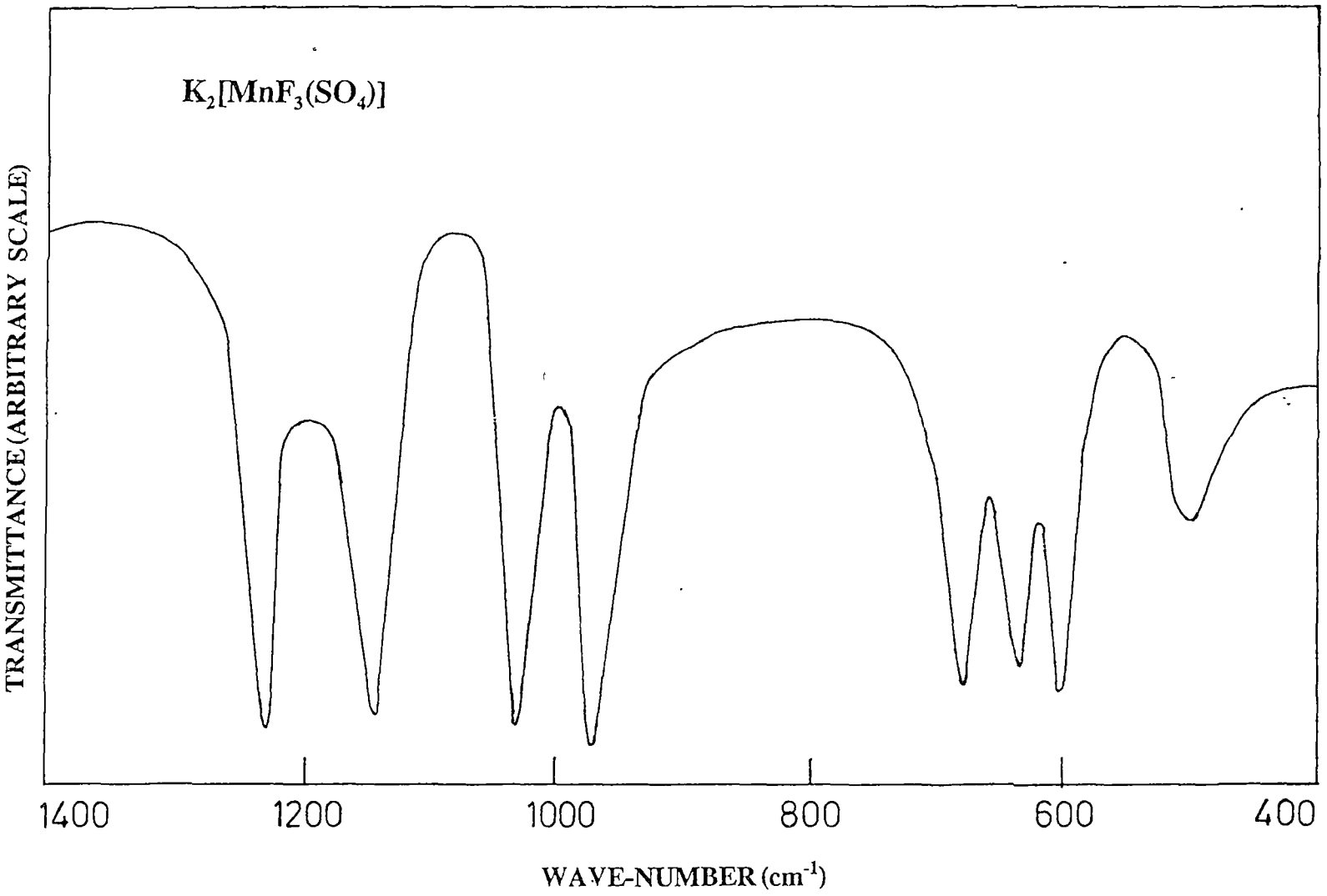

FIG. 3.2: IR SPECTRUM

sulphate group. The reflectance spectrum (Fig.3.3) exhibited three bands at 730, 550 and 462 nm, which have been attributed to $^5B_{1g} \longrightarrow {}^5A_{1g}$, $^5B_{1g} \longrightarrow {}^5B_{2g}$ and $^5B_{1g} \longrightarrow {}^5E_g$, transitions respectively. The observed spectral pattern indicates an appreciable splitting of the ^5E_g state, most probably as a consequence of Jahn-Teller effect. Based upon the empirical results, the compound was formulated as $K_2[MnF_3(SO_4)]$.

Incidentally, we have at our disposal dedicated methods[9] for the synthesis of $K_2[MnF_3(SO_4)]$ thus enabling a direct comparison. All the results obtained on the compound were similar to those obtained earlier,[9] which convincingly established its identity as $K_2[MnF_3(SO_4)]$.

$$KMnO_4 + 2SO_2.xH_2O + 3KHF_2 \longrightarrow K_2[MnF_3(SO_4)] + K_2SO_4 + 3HF + 2xH_2O$$

Rose-Pink product. ——— The compound that was obtained by conducting the $KMnO_4$ ——— $SO_2(g)$ reaction in the presence of a large excess of fluoride (Mn:F as 1:10) analysed positive for K^+, F^- and manganese(III) [as ascertained by redox titrimetry] only. No trace of sulphate was detected in it even spectroscopically. The atom ratio of K:Mn:F was determined to be 2:1:5 and the room temperature (300K) magnetic moment of the compound was found to be 3.2 μ_B, a value far less than that normally expected for a d^4

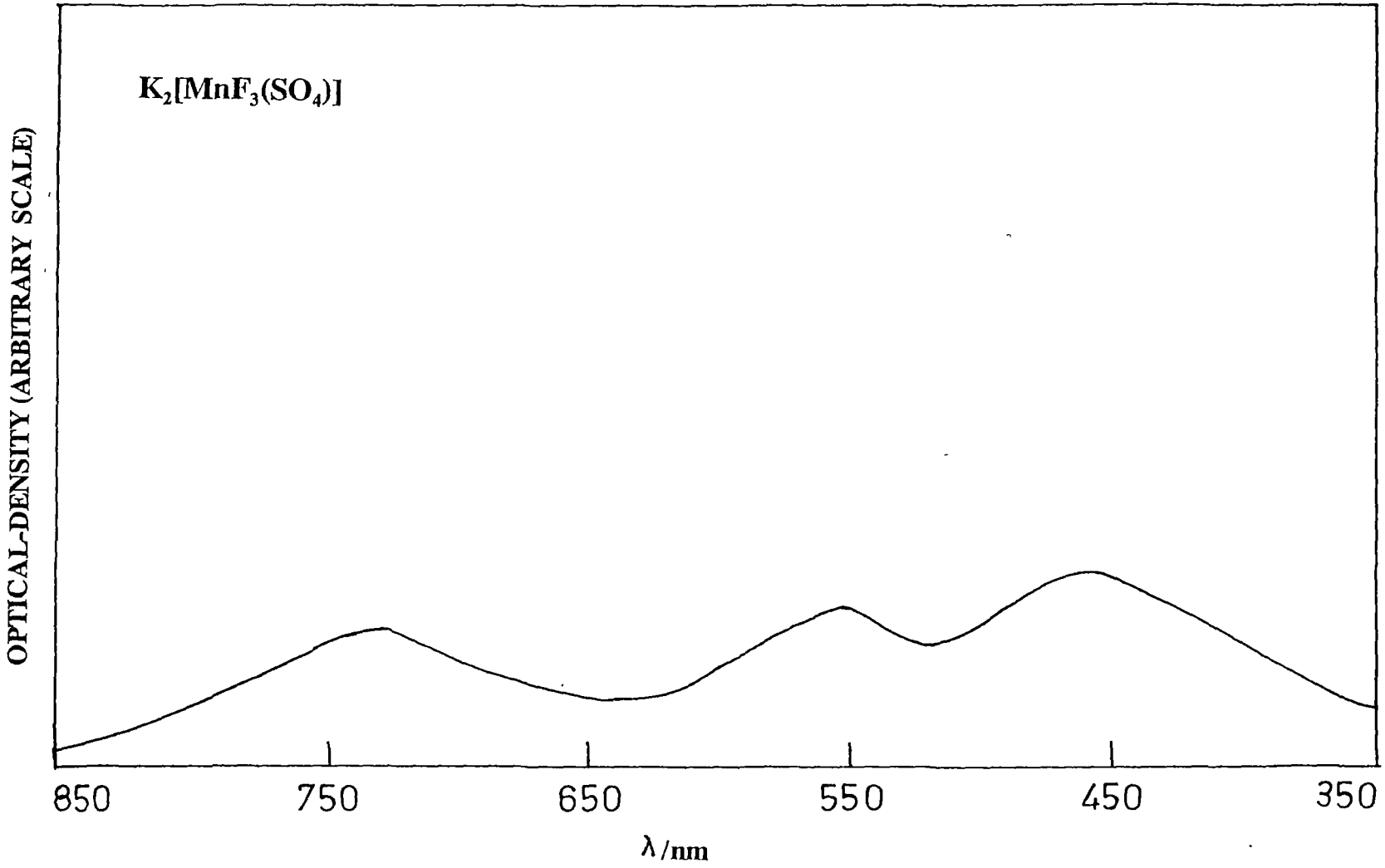

FIG. 3.3: DIFFUSE-REFLECTANCE SPECTRUM

system,presumably owing its origin to strong antiferromagnetic exchange interaction between the contiguous manganese(III) centres through -Mn-F-Mn-F- chains.

The compound was subjected to IR and Reflectance spectroscopic studies. Two bands bands observed in the IR spectrum (Fig.3.4) at *ca.* 615m and *ca.* 565s have been attributed to ν(Mn-F)ν_3 and ν(Mn-F)ν_4, respectively, implying the presence of distorted octahedral MF_6^{n-} environment.[13] The reflectance spectrum (Fig.3.5) exhibited three bands at *ca.*833, *ca.*540 and *ca.*476 nm, which have been assigned to the $^5B_{1g} \longrightarrow {}^5A_{1g}$, $^5B_{1g} \longrightarrow {}^5B_{2g}$ and $^5B_{1g} \longrightarrow {}^5E_g$, transitions, respectively. The results obtained are characteristic of potassium pentafluoromanganate(III) monohydrate, as reported by us[10,14] and others[2,15,16] therefore causing us to state that the rose-pink compound is $K_2[MnF_5].H_2O$.

$$KMnO_4 + 2SO_2.xH_2O + 5KHF_2 \longrightarrow K_2[MnF_5] + 2K_2SO_4 + 5HF + 2xH_2O$$

In situ methods for detecting reaction intermediates in the MnO_4^-/SO_2 redox reactions

In view of the above results there exists a finite possibility of manganese(III) being involved as an intermediate in the MnO_4^-/SO_2 redox process. But these results do not in themselves suffice to provide conclusive evidence. Therefore,

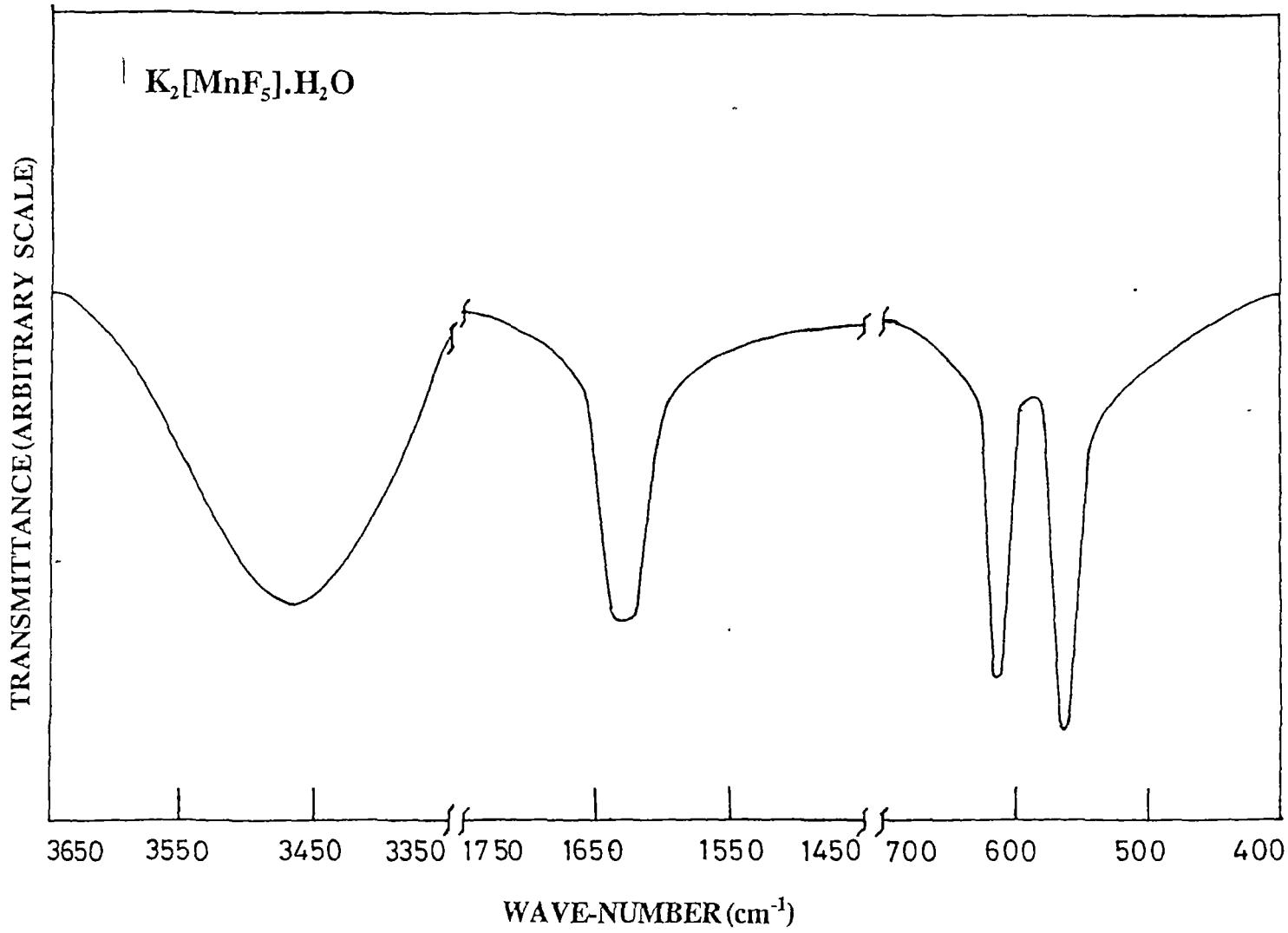

FIG. 3.4: IR SPECTRUM

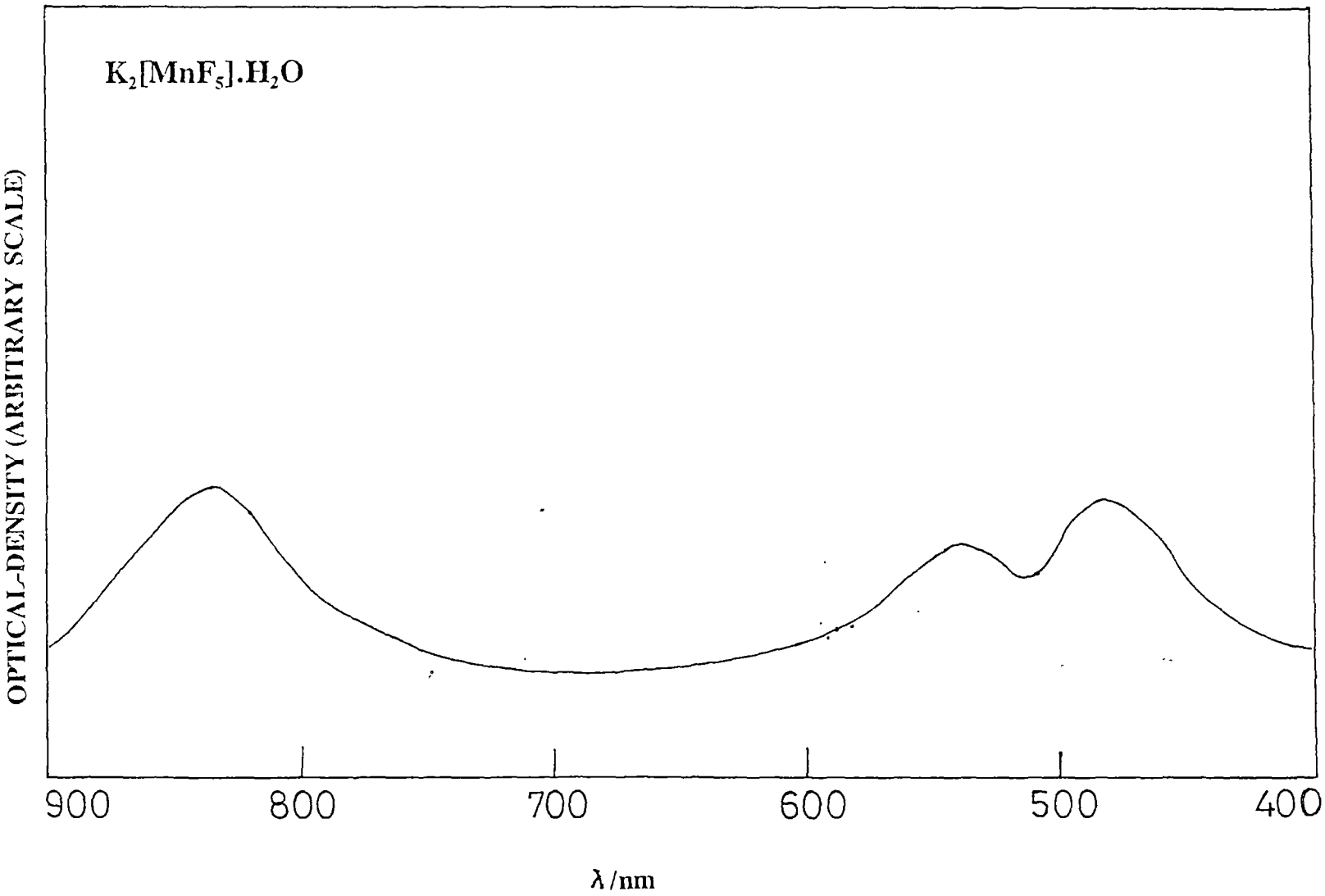

FIG. 3.5: DIFFUSE-REFLECTANCE SPECTRUM

further *in situ* experimentation for evidencing the occurrence of manganese(III) as the intermediate was called for. Thus, two different experiments viz. EPR and Electron absorption spectroscopies were conducted in solution.

The strength of the stock solution was maintained at 10^{-3}M with the molar stoichiometry of Mn:F as 1:4. The natural pH of the reaction solution was measured to be 5.5. The ESR spectra were recorded as a function of pH from the point of initiation of the reaction at every interval of pH of 0.2. The solution was ESR silent until a pH of 1.7. However, at this stage a characteristic six line spectrum typical of divalent manganese[17] was observed which persisted till pH 1.3, beyond which no scanning was made. The above results suggest that manganese(II) is not formed until the reaction pH is brought down to <2 by reacting with SO_2(g). The formation of manganese(III) at pH >2 is thus more likely.

In order to complement the results obtained from ESR experiments, electron absorption spectroscopic experiments were conducted. The electron absorption spectra (Fig.3.6) were recorded at pH values similar as those maintained for ESR experiments. As expected, the spectral pattern of the stock solution was similar to that of aqueous $KMnO_4$[18] with the charge-transfer bands appearing at *ca.*546, *ca.*526 and *ca.*311 nm. With the lowering in pH of the reaction solution with the bubbling of SO_2 through it,

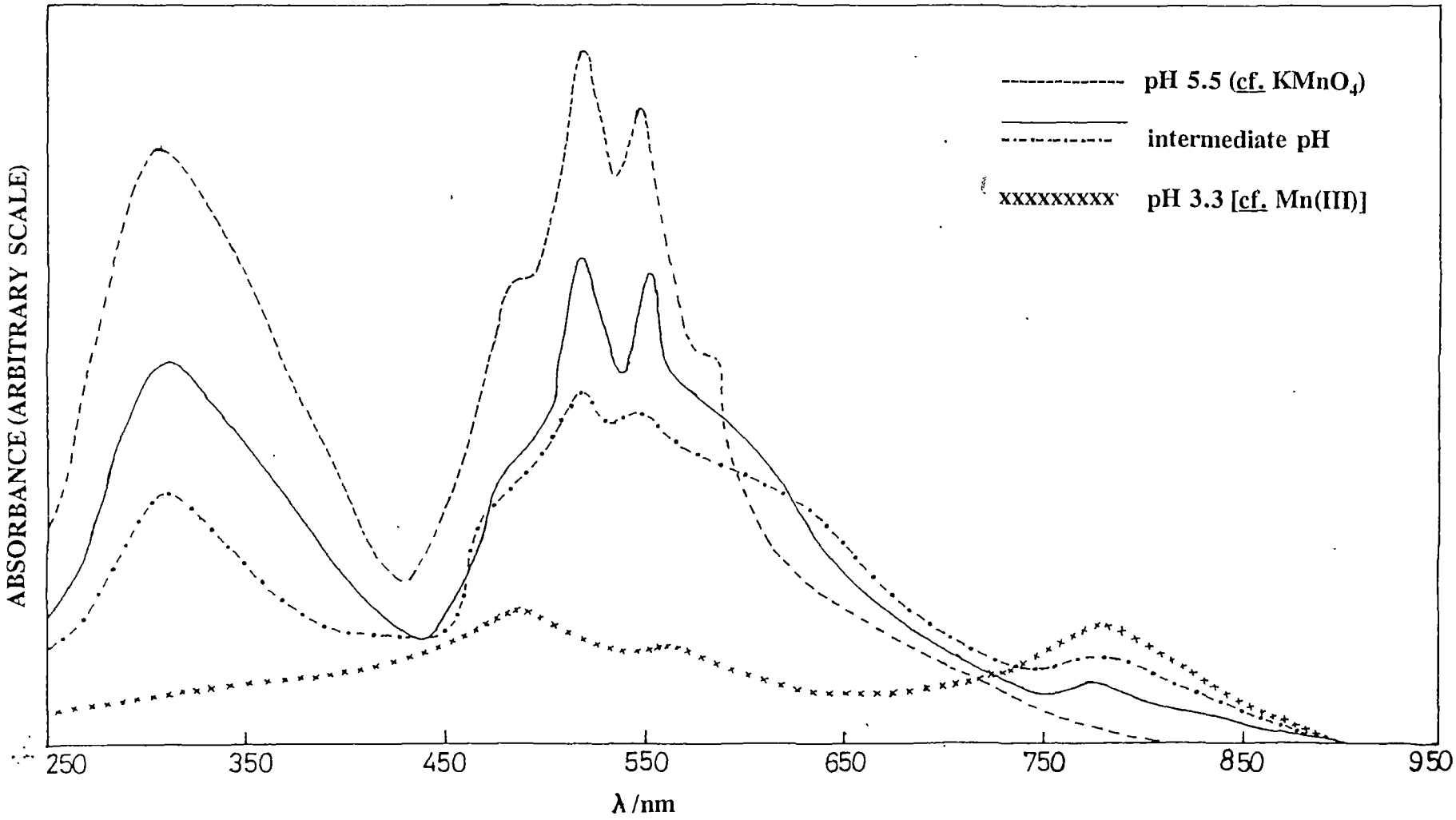

FIG. 3.6: ELECTRON ABSORPTION SPECTROSCOPY

(IN SITU EXPERIMENTS)

there was a gradual disappearance of the charge-transfer bands with the simultaneous appearance of newer bands at *ca.*775, *ca.*555 and *ca.*483 nm. The spectrum obtained at pH 3.3 showed absorptions only at 775, 555 and 483 nm. The observed spectral pattern is rather typical of manganese(III)[19] attributable to $^5B_{1g} \longrightarrow {}^5A_{1g}$, $^5B_{1g} \longrightarrow {}^5B_{2g}$ and $^5B_{1g} \longrightarrow {}^5E_g$, transitions, respectively. The spectral pattern remained unaltered till pH 2.1. However, on further passing of SO_2(g) through the solution led to lowering of pH of the reaction solution and the pattern that was observed till pH *ca.*2 disappeared, in fact, no absorption was apparent till pH 1.3 (the range covered in this experiment). This is in agreement with the formation of manganese(II) below pH *ca.*2, since a very dilute solution of it is not expected to exhibit any bands.[19]

Thus a combination of the results of EPR and electron absorption spectroscopic experiments provides strong evidence for the occurrence of manganese(III) intermediate in the MnO_4^-/SO_2 redox process.

Comments on the Reactions

It is thus evident that the $KMnO_4$——SO_2(g) reaction in the presence of F^- certainly involves tripositive level of manganese in the process under the present experimental conditions. There is a suggestion [in view of the "brown product" (!)] that the electron-transfer process involves a di- or multinuclear

manganese(III) species prior to the formation of $K_2[MnF_3(SO_4)]$ or $K_2[MnF_5].H_2O$. The nature of the brown product points to the deleterious effect of F^- ions on the formation of multinuclear manganese(III) complexes. Isolation of the other products in pure form implies that fluoride played a very important role, enabling the stabilization of Mn(III). That the product $K_2[MnF_5].H_2O$ instead of $K_2[MnF_3(SO_4)]$ resulted from the reaction carried out in a highly fluoridated medium suggests *interalia* that F^- is a better stabilizer for manganese(III), especially in an aqueous medium.

Probable Implications

The spontaneous separation of the metal as $K_2[MnF_3(SO_4)]$ and $K_2[MnF_5].H_2O$ from a fluoridated aqueous solution of its compound (*cf.* $KMnO_4$) may have a bearing upon the environmental pollution problem resulting from the current increase of SO_2 concentration in air. Probably the most important implications are: (i) that the results may provide a basis for developing manganese-based efficient system for fixation of atmospheric SO_2 and (ii) that there may be a necessity for adopting appropriate measures to compensate any depletion of the metal content in the fluoride containing water particularly of urban and/or industrial areas. A depletion of the desired Mn level is anticipated to cause ecological imbalance as the metal is an acknowledged bioessential trace element.

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CHAPTER IV

EFFECT OF FLUORIDE ON THE INTERACTION OF MANGANESE(III) WITH SALICYLIC ACID ($SalH_2$), 1,2-BIS(SALICYLIDENEIMINATO)-ETHANE ($SalenH_2$) AND N,N'-(ACETYL-ACETONATO)ETHYLENEDIAMINE ($AcacenH_2$) IN AN AQUEOUS MEDIUM ———— A SYNTHETIC STUDY

The importance of and interest in the manganese(III) chemistry has already been highlighted in Chapter I. The tripositive state of manganese is considered to be one of the unusual oxidation states of the metal. This is attributed mainly to the instability of manganese(III) in aqueous solution[1] and also

because many of its complexes demonstrate unusual magnetic and structural features.[2-6] In recent years, the efforts have been directed mainly towards developing potential models[7] for describing metallocentres in manganese containing biomolecules, particularly for enzymes involved in the oxidation of peroxide to dioxygen in dimanganese catalases[8] and the oxidation of water to dioxygen in the oxygen evolving center (OEC) of photosystem-II (PS-II),[9] while the usual interest on manganese(III) reagents as one electron oxidants never diminishes. A number of reports concerning multinuclear manganese systems involving a variety of oxygen and mixed nitrogen, oxygen (N,O) donor ligands like salicylate,[7,10-12] benzoate,[3,11] pyridine,[10,11] $OPPh_3$,[7] Schiff bases,[13] etc. have henceforth resulted in the recent past. It is important to note that while Cl^- ions are essential for the activity of PS-II,[7] F^- ions unfortunately inhibits its activity most probably by preventing di- or multinuclear complex formation. It was therefore considered worthwhile to study the effect of F^- on the interaction of Mn(III) with biochemically relevant ligands. Incidentally, there have not been many reports on fluoro complexes of manganese(III) with such ligands, even otherwise.

It may not be out of place to mention that there has been an ongoing programme in our laboratory[14] on fluoro chemistry of metals and non-metals. As a part of the programme, we had addressed earlier to fluoro and mixed-fluoro

manganates(III)[5,15-18] with the coligands being SO_4^{2-}, $C_2O_4^{2-}$, urea, bpy, phen, HPO_4^{2-} and Gly^{2-}.

For the present work, attention has been drawn towards $SalH_2$, $SalenH_2$ and $AcacenH_2$ as the coligands. Some of the reasons for this selection are as follows: Salicylic acid belongs to the class of hydroxy acids, which in general are known to stabilize and solubilize Mn(III) ions. It is worth mentioning here that amongst the various hydroxy ligands, the complexes of manganese(III) with catechol are reported[19] to be the most stable, whereas the corresponding salicylato complexes are relatively much weaker. Besides, salicylic acid, itself, in particular,[20] is well known for its medical applications viz. as an antipyretic and in the treatment of certain types of rheumatism. It is believed that the biological action[21] of this compound is connected with its ability to form complexes with metal ions. Owing to the pronounced stabilizing effect of F^- on manganese(III), it was conjectured that the presence of F^- might assist in bringing about stability to the manganese(III)-salicylato complexes in aqueous solution, wherein however, the possibility of formation of multinuclear complexes is very remote. In addition to $salH_2$, the other ligands $salenH_2$ and $acacenH_2$ belong to the Schiff base family. It was observed that manganese(III) complexes with schiff bases[22,23] evolve oxygen upon irradiation in the presence of p-benzoquinone.

Relevant to note here is that so far majority of the reports[7,10-13,22,23] concerning manganese(III) complexes with the said ligands are either di- or multinuclear ones with most of them being synthesized from non-aqueous medium.

In view of the above, our principal aim crystallized to investigate the interaction of manganese(III) with $SalH_2$, $SalenH_2$ and $AcacenH_2$ in the presence of F^- in an aqueous medium. The elicit strategy was to conduct the reactions amongst Mn(III), F^- and the chosen coligands under a variety of experimental conditions, isolate and characterize the products formed and then comment on the reactions and their implication.

Experimental

All the chemicals used were of reagent grade quality (B.D.H, SISCO chemicals, S.d-Fine chem., Qualigens Fine Chemicals, E.Merck(India) Ltd.). The details of the instruments equipment used for the characterization of the products are given in Chapter II.

I Reactions of MnO(OH) with Salicylic Acid in the Presence of F^-

(a) *Isolation of* $A_2[MnF_4(salH)]$, (A = K, Na or NH_4)

An amount of (0.89g, 10.11 mmol) freshly prepared MnO(OH) was added to an aqueous solution (10 cm^3) of 20.23 mmol of

AHF_2 maintaining the ratio of Mn:F at 1:4. This was followed by the addition of an ethanolic solution (20 cm^3) of (8.0g, 57.92 mmol) salicylic acid and the whole was then stirred for a period of *ca.* 30 min. at room temperature whereupon a green compound separated out. The compound on filtration and washing two or three times with acetone was identified to be $A_2[MnF_4(salH)]$, (A = K, Na or NH_4). The yields of $K_2[MnF_4(salH)]$, $Na_2[MnF_4(salH)]$ and $(NH_4)_2[MnF_4(salH)]$ were 2.5g (71.5%), 2.2g (69%) and 2.2g (71.4%), respectively.

(b) *Isolation of* $A[MnF_4(H_2O)_2].H_2O$ *and* $A_2[MnF_5].nH_2O$ (A = K, n=1; A = Na or NH_4, n=0)

Freshly prepared MnO(OH) (0.89g, 10.11 mmol) was reacted with an aqueous solution (10 cm^3) of 60.68 mmol of AHF_2 in the presence of ethanolic solution (20 cm^3) of 57.92 mmol of salicylic acid. The resultant reaction mixture upon stirring for *ca.* 30 min. at room temperature afforded $A[MnF_4(H_2O)_2].H_2O$ (A = K, Na or NH_4). However, on using similar concentrations of MnO(OH) and salicylic acid in the presence of a much higher concentration of F^- *ca.* 121.32 mmol of AHF_2, rose-pink $A_2[MnF_5].nH_2O$ (A = K, n=1; A = Na or NH_4, n=0) were isolated.

II Control Reactions

Reactions of MnO(OH) with F^- in the absence of salicylic acid

(a) *Isolation of* $A[MnF_4(H_2O)_2]$.(A = K, Na or NH_4)

Freshly prepared MnO(OH) (0.89g, 10.11 mmol) was added to an aqueous solution (20 cm^3) of 40.46 mmol of AHF_2. The reaction mixture was then stirred at room temperature for *ca.*30 min., wherein a brown compound separated out. The compound on isolation was analysed as $A[MnF_4(H_2O)_2]$.(A = K, Na or NH_4).

(b) *Isolation of* $A_2[MnF_5].nH_2O$ (A = K, n=1; A = Na or NH_4, n=0)

The reaction of freshly prepared MnO(OH) (0.89g, 10.11 mmol) with an aqueous solution (20 cm^3) of *ca.* 60.68 mmol of AHF_2 in the absence of salicylic acid, upon stirring at room temperature for *ca.* 30 min. afforded rose-pink $A_2[MnF_5].nH_2O$ (A = K, n=1; A = Na or NH_4, n=0).

III Reactions of $K_2[MnF_4(salH)]$ with F^-

An amount of (1.0g, 2.89 mmol) of $K_2[MnF_4(salH)]$ was reacted separately with aqueous solutions (20 cm^3) of 40.46 mmol and 113.37 mmol of KHF_2. The resultant reaction mixtures were stirred at room temperature for *ca.* 1.5h. No visible change could be observed during the entire time

period. The green $K_2[MnF_4(salH)]$ was recovered unchanged at the end of 1.5h.

IV Reactions of MnO(OH) with $SalenH_2$ and $AcacenH_2$ in the Presence of F^- and Isolation of $enH[MnF_4]$

MnO(OH) (0.89g, 10.11 mmol) was dissolved in (6.0 cm^3, 144 mmol) of 48% HF and stirred for *ca.* 10 min. To the resultant mixture, ethanolic solution (20 cm^3) of 20.22 mmol of $salenH_2$ or $acacenH_2$ was added and the whole was stirred for *ca.* 30 min. at room temperature, whereupon a brown compound precipitated out. The compound was isolated by filtration, washed twice with acetone and finally dried *in vacuo.* The yield of $enH[MnF_4]$ was (1.5g, 77%).

V Preparation of $A[MnF_4(H_2O)]$ (A = Rb or Cs) by Metathesis Reactions

To a suspension of (1.0g, 5.21 mmol) of $enH[MnF_4]$ in dilute HF solutions, aqueous solutions (5 cm^3) of Rb_2CO_3 (0.9g, 3.9 mmol) or $CsNO_3$ (1.52g, 7.8 mmol) was added separately with stirring. The stirring was continued for a period of another 5 min., whereupon solid $Rb[MnF_4(H_2O)]$ and $Cs[MnF_4(H_2O)]$ precipitated out. The products were separated by filtration, washed twice with acetone and finally dried *in vacuo.* over conc.H_2SO_4.

Elemental analyses and Chemical determination of oxidation state of manganese

Quantitative determinations of manganese, fluoride, carbon, nitrogen, hydrogen, potassium, sodium, rubidium and caesium contents as well as the chemical determination of oxidation state of manganese were made by the methods/procedure described in Chapter II.

The analytical and characterization data of the products are set out in Tables 4.1-4.7.

Results and Discussion

It has been observed that aqueous acidic conditions[10] are detrimental to the synthesis of manganese(III) complexes with biochemically relevant ligands. This can be accounted for by the following reasons: (i) excessive ligand protonation at low pH and (ii) instability of the products owing to hydrolysis. Hence, non-aqueous conditions were generally used by various other groups for the synthesis of a variety of Mn(III) complexes with such ligands. Notable among the ligands used were salicylate,[10-12] pyridine,[10] picolinic acid,[10] and Schiff bases,[7,13] etc.

Salicylic acid which is a very convenient substitute for tyrosine and phenoxide types of ligation, is a very widely used

Table 4.1:Analytical Data, Solution Electrical Conductance and Magnetic Moment Values of $A_2[MnF_4(salH)]$ (A = K, Na or NH_4)

Compound	Conductance ($\Omega^{-1}cm^2mol^{-1}$)	μ_B (BM)	Element	Found (%)	Calcd. (%)
$K_2[MnF_4(salH)]$	196	4.5	Mn	15.45	15.87
			F	20.8	21.95
			C	24.76	24.28
			H	1.62	1.46
			K	22.18	22.58
$Na_2[MnF_4(salH)]$	204	4.58	Mn	17.61	17.49
			F	24.31	24.20
			C	26.58	26.77
			H	1.81	1.61
			Na	14.25	14.64
$(NH_4)_2[MnF_4(salH)]$	206	4.6	Mn	18.76	18.06
			F	24.55	24.99
			C	27.83	27.64
			H	4.56	4.32
			N	9.11	9.21

$salH^-$ = salicylate ($C_7H_5O_3^-$).

Table 4.2: Analytical Data of $A[MnF_4(H_2O)_2].H_2O$, $A[MnF_4(H_2O)_2]$ and $A_2[MnF_5].nH_2O$, (A = K, Na or NH_4)

Compound	Element	Found (%)	Calcd. (%)
$K[MnF_4(H_2O)_2].H_2O$	Mn	23.83	24.52
	F	32.97	33.91
	H	2.61	2.70
	K	17.14	17.45
$Na[MnF_4(H_2O)_2].H_2O$	Mn	27.02	26.41
	F	37.14	36.54
	H	2.73	2.91
	Na	11.29	11.05
$NH_4[MnF_4(H_2O)_2].H_2O$	Mn	27.56	27.06
	F	37.88	37.43
	H	4.93	4.97
	N	6.78	6.90
$K[MnF_4(H_2O)_2]$	Mn	25.17	26.66
	F	37.33	36.88
	H	1.88	1.96
	K	18.58	18.97

Table 4.2 contd.

Compound	Element	Found (%)	Calcd. (%)
$Na[MnF_4(H_2O)_2]$	Mn	28.46	28.92
	F	39.79	40.01
	H	2.34	2.13
	Na	19.8	12.10
$NH_4[MnF_4(H_2O)_2]$	Mn	29.24	29.69
	F	40.77	41.07
	H	4.61	4.37
	N	7.42	7.57
$K_2[MnF_5].H_2O$	Mn	21.84	22.32
	F	38.62	38.59
	K	32.77	31.77
$Na_2[MnF_5]$	Mn	28.26	28.04
	F	49.11	48.49
	Na	23.76	23.47
$(NH_4)_2[MnF_5]$	Mn	30.25	29.53
	F	50.73	51.06
	H	4.54	4.34
	N	15.61	15.06

Table 4.3:Analytical Data and Magnetic Moment Values of enH[MnF_4], $Rb[MnF_4(H_2O)$ and $Cs[MnF_4(H_2O)$

Compound	μ_B (BM)	Element	Found (%)	Calcd. (%)
enH[MnF_4]	4.2	Mn	28.16	28.60
		F	40.17	39.57
		C	12.63	12.51
		H	4.58	4.73
		N	13.93	14.59
$Rb[MnF_4(H_2O)]$	4.8	Mn	24.16	23.44
		F	33.58	32.42
		Rb	36.68	36.46
$Cs[MnF_4(H_2O)]$	4.85	Mn	20.23	19.49
		F	26.52	26.96
		Cs	47.61	47.15

enH = protonated ethylenediamine ($C_2N_2H_9^+$).

Table 4.4: IR and LR Spectral Data of $A_2[MnF_4(salH)]$ (A = K, Na or NH_4) with their Assignments

Compound	IR (cm^{-1})	LR (cm^{-1})	Assignment
$K_2[MnF_4(salH)]$	1603s	1597m	$\nu_{as}(COO^-)$
	1383s	1315s	$\nu_s(COO^-)$
	1231m	1237m	δ(O-H)
	474m		ν(Mn-F)
	373m		ν(Mn-O)
	3256s		ν(O-H)
$Na_2[MnF_4(salH)]$	1606s	1600m	$\nu_{as}(COO^-)$
	1383s	1320s	$\nu_s(COO^-)$
	1230m	1235m	δ(O-H)
	468m		ν(Mn-F)
	364m		ν(Mn-O)
	3244s		ν(O-H)

Table 4.4 contd.

Compound	IR (cm^{-1})	LR (cm^{-1})	Assignment
$(NH_4)_2[MnF_4(salH)]$	1604s	1595m	$\nu_{as}(COO^-)$
	1381s	1325s	$\nu_s(COO^-)$
	1237m	1230m	δ(O-H)
	468m		ν(Mn-F)
	374m		ν(Mn-O)
	3243s		ν(O-H)
	1444s		ν(N-H)ν_4
	3039s		ν(N-H)ν_1
	3079m		ν(N-H)ν_3

Table 4.5 Electron Absorption Spectral Data of $A_2[MnF_4(salH)]$ (A = K, Na or NH_4) with their Assignments

Compound	UV-VIS λ_{nm}	ε ($Lmol^{-1}cm^{-1}$)	Assignment
$K_2[MnF_4(salH)]$	590	74	$^5B_{1g} \longrightarrow {}^5B_{2g}$
	510	75	$^5B_{1g} \longrightarrow {}^5E_g$
	290	8700	C T band
$Na_2[MnF_4(salH)]$	590	80	$^5B_{1g} \longrightarrow {}^5B_{2g}$
	510	85	$^5B_{1g} \longrightarrow {}^5E_g$
	290	9500	C T band
$(NH_4)_2[MnF_4(salH)]$	590	76	$^5B_{1g} \longrightarrow {}^5B_{2g}$
	510	75	$^5B_{1g} \longrightarrow {}^5E_g$
	290	10300	C T band

Table 4.6: IR Spectral Data of $A[MnF_4(H_2O)_2].H_2O$ and $A[MnF_4(H_2O)_2]$ (A = K, Na or NH_4) with their Assignments

Compound	IR (cm^{-1})	Assignment
$K[MnF_4(H_2O)_2].H_2O$	590m	$\nu(Mn-F)\nu_3$
	560s	$\nu(Mn-F)\nu_4$
	735m	$\rho_r(H_2O)$
	1665m	$\delta(H-O-H)$
	3450s	$\nu(O-H)$
$Na[MnF_4(H_2O)_2].H_2O$	550s	$\nu(Mn-F)\nu_4$
	588m	$\nu(Mn-F)\nu_3$
	730m	$\rho_r(H_2O)$
	1660m	$\delta(H-O-H)$
	3440s	$\nu(O-H)$
$NH_4[MnF_4(H_2O)_2].H_2O$	540s	$\nu(Mn-F)\nu_4$
	580m	$\nu(Mn-F)\nu_3$
	760m	$\rho_r(H_2O)$
	1650m	$\delta(H-O-H)$
	3450s	$\nu(O-H)$
	1400s	$\nu(N-H)\nu_4$
	3065s	$\nu(N-H)\nu_1$
	3142m	$\nu(N-H)\nu_3$

Table 4.6 contd.

Compound	IR (cm^{-1})	Assignment
$K[MnF_4(H_2O)_2]$	585m	$\nu(Mn-F)\nu_3$
	560s	$\nu(Mn-F)\nu_4$
	740m	$\rho_r(H_2O)$
	1660m	$\delta(H-O-H)$
	3442s	$\nu(O-H)$
$Na[MnF_4(H_2O)_2]$	555s	$\nu(Mn-F)\nu_4$
	590m	$\nu(Mn-F)\nu_3$
	735m	$\rho_r(H_2O)$
	1665m	$\delta(H-O-H)$
	3440s	$\nu(O-H)$
$NH_4[MnF_4(H_2O)_2]$	525s	$\nu(Mn-F)\nu_4$
	586m	$\nu(Mn-F)\nu_3$
	769m	$\rho_r(H_2O)$
	1665m	$\delta(H-O-H)$
	3449s	$\nu(O-H)$
	1405s	$\nu(N-H)\nu_4$
	3055s	$\nu(N-H)\nu_1$
	3126m	$\nu(N-H)\nu_3$

Table 4.6 contd.

Compound	IR (cm^{-1})	Assignment
$(NH_4)_2[MnF_5]$	614m	$\nu(Mn-F)\nu_3$
	564s	$\nu(Mn-F)\nu_4$
	3040s	$\nu(N-H)\nu_1$
	3157m	$\nu(N-H)\nu_3$
	1400s	$\nu(N-H)\nu_4$
$Na_2[MnF_5]$	615m	$\nu(Mn-F)\nu_3$
	565s	$\nu(Mn-F)\nu_4$

Table 4.7: IR Spectral Data of $enH[MnF_4]$ and $Rb[MnF_4(H_2O)]$ $Cs[MnF_4(H_2O)]$ with their assignments

Compound	IR (cm^{-1})	Assignment
$enH[MnF_4]$	1007m, 1040m, 1110w	ν(C-C)
	1330w, 1350w	$\phi_r(NH_3^+)$
	1510m, 1570m	$\delta(CH_2)$
	1600m	$\delta(NH_2)$
	578s	ν(Mn-F)
	625m	ν(Mn-F)
$Rb[MnF_4(H_2O)]$	530s	ν(Mn-F)
	600m	ν(Mn-F)
	740m	$\rho_r(H_2O)$
	1640m	δ(H-O-H)
	3460s	ν(O-H)
$Cs[MnF_4(H_2O)]$	535s	ν(Mn-F)
	600m	ν(Mn-F)
	735m	$\rho_r(H_2O)$
	1630m	δ(H-O-H)
	3450s	ν(O-H)

ligand as far as complexation with Mn(III) is concerned. Most of the earlier reports[10-12] dealt with the synthesis of mixed-ligand salicylato complexes of manganese(III) (generally di- or multi-nuclear) from non-aqueous medium and their study[7,10-12] as potential models for the water oxidizing complex.

In the context of some polarographic studies[19] conducted earlier on aromatic hydroxy ligands as regards complexation with Mn(III), it was observed that the ability of the ligands to stabilize the manganese(III) ion decreases in the order ditertiarybutylcatechol (DTBC) > 4,5-dihydroxynaphthalene-2,7-disulfonate (DHNDSA), catechol > dihydroxybenzoic acid > Tiron > salicylate. This clearly shows that the manganese(III)-salicylato complexes are the relatively more unstable ones as compared with the corresponding catecholate or substituted catecholate complexes, thereby indicating that two adjacent aromatic hydroxyl groups bind manganese(III) more effectively than adjacent aromatic hydroxyl and carboxyl groups. Thus, it is also evident that salicylate alone is not very efficient in stabilizing the manganese(III) ion.

It was hence conjectured that the presence of F^- would enhance the stability of manganese(III)-salicylato system and might as well permit isolation in the solid state. In accord with this Mn(OH) was reacted with AHF_2 (A = K, Na or NH_4) and an

ethanolic solution of salicylic acid at pH 4 which finally afforded novel mixed-fluoro(salicylato)manganates(III) $A_2[MnF_4(salH)]$, (A = K, Na or NH_4). The alkali hydrofluoride is believed to have played two roles. Firstly, it functioned as a fluorinating agent and secondly it also acted as a buffer and thereby preventing hydrolysis. These in conjunction with the pronounced tendency of F^- to form stable fluoromanganates(III) at low pH must have been responsible for the success.

Characterization and Identity of the Products

The mixed-fluoro(salicylato) complexes $A_2[MnF_4(salH)]$, (A = K, Na or NH_4) are green in colour and stable for prolonged periods in the absence of air. It is very important to note here that a large number of fluoro-manganese(III) complexes are known to be insoluble in most of the commonly used organic solvents (in water most of them decompose, anyway). But the newly synthesized mixed-ligand complexes are, to the contrary, soluble in some such solvents. One such solvent is methanol. All the solution studies have hence been carried out in this solvent. The solution electrical conductances of 10^{-3}M solutions of $A_2[MnF_4(salH)]$, (A = K, Na or NH_4) in methanol recorded values in the range 210-220 $\Omega^{-1}cm^2mol^{-1}$ conforming to their 1:2 electrolytic nature in full accord with the assigned formula. Further, the unaltered solution

conductivities over a period of two or three days attests to their stability in methanol under the present experimental conditions.

In view of the anamolous magnetic behaviour of many manganese(III) complexes, the chemical determination of oxidation state of manganese was extremely important. The iodometrically estimated oxidation level of the metal in $A_2[MnF_4(salH)]$, (A = K, Na or NH_4) was found to be +3. The ambient temperature (300K) magnetic moments of the complexes were found to lie in the range of 4.5 - 4.6 BM. This somewhat lowering in the magnetic moment values as compared to that of 4.9 BM expected for an ideal d^4 system may be attributed to weak antiferromagnetic exchange interactions between the contiguous manganese atoms and the complexes may have a polymeric structure through -Mn-F-Mn-F- interactions. This kind of a situation though not common for mixed-fluormanganates(III), has been observed earlier in the cases of $[MnF_3(SO_4)]^{2-}$,[16] $[MnF_3(C_2O_4)]^{2-}$,[17] and $[MnF_3(urea)_2]$.[18] These interactions are however, more pronounced in binary fluoromanganates(III) for eg. $[MnF_5]^{2-}$.[5]

In order to probe into the homogeneity as well as the crystallinity of the products obtained by the newer synthetic methodology, they were subjected to Scanning Electron Microscopy (SEM). The results of the SEM experiments (Fig.4.1) conducted on $K_2[MnF_4(salH)]$, taken as a representative example, give evidence

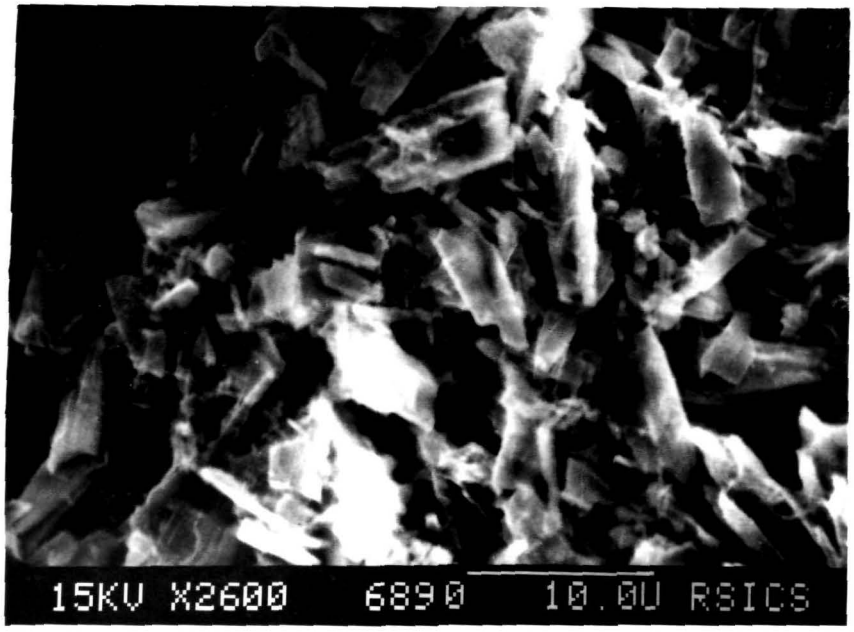

FIG. 4.1: SE MICROGRAPH OF $K_2[MnF_4(salH)]$

for the mixed-fluoro(salicylato)manganates(III) to be composed of an accumlation of highly crystalline rod shaped units with the average dimension of the crystal being *ca.* 10μ.

The electron absorption spectra (Figs.4.2-4.4) of freshly prepared solutions of $A_2[MnF_4(salH)]$, (A = K, Na or NH_4) in methanol exhibited bands at *ca.* 600 , *ca.* 510 and *ca.* 290 nm (ε = 9000 $Lmol^{-1}cm^{-1}$). While the the weaker absorptions are assigned to the $^5B_{1g} \longrightarrow {}^5B_{2g}$ and $^5B_{1g} \longrightarrow {}^5E_g$ transitions, respectively, the stronger one is attributed to the salH to manganese, LMCT transition. The absence of a low energy band (*cf.* $^5B_{1g} \longrightarrow {}^5A_{1g}$) at *ca.* 800 nm, may be due to the complexes not being distorted to the extent needed to produce it. This kind of a situation though not very common, is certainly not unprecedented.[24] The observed spectral pattern, however, lends support to the distorted octahedral structure of the complexes.

IR spectroscopy has been a very powerful tool for the characterization of metal salicylates, particularly to decipher the various modes of coordination of salicylato ligand. The interpretation of the IR spectra of such compounds is generally based[25,26] upon the extensive information available on the IR spectra of carboxylic acids and alcohols.

The IR spectra (Figs.4.5-4.7) of the complexes $A_2[MnF_4(salH)]$, (A = K, Na or NH_4) displayed a pattern typical of coordinated salicylate and coordinated fluoride. The $\nu_{as}(COO^-)$ and

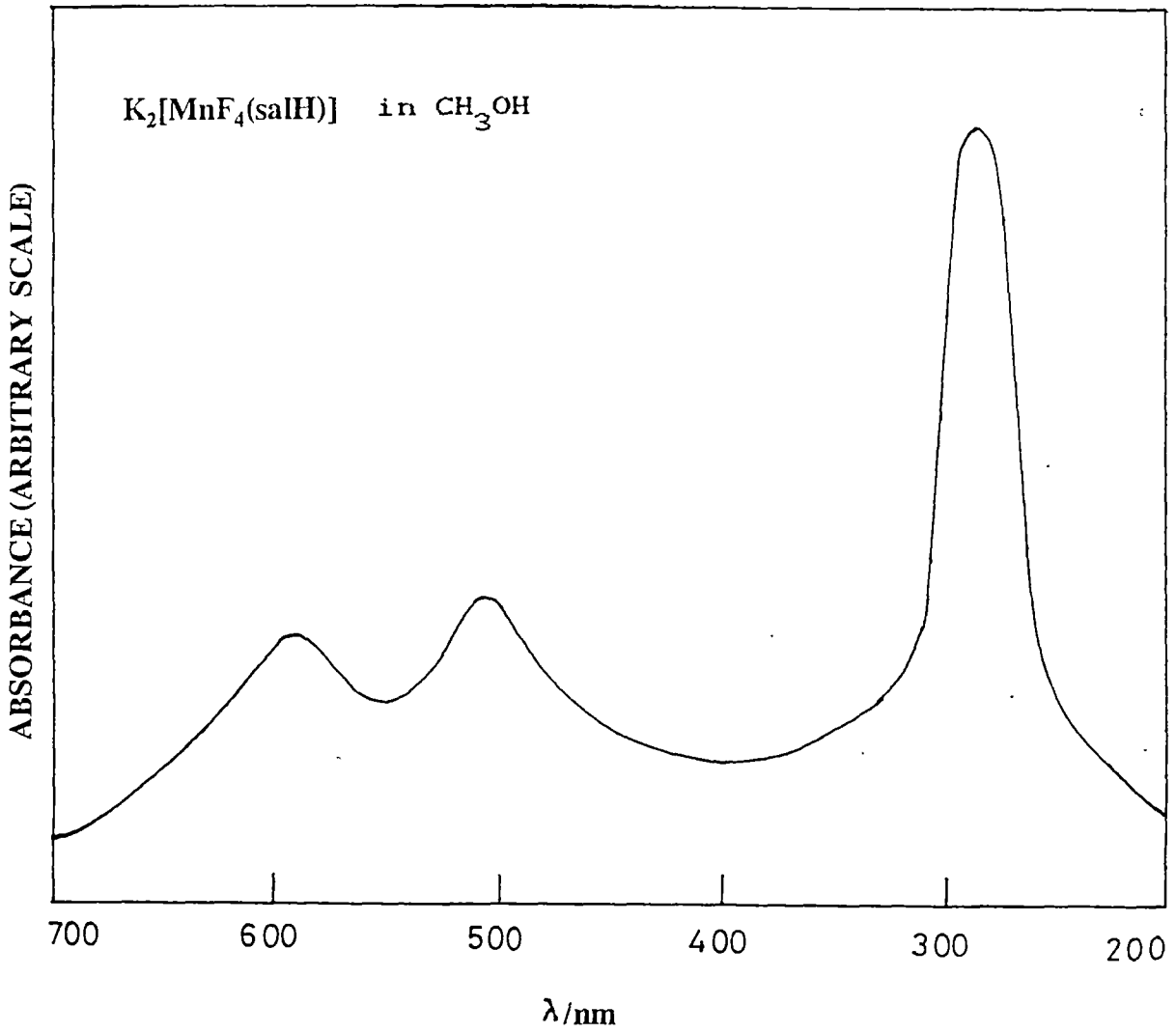

FIG. 4.2: ELECTRON ABSORPTION SPECTRUM

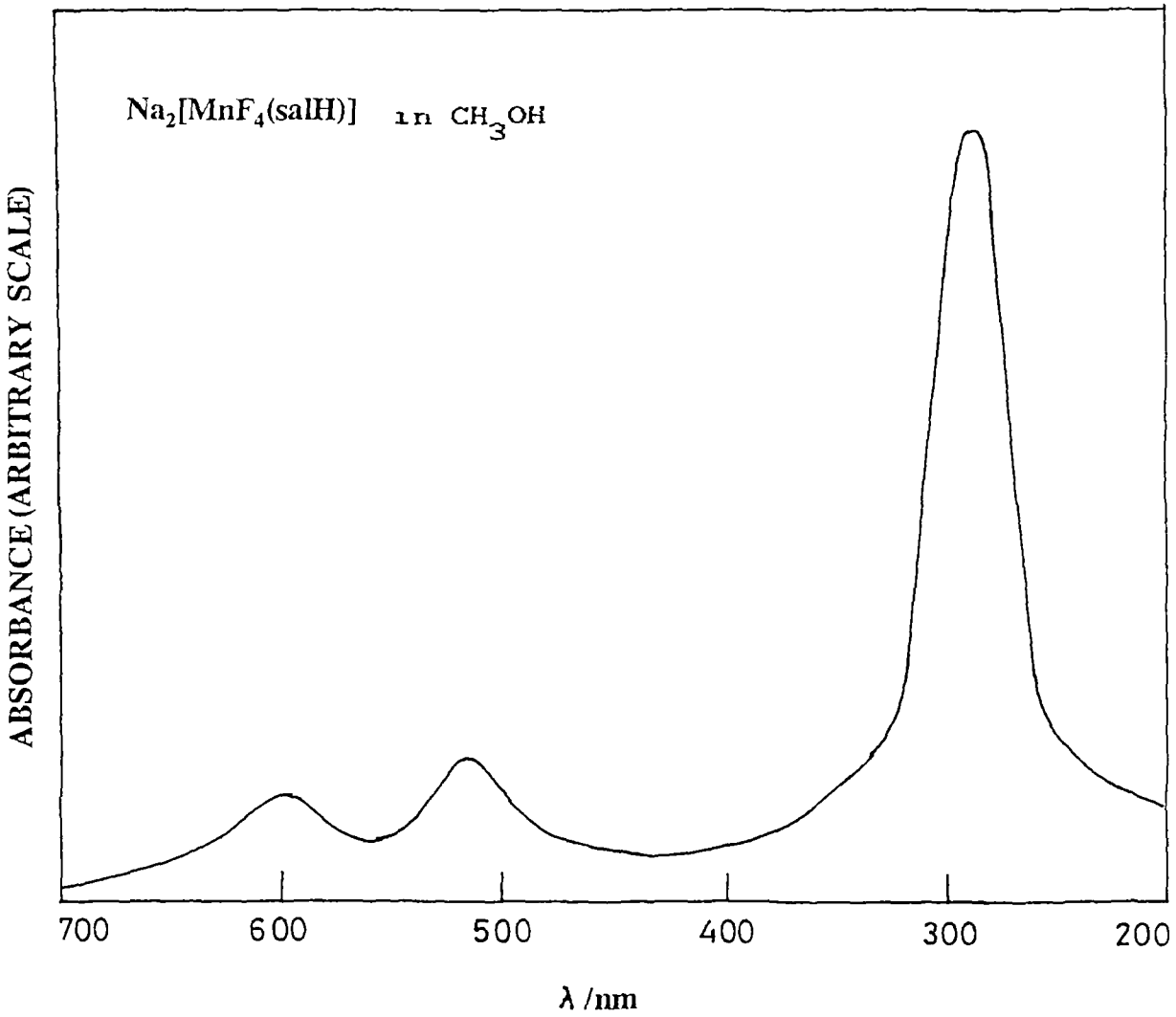

FIG. 4.3: ELECTRON ABSORPTION SPECTRUM

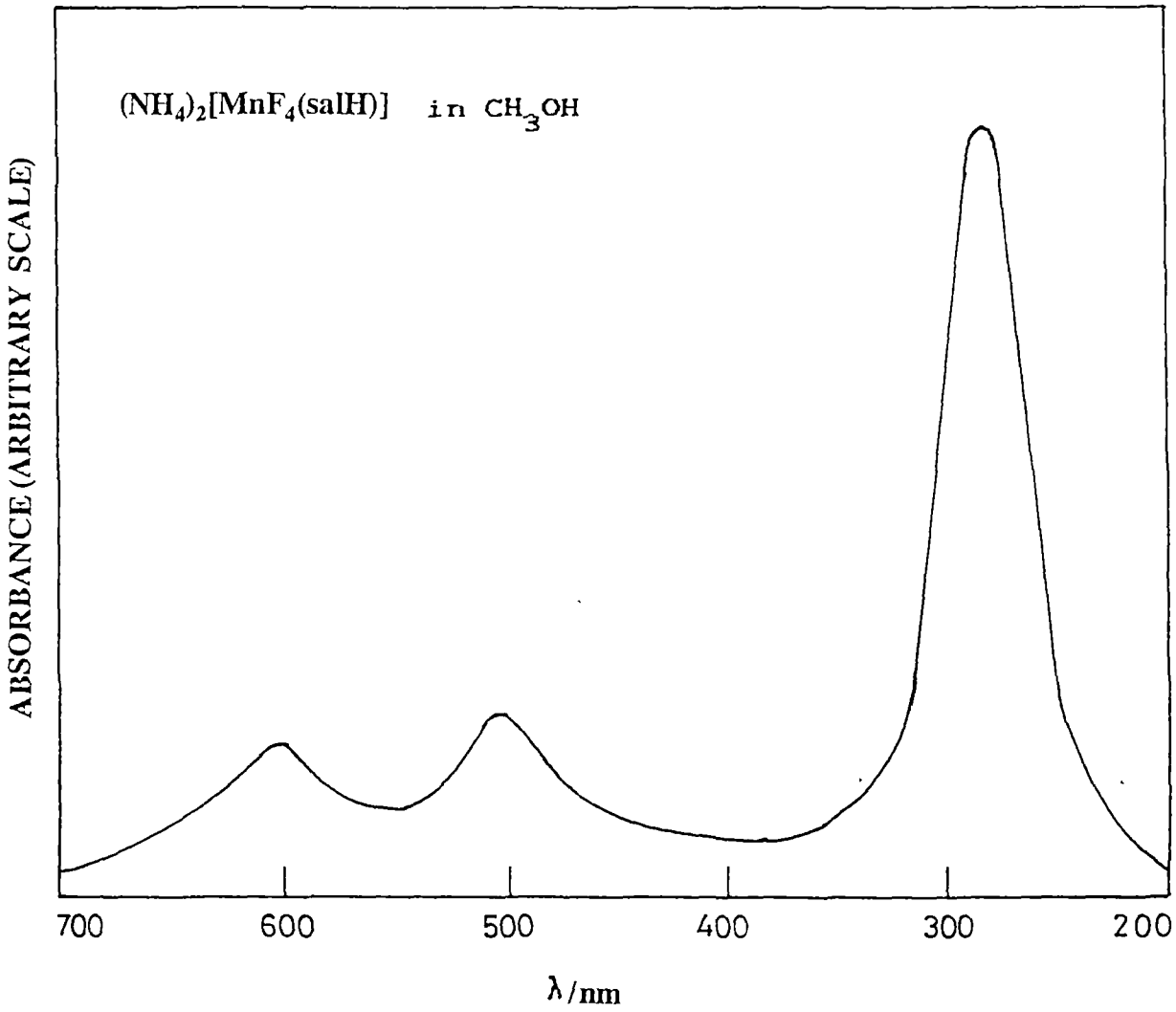

FIG. 4.4: ELECTRON ABSORPTION SPECTRUM

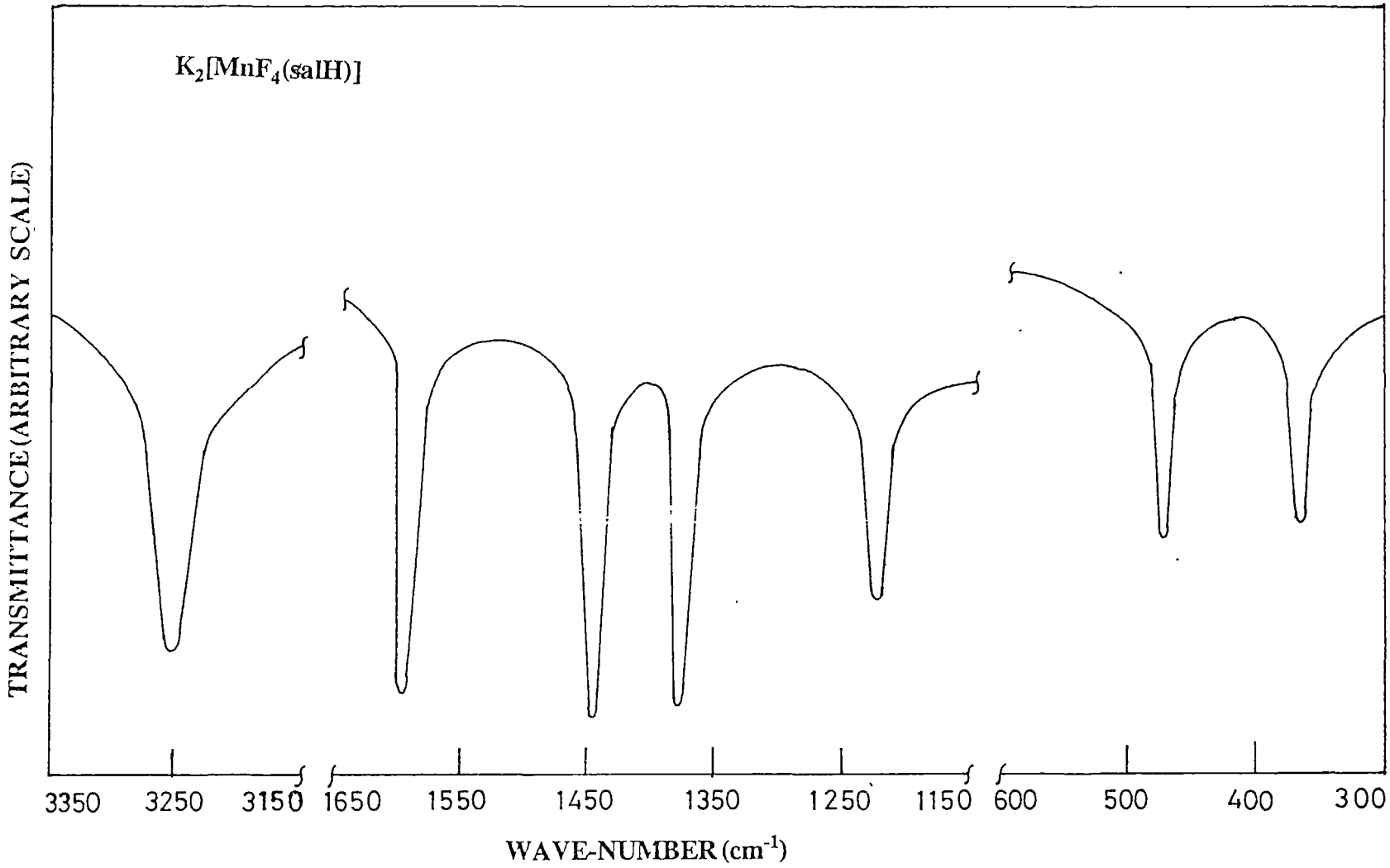

FIG. 4.5: IR SPECTRUM

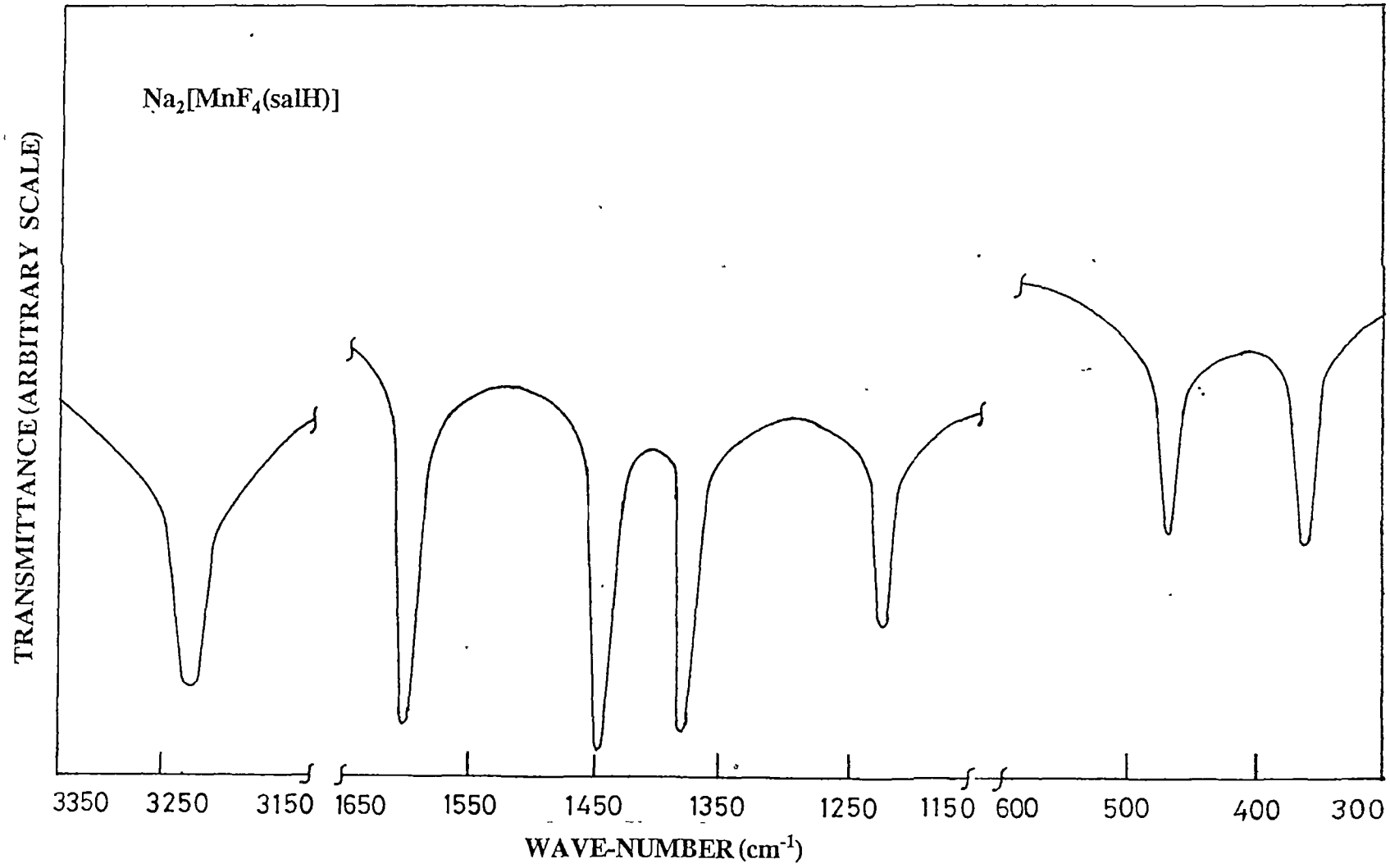

FIG. 4.6: IR SPECTRUM

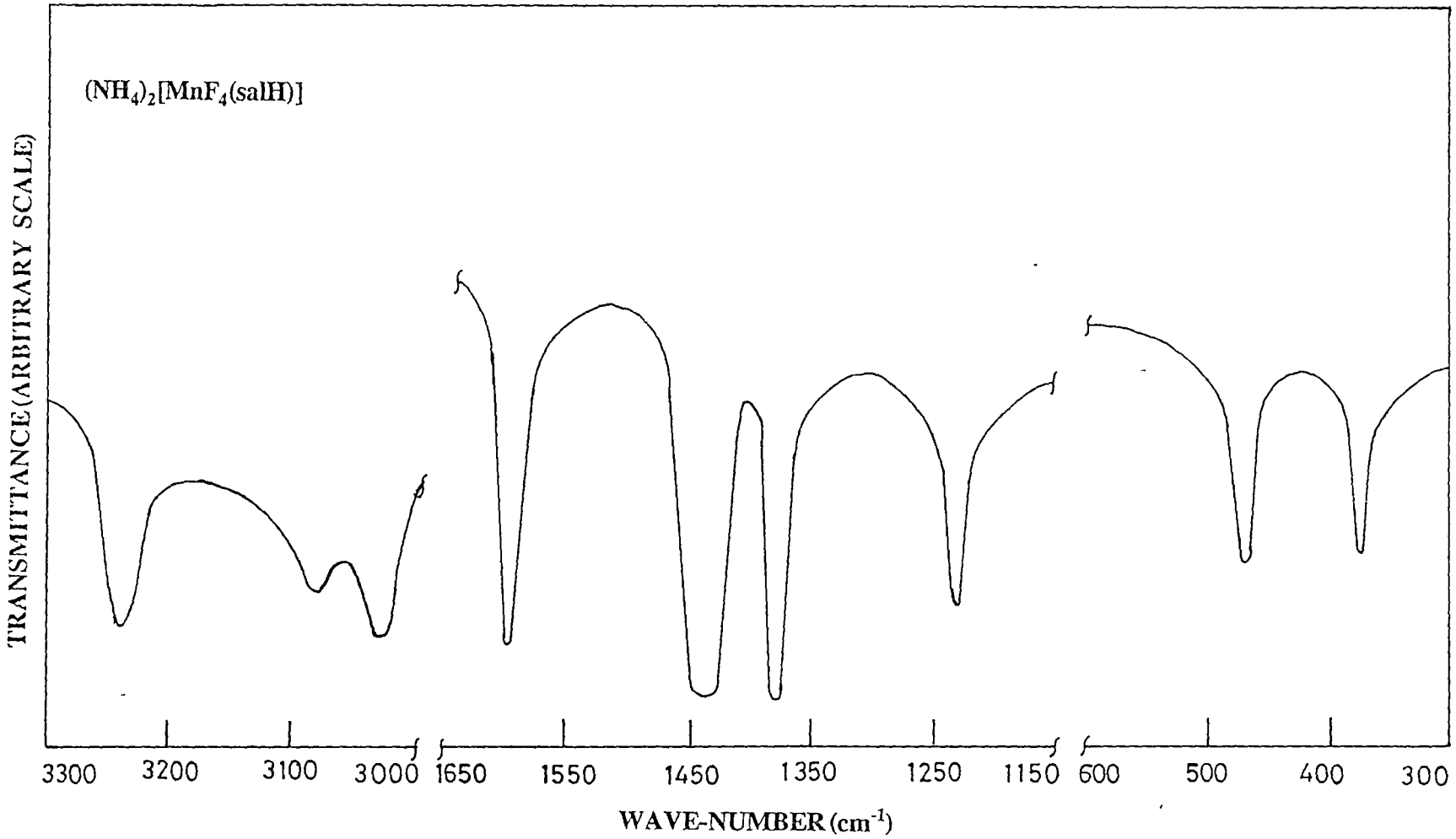

FIG. 4.7: IR SPECTRUM

$\nu_s(COO^-)$ which normally appear[27] at *ca.* 1640 and *ca.* 1355 cm^{-1} are known to shift to different frequencies upon coordination. Characteristically, the energy difference between the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ is used as the most important criterion for distinguishing mono- and bidentate types of coordination[27] with the energy difference being in the order of >*ca.* 200 cm^{-1} for the former and *ca.* 50 cm^{-1} for the latter. In the present case, the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ frequencies have been observed at *ca.* 1604 and *ca.* 1382 cm^{-1} with the difference between them being *ca.* 222 cm^{-1}. It is thus logical for us to assume that the ligand salicylate in the complexes $A_2[MnF_4(salH)]$, (A = K, Na or NH_4) is coordinated to the metal centre through its carboxylate oxygen in an unidentate fashion.

In order to ascertain the fate of the hydroxyl group of the salicylate ligand in metal-salicylates, it is most important for one to locate the ν(O-H) and δ(O-H) band positions in the IR spectra of the compounds.[26] For the $A_2[MnF_4(salH)]$, (A = K, Na or NH_4) complexes, the ν(O-H) and δ(O-H) modes have been observed at *ca.* 3250 and *ca.* 1230 cm^{-1}, respectively. These positions are somewhat lower than those normally observed for an uncoordinated hydroxyl group. These therefore provide definite indications for the presence of a protonated hydroxyl functionality in the complexes with the OH group being coordinated to the metal centre. This view is further supported by the observance of a band at *ca.*

340 cm^{-1} which has been assigned to the Mn-O stretching[28] mode from O-bonded OH group. Incidentally, the adopted synthetic methodology wherein the natural pH of the reaction medium was 4, might have favoured the retention of the phenolic proton, as the phenolic protons are not expected to be ionised at pH < 7.

It is thus evident from the observed spectral pattern that the salicylate in the complexes $A_2[MnF_4(salH)]$, (A = K, Na or NH_4) exists as $Hsal^-$ coordinated to the metal centre in a bidentate manner through the oxygens of the protonated phenolic and deprotonated carboxyl groups, respectively. This kind of a situation for coordinated salicylate present as $Hsal^-$ though unusual, has precedence in the literature.[26] In fact, X-ray diffraction studies on $[Cu(Hsal)_2].2H_2O$[26] revealed that salicylate is coordinated in a bidentate fashion to two distinct copper atoms through protonated alcoholic and deprotonated carboxyl groups.

In order to complement the results obtained from IR spectral studies, laser Raman spectroscopic experiments were conducted on the complexes $A_2[MnF_4(salH)]$, (A = K, Na or NH_4). The Raman spectra (Figs.4.8-4.10) of the mixed-fluoro(salicylato) complexes exhibited three bands at *ca.* 1597, *ca.* 1385 and *ca.* 1237 cm^{-1}. The spectral pattern and the band positions were essentially similar to the IR spectral pattern of the complexes. The bands have thus been assigned to the absorptions originating from $\nu_{as}(COO^-)$, $\nu_s(COO^-)$ and δ(O-H) modes of the coordinated salicylate ligand.

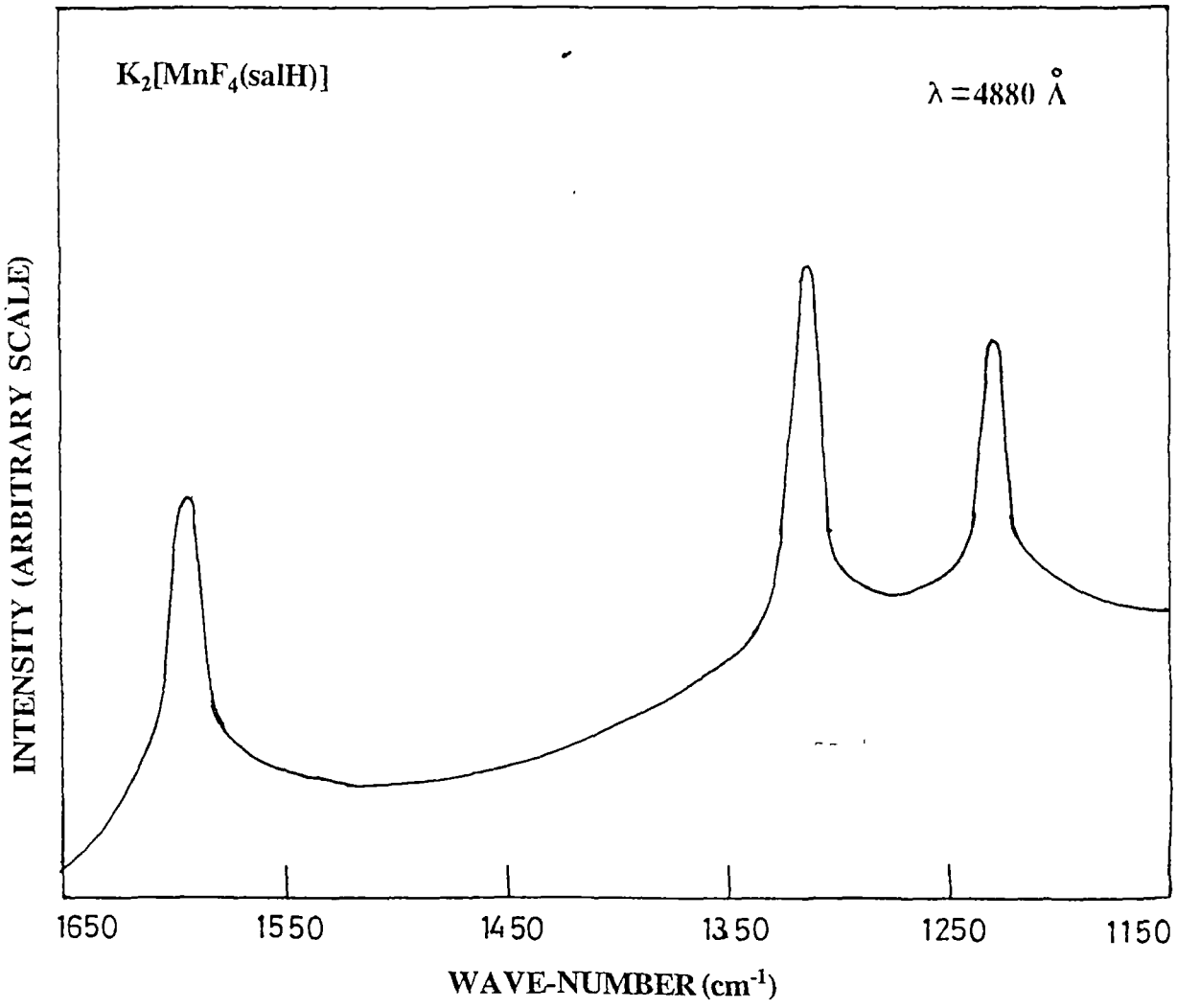

FIG. 4.8: RAMAN SPECTRUM

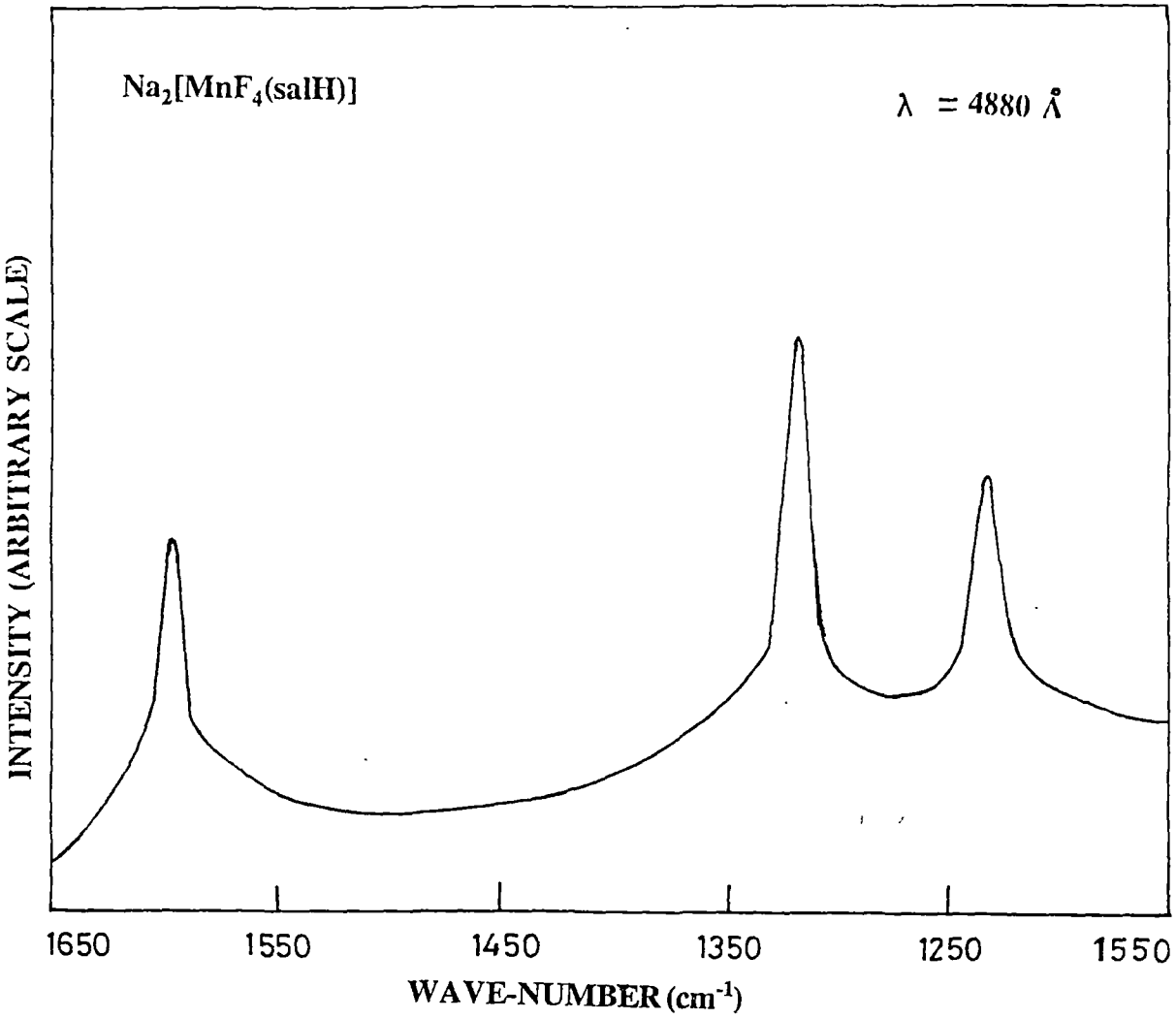

FIG. 4.9: RAMAN SPECTRUM

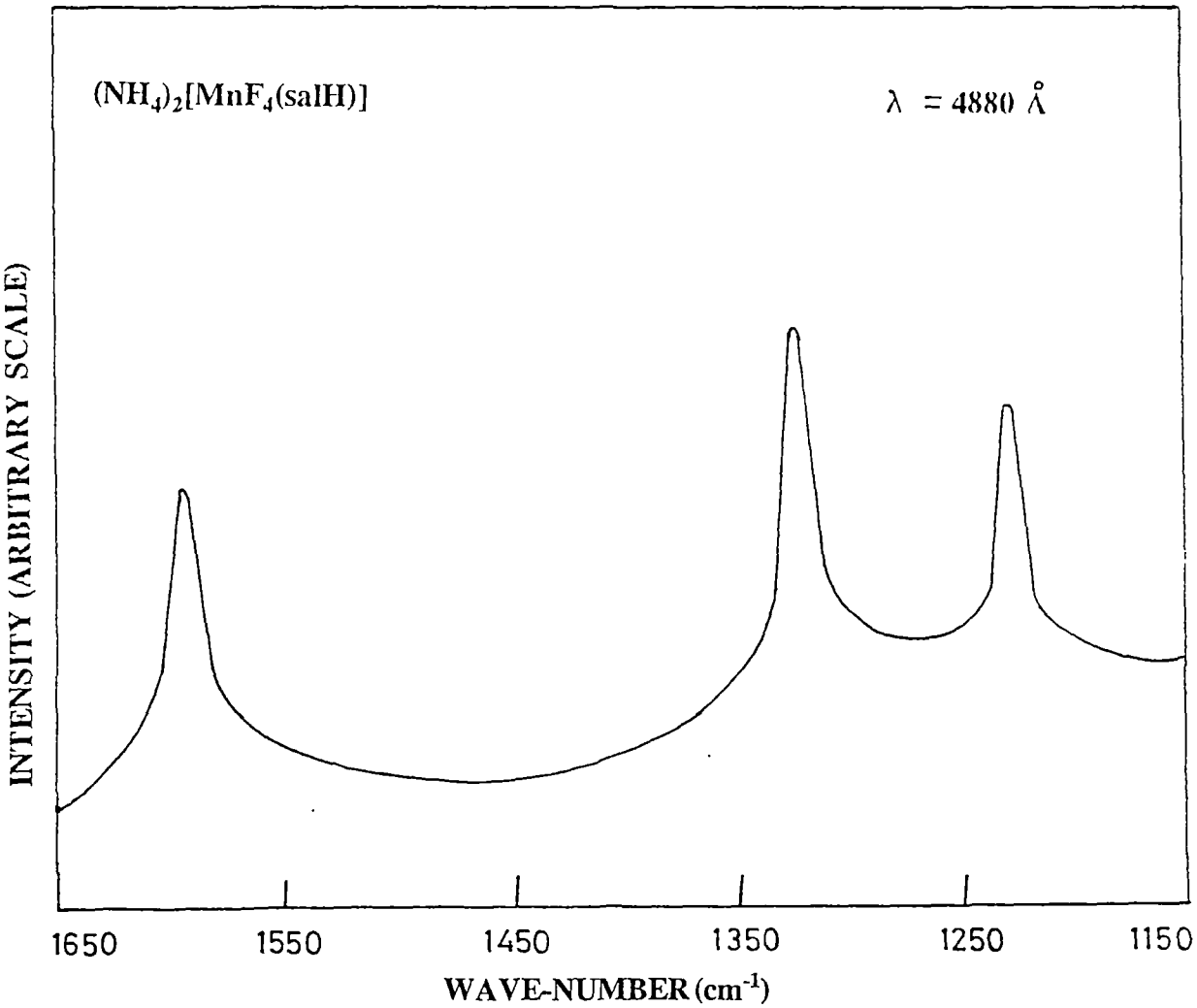

FIG. 4.10: RAMAN SPECTRUM

This therefore further augments our contention that salicylate ligand in the complexes $A_2[MnF_4(salH)]$, (A = K, Na or NH_4) is present as $Hsal^-$ coordinated to the metal centre in a bidentate fashion through both the protonated phenolic and deprotonated carboxyl groups.

Thus a combination of chemical analyses, chemical determination of oxidation state of manganese, magnetic susceptibility measurements, solution electrical conductivity experiments, IR, laser Raman and electron absorption spectroscopies and Scanning Electron Microscopy enables us to ascertain the identity of the compounds to be $A_2[MnF_4(salH)]$, (A = K, Na or NH_4).

Investigation of the effect of relatively higher concentrations of F^- on the reaction amongst manganese(III), F^- and salicylic acid

As discussed earlier in this section, a concentration of *ca.* 20.23 mmol of AHF_2 for 10.11 mmol of MnC(OH) (vide experimental) was found conducive to the successful synthesis of $A_2[MnF_4(salH)]$, (A = K, Na or NH_4). In order to study the effect of an excess of F^- in the reaction medium, the reactions were strategically conducted with varying amounts of higher fluoride ion concentrations but similar concentrations of $salH_2$ as required for the preparation of $A_2[MnF_4(salH)]$, (A = K, Na or NH_4). The reaction of MnC(OH) (10.11

mmol) with 60.68 mmol of AHF_2 and 57.97 mmol of $salH_2$ afforded $A[MnF_4(H_2O)_2].H_2O$ (A = K, Na or NH_4). Incidentally, only the sodium salt of the trihydrate complex has been reported in the literature[29] earlier. This therefore enables us to make the first report on the corresponding NH_4^+ and K^+ salts as well as devising a general methodology for the tetrafluoromanganates(III) trihydrates. However, reactions conducted with still larger concentrations of F^- (*ca.* 121.38 mmol of AHF_2) afforded the binary pentafluoromanganates(III), for which very well dedicated methods were improvised.[5]

In order to be able to comment on the role of the hetero-ligand, control reactions involving higher concentrations of F^- were necessary. Thus independent reactions of MnO(OH) (10.11 mmol) with 40.46 mmol of AHF_2 afforded the diaquotetrafluoro-manganates(III), $A[MnF_4(H_2O)_2]$ (A = K, Na or NH_4). However, on conducting the reactions at similar concentrations of F^- (*ca.* 60.68 mmol of AHF_2) as that used for $A[MnF_4(H_2O)_2].H_2O$ (A = K, Na or NH_4), the pentafluoromanganates(III) were obtained. Further, our attempts to convert an amount of 2.89 mmol of preformed $K_2[MnF_4(salH)]$ isolated from the reaction of MnOOH with KHF_2 and $salH_2$ at pH 4, to binary fluoromanganates(III) by treatment with excess of F^- (*ca.* 60.68 mmol to *ca.* 121.38 mmol of KHF_2) met with failure.

The alkali diaquotetrafluoromanganates(III) $A[MnF_4(H_2O)_2].H_2O$ and $A[MnF_4(H_2O)_2]$ (A = K, Na or NH_4) are brown in colour and highly insoluble in most of the commonly used solvents. The chemically determined oxidation state of manganese in each of the compounds was found to be +3. The room temperature (300K) magnetic moments of $A[MnF_4(H_2O)_2].H_2O$ and $A[MnF_4(H_2O)_2]$ (A = K, Na or NH_4) were found to lie in the range of 4.9-5.0 BM. The observed values are very much in line with those expected normally for a d^4 system which also concurs with the values reported earlier for tetrafluoromanganates(III).[16,30,31] Incidentally, there are literature[29-31] precedences for the Na, Rb and Cs salts of $[MnF_4(H_2O)_2]^-$ anion. The crystallographically characterized structures were shown to consist of $[MnF_4(H_2O)_2]^-$ octahedra[30,31] interlinked by an array of hydrogen bonds of the type OH.....F with tetragonal elongation of the manganese octahedron. The compounds reported herein other than the sodium salt may also most likely have similar tetragonally distorted octahedral geometry.

The IR spectra (Figs.4.11-4.16) of $A[MnF_4(H_2O)_2].H_2O$ and $A[MnF_4(H_2O)_2]$ (A = K, Na or NH_4) bear a close resemblance to each other in the 450-700 cm^{-1} region. Two strong bands at *ca.* 550 and *ca.* 590 cm^{-1} have been assigned to the ν(Mn-F) stretching modes. The band positions get along very well with those of the crystallographically characterized complexes of similar type.[29-31]

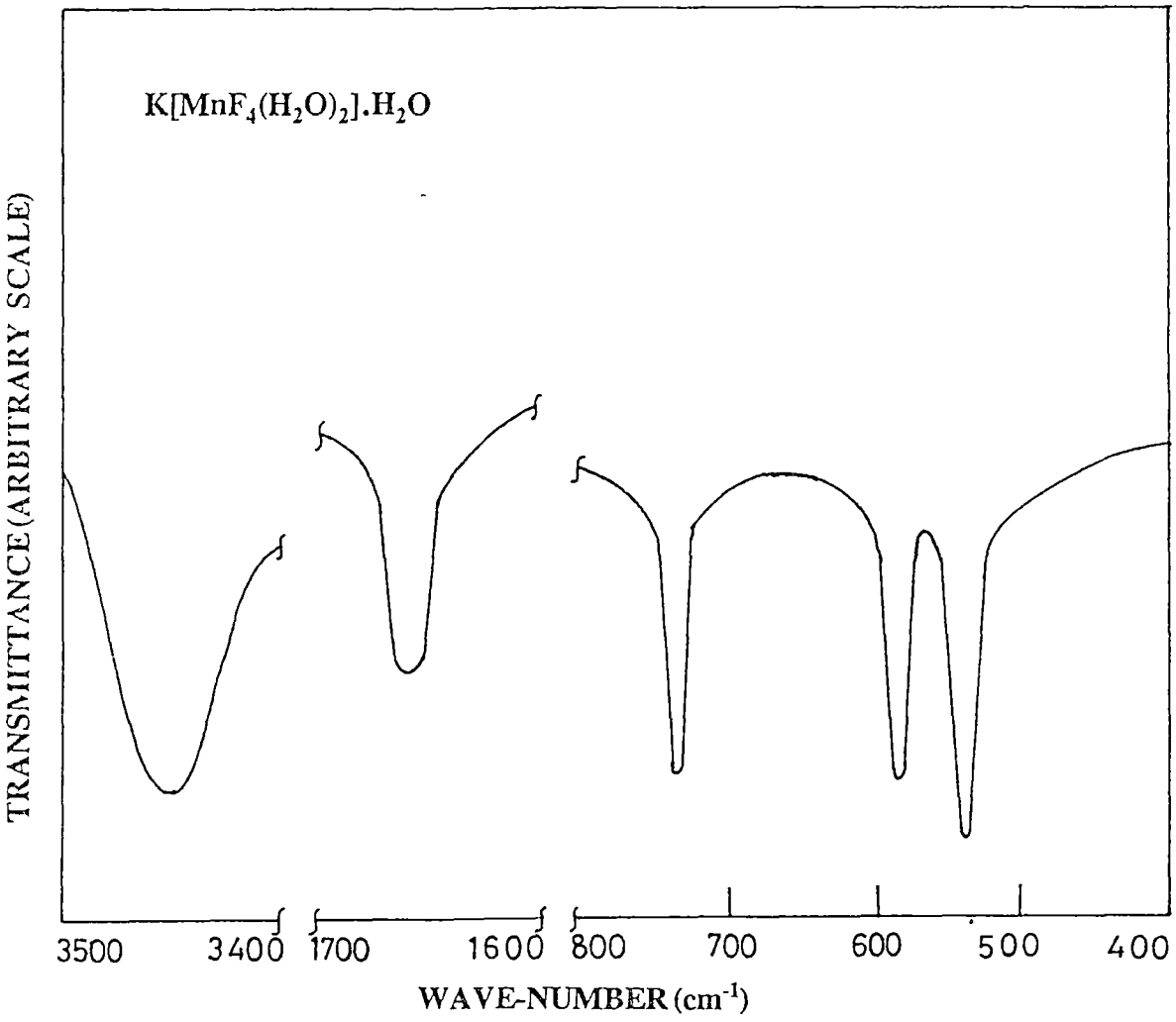

FIG. 4.11: IR SPECTRUM

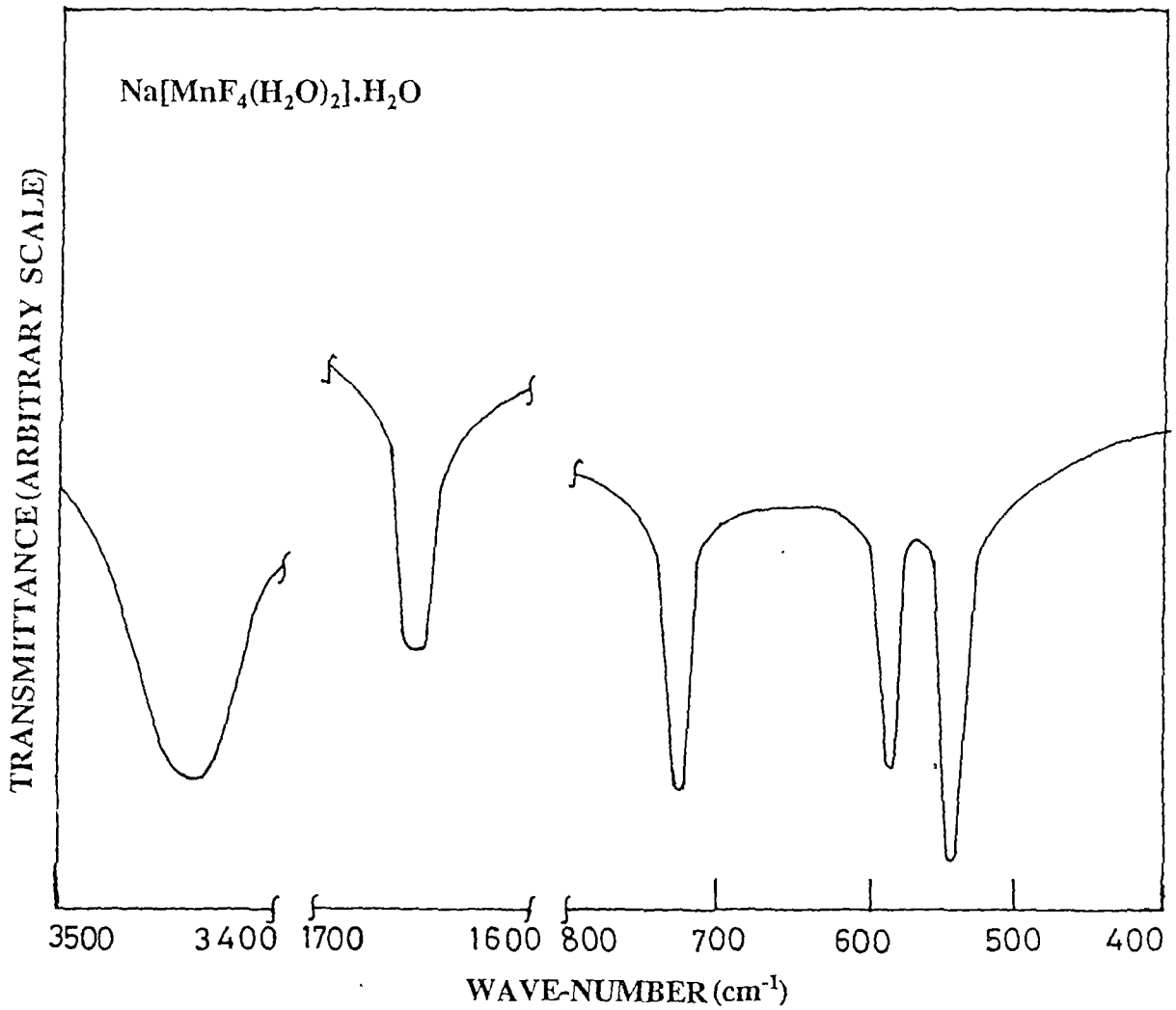

FIG. 4.12: IR SPECTRUM

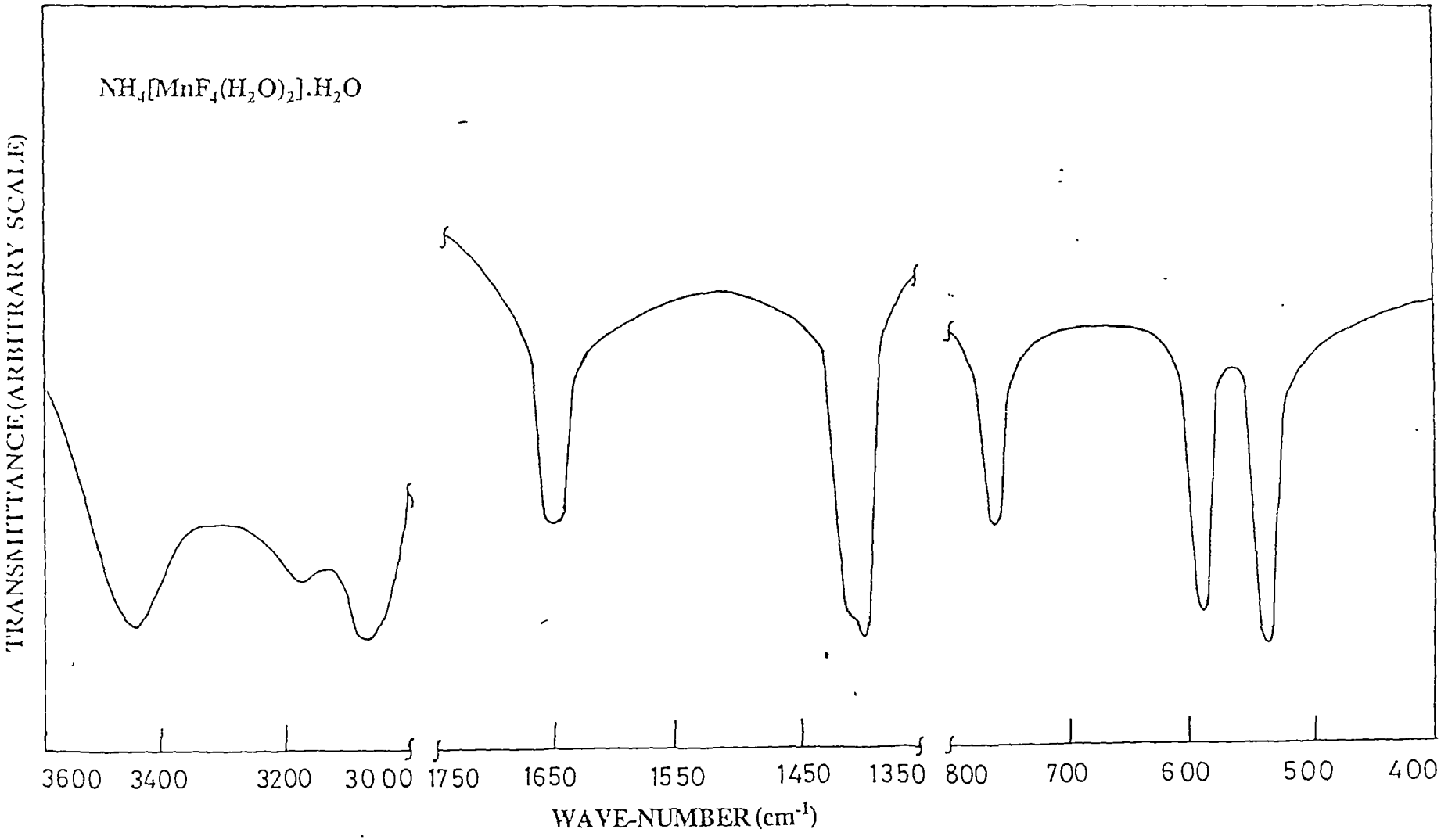

FIG. 4.13: IR SPECTRUM

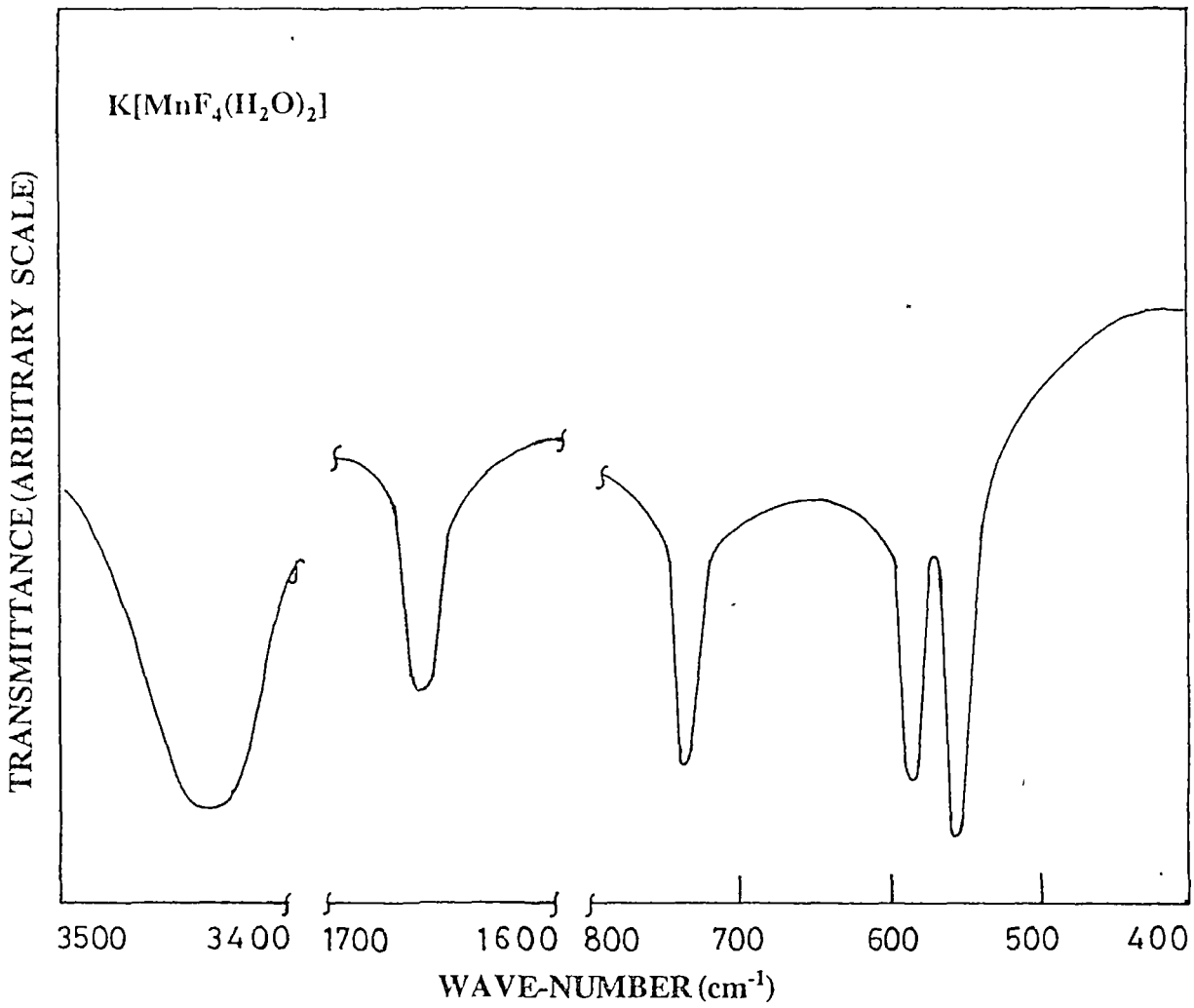

FIG. 4.14: IR SPECTRUM

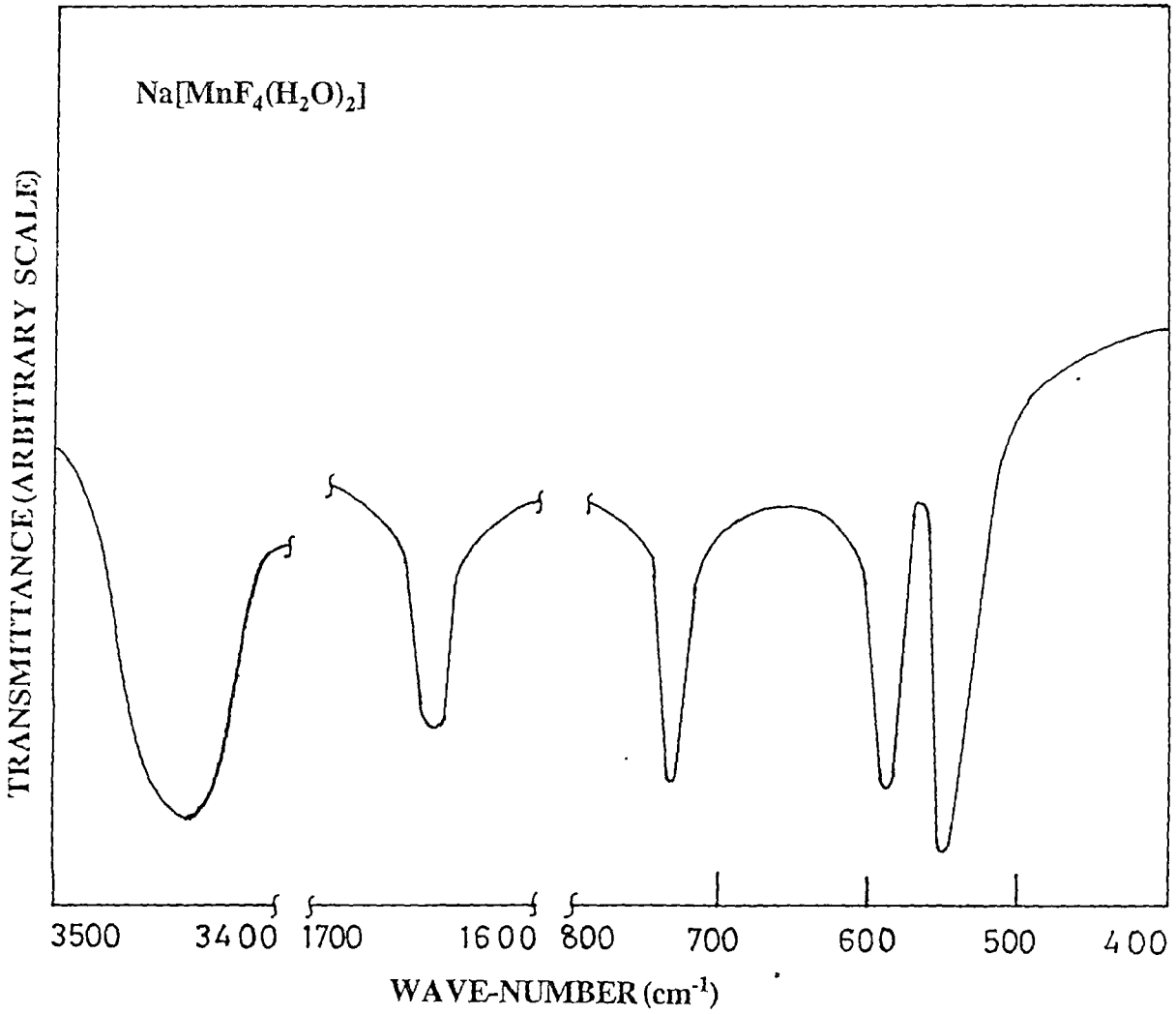

FIG. 4.15: IR SPECTRUM

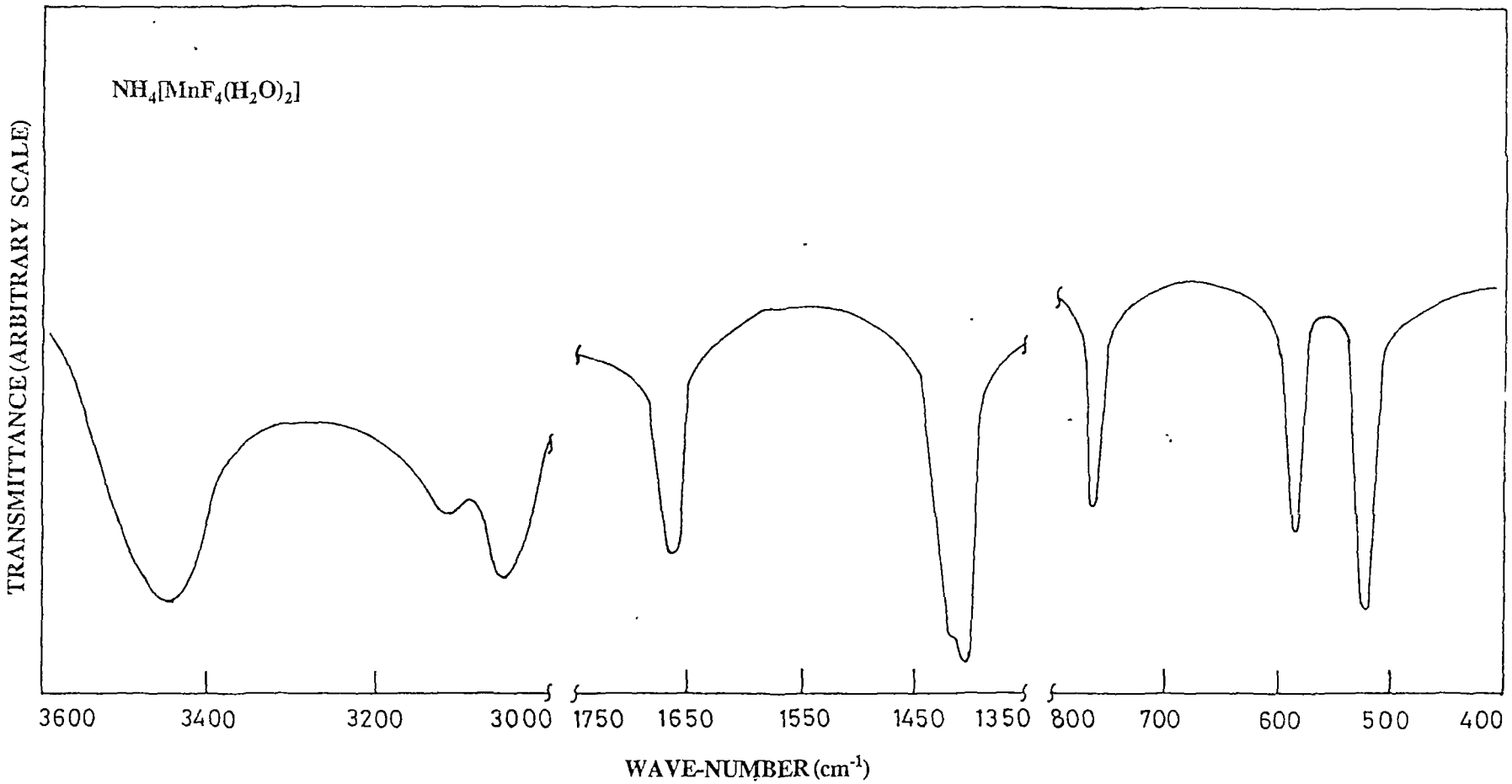

FIG. 4.16: IR SPECTRUM

Additional bands at *ca.* 745, *ca.* 1660 and *ca.* 3445 cm^{-1} have been attributed to the rocking mode of coordinated water, δ(H-O-H) and ν(O-H) modes, in conformity to the presence of water molecules in the compounds. However, the ammonium salts of the corresponding complexes displayed additional bands at *ca.* 1420, *ca.* 3030 and *ca.* 3150 cm^{-1} in their IR spectra. These were attributed to the absorptions originating from NH_4^+ ion and have been assigned to the ν_3, ν_1 and ν_4 modes, respectively, of NH_4^+ ion.[27b]

The pentafluoromanganates(III), $A_2[MnF_5].nH_2O$ (A = K, n = 1; A = Na or NH_4, n = 0), have also been characterized by a combination of elemental analyses, chemical determination of oxidation state of the metal, magnetic susceptibility measurements and IR spectroscopy. The characterization data are very much similar to that described for a similar compound in Chapter III and to those reported earlier in the literature.[5]

Comments on the Reactions

Based upon the isolation of $A_2[MnF_4(salH)]$, $A[MnF_4(H_2O)_2].H_2O$, $A[MnF_4(H_2O)_2]$ and $A_2[MnF_5].nH_2O$ (A = K, Na or NH_4), a few comments on the reactions are essential.

That in the presence of salicylic acid, a larger concentration of fluoride is required for the preparation of diaquotetrafluoromanganates(III), which however, can also be obtained by using a lesser amount of F^- in the absence of

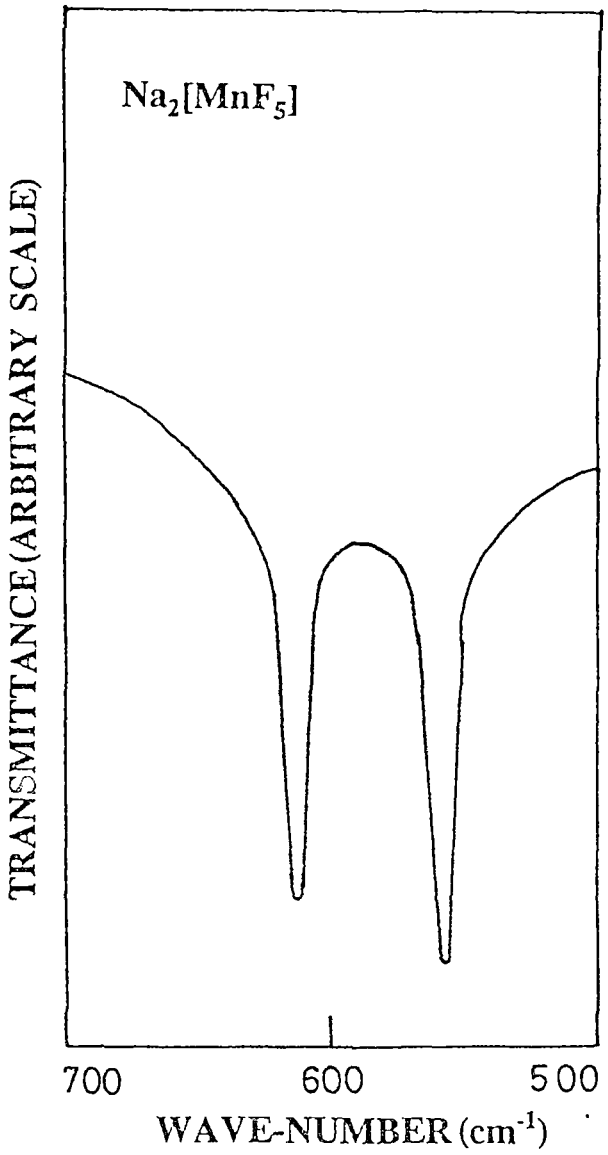

FIG. 4.17: IR SPECTRUM

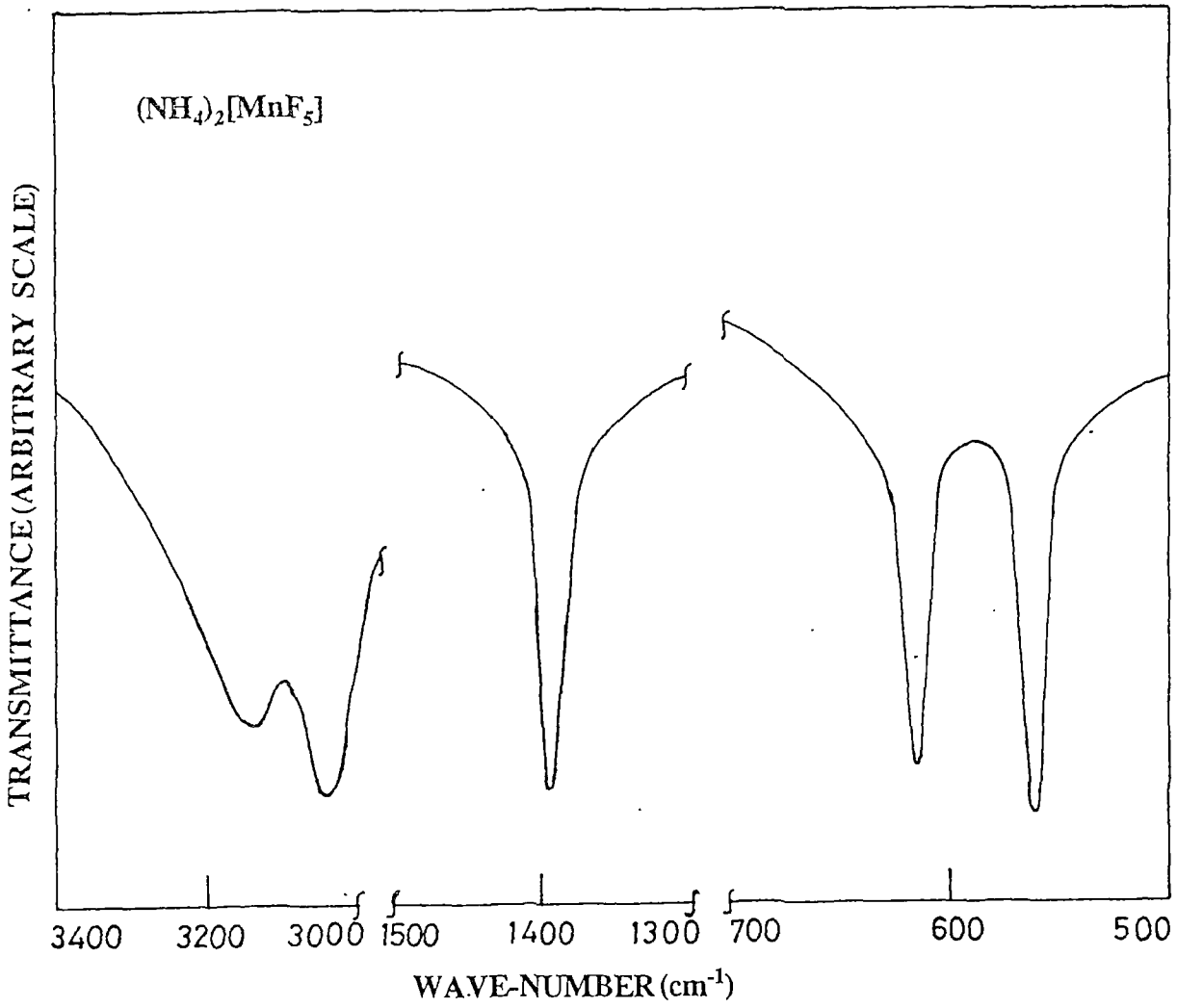

FIG. 4.18: IR SPECTRUM

salicylic acid, thereby implying that an excess of F^- in the reaction medium as well as a lowering of pH is essential for the isolation of binary fluoromanganates(III) in the presence of different co-ligands in the reaction medium. Further, the presence of F^- itself in the reaction medium as well as the aqueous acidic conditions used for the investigation might have most probably inhibited di- or multi- nuclear complex formation. This observation supports the comments made by Wieghardt[7] in the context of formation of multinuclear complexes favoured by Cl^-, but inhibition of such complex formation by F^-. However, one should not lose sight of the fact that hetero-ligands viz., pyridine, benzoate and CH_3OH assisted formation of multinuclear manganese-salicylato complexes. It is thus evident that by simultaneous lowering of pH and addition of a large excess of F^- to the reaction medium, $salH_2$ loses its capability of binding to manganese(III) owing to the pronounced complexing nature of F^-. But an optimum molar stoichiometry of Mn:F:$salH_2$ as 1:4:3 provides a conducive pH of *ca.*4 facilitating the simultaneous complexation of salicylate and F^- to manganese(III) leading to $A_2[MnF_4(salH)]$, (A = K, Na or NH_4) as isolated. The complex once isolated in the solid state has been found to be highly stable. The contention is supported by the fact that our attempts to convert the preformed $K_2[MnF_4(salH)]$ to binary fluoromanganates(III) by reacting with excess of F^- were not successful (vide experimental).

Interaction of manganese(III) with Schiff bases in the presence of F^-

In addition to salicylic acid, our attention was also drawn for studying the effect of F^- on the complexation of manganese(III) with N,O donor ligands under aqueous conditions. The N,O donor ligands chosen for the present work were drawn from Schiff bases viz., salenH_2 (condensed product of salicylaldehyde and ethylenediamine) and acacenH_2 (condensed product of acetylacetone and ethylenediamine). The manganese(III)-schiff base complexes are important in their own right as described in the introduction section. It was therefore planned to carry out separate reactions of manganese(III) with salenH_2 and acacenH_2 in the presence of F^- in an aqueous medium. Accordingly, independent reactions of MnO(OH) with aqueous HF and ethanolic solutions of salenH_2 or acacenH_2 afforded the heretofore unreported tetrafluoromangante(III), enH[MnF_4]. Similar reactions conducted by using ethylenediamine instead of the schiff base did not provide any tractable product. The natural pH of *ca.* 4 attained during the course of the reaction must have facilitated the cleavage of the C-N bond of the schiff bases and further subsequent protonation of ethylenediamine formed in the process, thereby resulting into enH[MnF_4], since in an acidic medium the posibility of coordination of ethylenediamine is rather remote. In

order to further substantiate the existence of en as enH in the complex, metathesis reactions employing the complex enH[MnF_4] with Rb_2CO_3 and $CsNO_3$ were conducted. The products isolated from the above reactions were identified as $Rb[MnF_4(H_2O)]$ and $Cs[MnF_4(H_2O)]$, respectively, supporting our contention and attesting to the assigned formula.

The colour, stability and solubility properties of the newly isolated enH[MnF_4] are similar to that of binary tetrafluoro-manganates(III) reported earlier by us[16] and others.[30,31] The iodometrically estimated oxidation level of manganese in the complex was +3. The room temperature (300K) magnetic moment of the complex was 4.2 BM, a value somewhat lower than that normally expected for an ideal d^4 system. Noteworthy is that this value is also lower than those reported for other tetrafluoro-manganates(III)[16,30,31] earlier. This therefore indicates that there is some degree of antiferromagnetic exchange interactions operative in the complex through -Mn-F-Mn-F- chains and that the counterion must have played a role in this regard. The presence of enH might have most probably been responsible for the polymeric structure of the complex through enhanced hydrogen bonding (*cf.* corresponding alkali salts of tetrafluoromanganates(III)).[16,30,31]

The structurally most significant bands in the IR spectrum (Fig.4.19) of the complex enH[MnF_4] have been the absorptions at

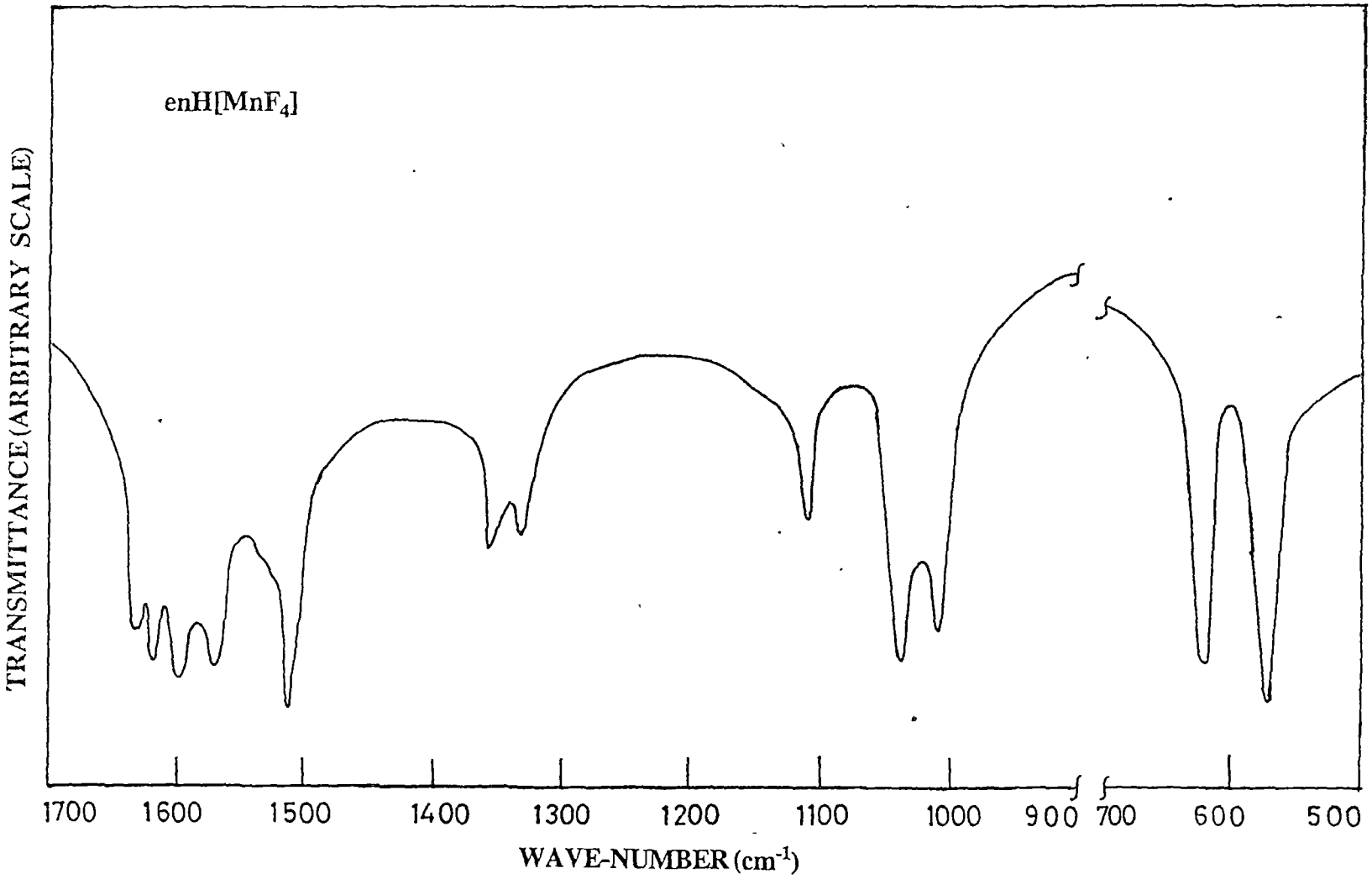

FIG. 4.19: IR SPECTRUM

578 and 625 cm^{-1} which have been attributed to the Mn-F modes. Repeated scanning of the IR spectrum in the 500-700 cm^{-1} region led to the observance of only these two bands at similar positions. Owing to the fact that manganese(III) ion generally favours a octahedral or distorted octahedral geometry and that the octahedral $[MF_6]^{n-}$ (Ref. 32) complex should have two IR active vibrations, it should be reasonable to assume that the manganese(III) ion in the $enH[MnF_4]$ complex finds itself in a distorted octahedral environment with a D_{4h} symmetry consisting of $[MnF_6]^{3-}$ octahedra, thereby forming infinite chains of $[MnF_4]^{-}$ in the crystal lattice. In addition to the absorptions due to Mn-F, bands due to ethylenediamine moiety were also observed in their usual positions, which were in agreement with the reported IR data of compounds containing uncoordinated en.[27] Further, the absence of any absorption in the 450-350 cm^{-1} region due to Mn-N stretching vibration rules out the possibility of coordination of en, thereby lending additional support to the assigned formula.

The scanning electron micrograph (Fig.4.20) attests to the homogenous and crystalline character of the complex $enH[MnF_4]$ having a rod shaped external morphology. The micrograph also indicates to the compound being present in a single phase. The crystal dimension is of the order of 20μ.

The rubidium and caesium salts of tetrafluoromanganates(III) were also characterized by a combination of elemental analyses,

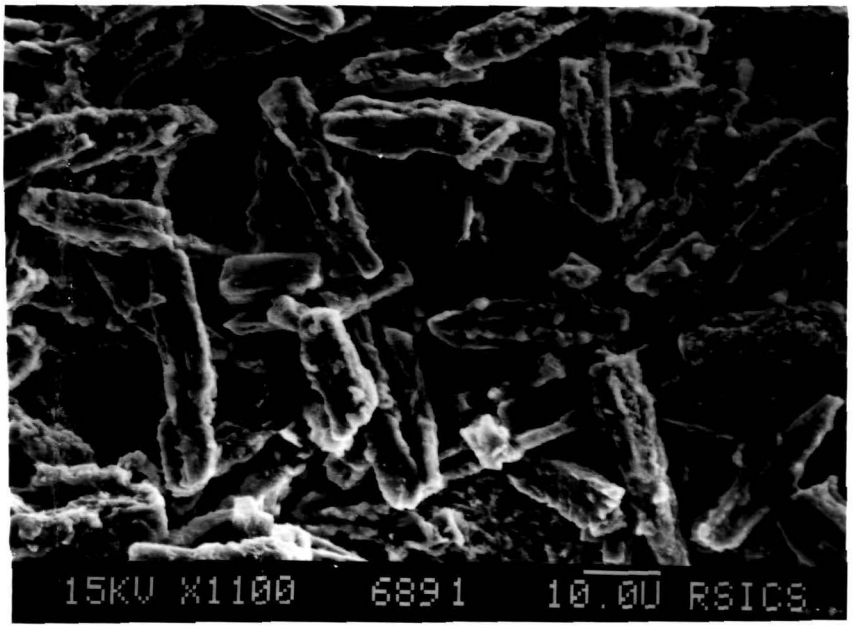

FIG. 4.20: SE MICROGRAPH OF enH[MnF_4]

chemical determination of oxidation state of manganese, magnetic susceptibility measurements and IR spectroscopic studies.

The room temperature magnetic moments of $A[MnF_4(H_2O)]$ (A = Rb or Cs) were found to be 4.8 and 4.85 BM, respectively, in agreement with the values reported earlier in the literature[16,30,31] for similar compounds. The rubidium salt of monoaquotetrafluoromanganate(III) has got a precedence in the literature[16,31] with the structure being crystallographically characterized as consisting of $[MnF_6]^{3-}$ and $[MnF_4(H_2O)_2]^-$ octahedra forming infinite chains of composition $[MnF_4(H_2O)]^-$. The compounds described herein, both the Rb and Cs salts may also most likely have similar structures.

The IR spectral features (Figs.4.21 and 4.22) of the compounds $A[MnF_4(H_2O)]$ (A = Rb or Cs) were essentially similar to the other tetrafluoromanganates(III) described earlier in this section and also to similar compounds reported earlier in the literature.[16,30,31]

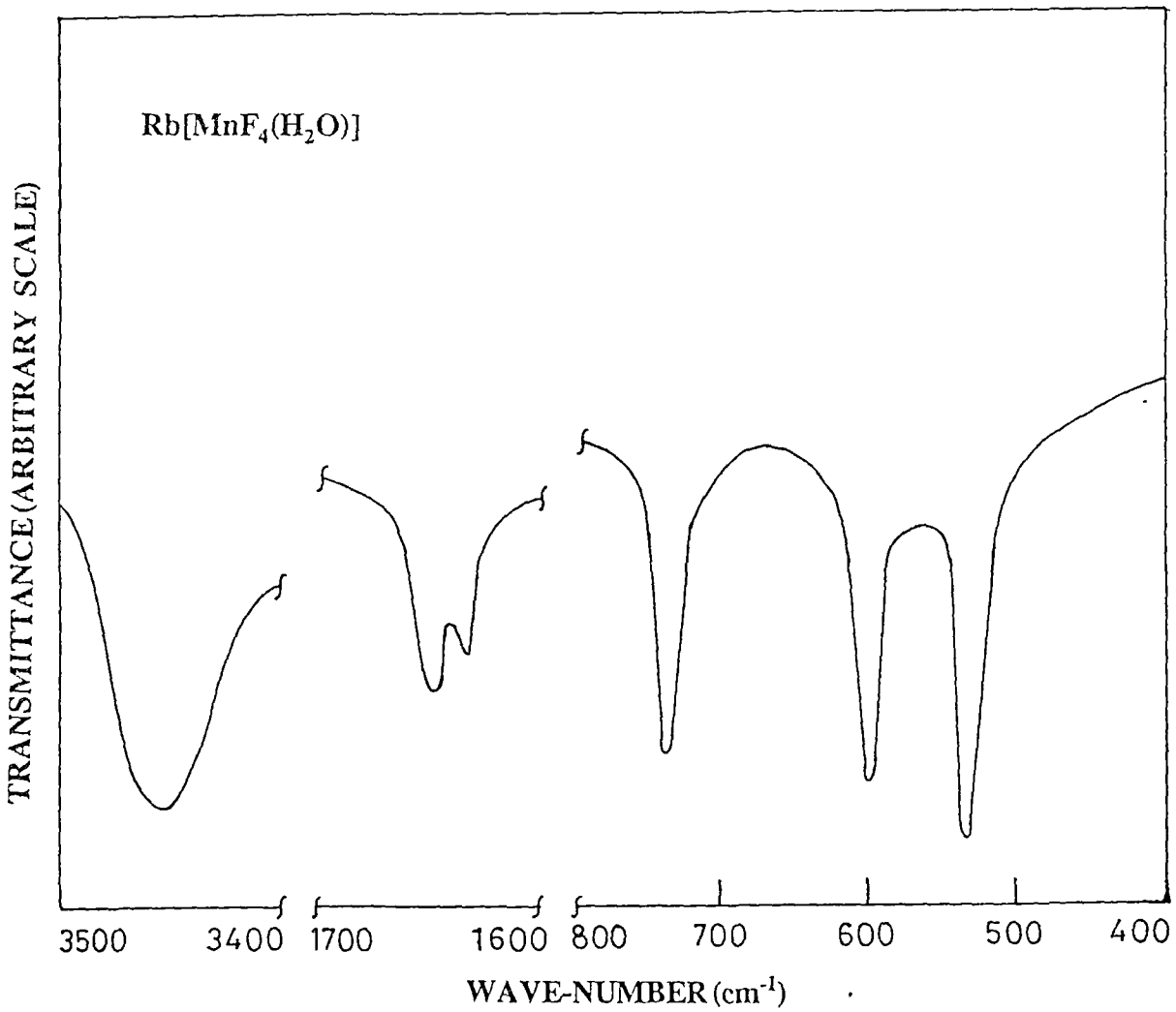

FIG. 4.21: IR SPECTRUM

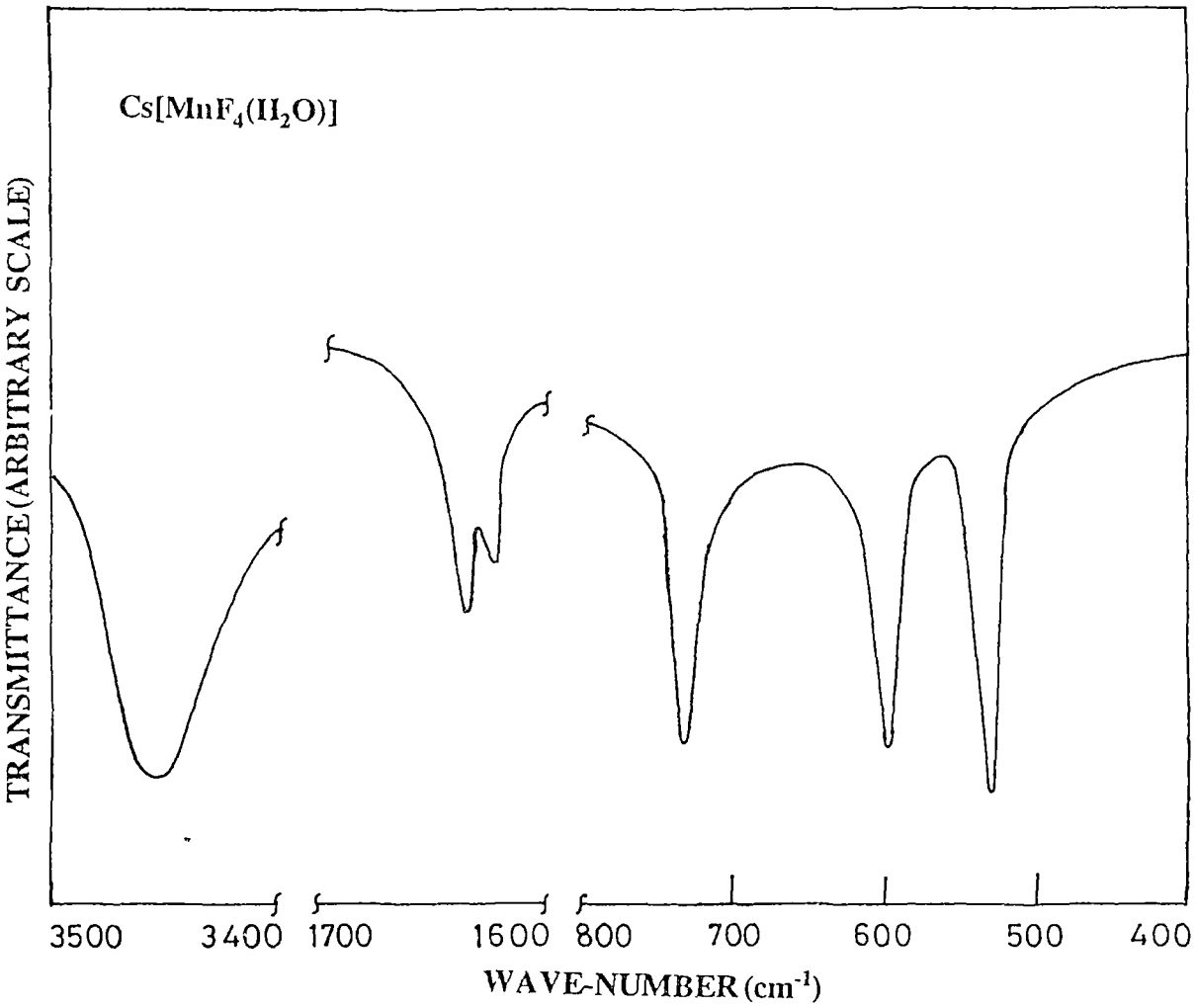

FIG. 4.22: IR SPECTRUM

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CHAPTER V

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF MIXED-FLUORO COMPLEXES OF UO_2^{2+} WITH ORGANIC CO-LIGANDS NAMELY AMINO ACIDS, ACETYLACETONATE AND ACETATE AND THE FIRST SYNTHESES OF $[UO_2F_6]^{4-}$ AND $[UO_2F_7]^{5-}$ COMPLEXES*

Chemistry involving fluoro containing compounds is one of the active areas of contemporary research in inorganic chemistry. This

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* The work described herein has been published in parts in:

(a) *Proc.Indian Acad.Sci.*, 1992, 104, 479.

(b) *J.Fluorine Chem.*, 1992, 56, 305.

(c) *Polyhedron*, 1993, 12, 227.

is mainly owing to an intrinsic interest[1-6] in fluoro metal compounds as well as their use in practice.[8-12] Uranyl, UO_2^{2+} ion is known to form stable fluoro and mixed-fluoro complexes. Notable among the binary fluoro complexes are $[UO_2F_2]$,[13-19] $[UO_2F_3]^-$,[13,20] $[UO_2F_4]^{2-}$,[21] $[UO_2F_5]^{3-}$,[13] $[(UO_2)_2F_7]^{3-}$,[22,23] $[(UO_2)_2F_9]^{5-}$,[13] whose syntheses are well documented in the literature. However, to the best of our knowledge $[UO_2F_6]^{4-}$ and $[UO_2F_7]^{5-}$ seem to be unprecedented. Interestingly, some physico-chemical studies[24,25] involving the complex $[UO_2F_6]^{4-}$ were conducted without making any mention of its preparation. Hence synthetic procedures for hexafluorodioxouranate(VI) and heptafluorodioxouranate(VI) were warranted.

As mentioned in Chapter I of the thesis, one of the possible ways of accessing these compounds could be by using $UO_2(acac)_2.2H_2O$ as the precursor. Thus it was imperative to prepare $UO_2(acac)_2.2H_2O$. The widely used method[26] for the preparation of $UO_2(acac)_2.2H_2O$ requires sodium hydroxide for maintaining an appropriate pH of the reaction medium. The chances of contamination of the end product owing to the use of such a large amount of alkali cannot be discounted. Recently, a new method[27] was described which did not require any alkali or buffer. But the procedure requires an extra step for obtaining an intermediate uranium product of unknown composition and also a very thorough washing in order to make it free from alkali prior

to the final step of synthesis. In view of the problems encountered in the literature methods, it was decided to develop a straight method for the synthesis of the compound and then use it to investigate its nucleophilic substitution reactions with F^- being the nucleophile to provide an access to fluoro compounds of uranium. It was also our concern to improvise a direct route to uranyl fluoride hydrate. There have been several methods for the synthesis of UO_2F_2, but most of the procedures involve dry reaction techniques[13-19] namely use of anhydrous HF or UF_4 and dry oxygen which are difficult to handle and which also require high temperature. A recent method developed by Chakravorti and Chowdhury[14] initially requires the preparation of $UO(O_2).2H_2O$ that is then converted to $H[UO_2F_3].H_2O$ which finally afforded UO_2F_2.

Though there are a number of reports on mixed-ligand complexes of UO_2^{2+}, the area of hetero-ligand fluoro chemistry of uranyl seems to be far less attended to. The co-ligands had been largely drawn from sulphate,[28] oxalate,[29] Cl^- or Br^-,[30] CO_3^{2-},[31] acetylacetonate,[32] propionate,[33] malonate,[34] urea[35] and DMSO.[36] Relevant to mention here is that, we have been interested in the chemistry of UO_2^{2+} and some of our previous publications dealt with mixed ligand peroxo complexes including fluoroperoxo-uranates(VI).[5]

As part of a general programme of the laboratory on fluorometallates, we sought to address to such aspects of uranyl

chemistry. In this context, attention has been drawn to the synthesis and structural characterization of heretofore unreported fluoro and mixed-fluoro complexes of UO_2^{2+} for the present investigation.

Thus the main aim of the present work crystallized to improvise a straight methodology for obtaining $UO_2(acac)_2.2H_2O$, investigate its nucleophilic reaction profile by the interaction with fluoride, and to gain an access to the hitherto unreported complexes, $[UO_2F_6]^{4-}$ and $[UO_2F_7]^{5-}$. The other concern was to achieve the synthesis of newer mixed-fluoro compounds of the metal by drawing the coligands from amino acids viz. glycine, L-alanine and L-cysteine, acetylacetonate and acetate.

Experimental

All the chemicals used for the present work were of reagent-grade quality (E.Merck (India) Ltd., SISCO Chemicals, Qualigens Fine Chemicals, S.d. Fine Chem.). The details of the instruments/equipment used for the characterization of the complexes are described in Chapter II.

Synthesis of bis(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2.2H_2O$

To 1.0g (2.79 mmol) of $UO_3.4H_2O$ was added 4 cm^3 (39.95 mmol) of distilled acetylacetone and stirred constantly over a

steam-bath for *ca.*10 min until an orange-yellow solution resulted. pH value of the solution at this stage was found to be 5-5.5. The solution on cooling to room temperature (*ca.*20^{o}C) afforded orange-yellow crystals of $UO_2(C_5H_7O_2)_2.2H_2O$. The yield of $UO_2(C_5H_7O_2)_2.2H_2O$ was 1.3g (92.2%).

Synthesis of ammonium hexafluorodioxouranate(VI), $(NH_4)_4[UO_2F_6]$

A mixture of 1.0g (1.98 mmol) of $UO_2(C_5H_7O_2)_2.2H_2O$ and 0.3g (8.1 mmol) of NH_4F was allowed to react in the presence of 20.0 cm^3 (199.75 mmol) of distilled acetylacetone and a trace of water (1 cm^3). The atom ratio of U:F was maintained as 1:4. The solution was stirred continuously in a 100 cm^3 polyethylene beaker and heated over a steam-bath for *ca.* 6 h until a yellow solid formed. The pH of the mother liquor was found to be *ca.* 4. The yellow solid thus formed was separated by filtration, washed several times with ethanol, and finally dried *in vacuo* over conc.H_2SO_4. The yield of $(NH_4)_4[UO_2F_6]$ was 0.6g (66.7%).

Synthesis of $[UO_2(acac)F(H_2O)_2].3H_2O$

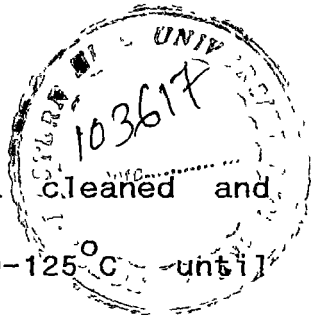
(i) An amount of 1.0g (2.79 mmol) of $UO_3.4H_2O$ in 5 cm^3 of water was reacted with 0.2 cm^3 (4.8 mmol) of 48% HF in the presence of 1.0 cm^3 (10 mmol) acacH and the resultant reaction

mixture was stirred constantly on a steam-bath for *ca.*15 min whereupon a yellow solid precipitated out.The pH of the reaction solution was found to be *ca.*3.5. The yellow solid was collected by filtration and washed with ethanol. The yield of $[UO_2(acac)F(H_2O)_2].3H_2O$ was 1.0g (77%).

(ii) Alternatively, to an aqueous suspension (5 cm^3) of 1.0g (1.98 mmol) of $UO_2(acac)_2.2H_2O$ was added 0.2 cm^3 (4.8 mmol) of 48% HF. The whole of the reaction solution upon stirring on a steam-bath for *ca.*15 min afforded a yellow solid. The pH of the reaction solution measured at this stage was *ca.*3.5. The yield of $[UO_2(acac)F(H_2O)_2].3H_2O$ was 0.7g (74%).

Synthesis of difluorodioxouranium(VI) trihydrate, $[UO_2F_2].3H_2O$

To an aqueous suspension (5 cm^3) of 1.0g (1.98 mmol) of $UO_2(C_5H_7O_2)_2.2H_2O$ in a small polyethylene beaker was added 0.5 cm^3 (12 mmol) of 48% hydrofluoric acid whereupon a clear yellow solution was formed. The pH of the solution was measured to be *ca.*2. This solution on concentration over a steam-bath produced a yellow crystalline solid, $[UO_2F_2].3H_2O$. The compound was separated by centrifugation , washed with ethanol (four or five times), and finally dried *in vacuo* over conc.H_2SO_4. Yield of the compound was 0.36g (50%).



Pyrolysis of $[UO_2F_2].3H_2O$

1.0g (2.76 mmol) of $[UO_2F_2].3H_2O$ was taken in a cleaned and preweighed platinum crucible and heated at 120-125 °C until constant weight. On cooling to room temperature, yellow UO_2F_2 was obtained. The starting compound underwent 14.6% loss in weight. The calculated weight loss corresponding to the expulsion of three molecules of water per formula weight was 14.93%.

Synthesis of $K_2[UO_2(acac)F_3]$

Uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$ (1.0g, 1.99 mmol) was dissolved in water (15 cm^3) followed by the addition of 20% KOH solution until a yellow precipitate ceased to appear. The precipitate was filtered off and washed free from alkali and nitrate. To a suspension of the yellow precipitate in an excess of acetylacetone (10 cm^3, 100 mmol) was added (0.7g, 12 mmol) of KF maintaining the atom ratio of U:F at 1:6. The reaction solution was stirred constantly over a steam-bath for *ca.*2h until the formation of a bright yellow compound was complete. The pH of the reaction solution at this stage was measured to be *ca.*3.5. The compound was separated by filtration and dried *in vacuo* over conc.H_2SO_4. The yield of $K_2[UO_2(acac)F_3]$ was 0.7g (70%).

Synthesis of $A[UO_2(CH_3COO)_2F].3H_2O$ (A = K, Na or NH_4)

An amount of (1.0g, 1.99 mmol) of uranyl nitrate hexahydrate,

$UO_2(NO_3)_2.6H_2O$ was dissolved in water (15 cm^3) followed by the addition of 20% AOH (A = K or Na) solution or aqueous ammonia (sp.gr.0.91) until a yellow precipitate ceased to appear. The precipitate was filtered off and washed free from alkali and nitrate. This was then dissolved in a minimum amount of glacial acetic acid (2 cm^3, 35 mmol). To the resulting clear solution, 0.5 cm^3 (12 mmol) of 48% HF was added. The whole upon concentration over a steam-bath afforded a lemon-yellow solid. The solid was isolated by filtration, washed with ethanol and finally dried *in vacuo* over conc.H_2SO_4. The yields of $K[UO_2(CH_3COO)_2F].3H_2O$, $Na[UO_2(CH_3COO)_2F].3H_2O$ and $NH_4[UO_2(CH_3COO)_2F].3H_2O$ were 0.6g (60%), 0.6g (62%) and 0.65g (68%), respectively.

Synthesis of $[UO_2(CH_3COO)F(H_2O)_2]$

A quantity of 1.0g (2.79 mmol) of $UO_3.4H_2O$ was dissolved in a minimum amount of glacial acetic acid (2 cm^3, 35 mmol). To the resulting clear solution, 0.2 cm^3 (4.8 mmol) of 48% HF was added and the reaction solution was concentrated over a steam-bath to afford a lemon-yellow solid. The pH of the reaction solution was *ca.*2.5. The solid was isolated by filtration, washed with ethanol and finally dried *in vacuo* over conc.H_2SO_4. The yield of $[UO_2(CH_3COO)F(H_2O)_2]$ was 0.8g (74%).

Synthesis of $A_3[UO_2(GlyH)_2F_5].3H_2O$ (A = K or NH_4)

An amount of 1.0g (2.79 mmol) of $UO_3.4H_2O$ was dissolved in an aqueous solution of a combination of aqueous HF (12 mmol) and AF (8.38 mmol) (A=K or NH_4). To the clear lemon yellow solution thus obtained, an aqueous solution (5 cm^3) of 0.42g (5.57 mmol) of glycine was added and stirred for *ca.* 10 min. The solution on being concentrated by heating on a steam-bath to nearly half of its volume afforded a lemon-yellow solid. The pH of the reaction solution recorded to be *ca.*2.5. The compound was isolated by filtration and dried *in vacuo* over conc.H_2SO_4. The yields of $K_3[UO_2(GlyH)_2F_5].3H_2O$ and $(NH_4)_3[UO_2(GlyH)_2F_5].3H_2O$ were 1.2g (63%) and 1.1g (65%), respectively.

Synthesis of $K_3[UO_2(AlanH)_2F_5].2H_2O$ and $(NH_4)_5[UO_2(CysH)_2F_5].2H_2O$

These complexes were prepared by a method similar to that employed for $A_3[UO_2(GlyH)_2F_5].3H_2O$ (A = K or NH_4), except that AHF_2 was used as the fluoridating agent instead of AF and HF. 1.0g (2.79 mmol) of $UO_3.4H_2O$ was dissolved in an aqueous solution (5 cm^3) of AHF_2 (8.37 mmol). This was followed by the addition of 5.57 mmol of L-alanine or L-cysteine to it. The pH of the resultant clear solution was measured to be *ca.*2.5. The solution on concentration on a steam-bath produced $K_3[UO_2(AlanH)_2F_5].2H_2O$ and $(NH_4)_5[UO_2(CysH)_2F_5].2H_2O$, respectively. The compounds were isolated in a manner similar to that of $A_3[UO_2(GlyH)_2F_5].3H_2O$

(A = K or NH_4). The yields of $K_3[UO_2(AlanH)_2F_5].2H_2O$ and $(NH_4)_5[UO_2(CysH)_2F_5].2H_2O$ were 1.3g (66%) and 1.4g (68%), respectively.

Treatment of $K_3[UO_2(GlyH)_2F_5].3H_2O$ *with water and isolation of* $K_5[UO_2F_7].2H_2O$

A suspension of 1.0g (1.46 mmol) of $K_3[UO_2(GlyH)_2F_5].3H_2O$ in 10 cm^3 of water was stirred constantly for *ca.*5 min whereupon the solid slowly dissolved. On further agitation, the solution deposited a bright lemon-yellow crystalline solid. The pH of the mother liquor was recorded to be *ca.*1.7. The solid thus obtained was collected by filtration and finally dried *in vacuo* over conc.H_2SO_4. The yield of $K_5[UO_2F_7].2H_2O$ was 0.7g (76%).

Elemental Analyses

Quantitative determinations of uranium, fluoride, potassium, sodium, carbon, hydrogen and nitrogen were made by the methods described in Chapter II.

The analytical and characterization data are summarized in Tables 5.1-5.7.

Results and Discussion

From the experience gathered by our group of having worked in the field of acetylacetonato compounds of metals,[37] it was

Table 5.1: Analytical Data and Solution Electrical Conductance Values of Bis(acetylacetonato) and Mixed - fluoro-(acetylacetonato) Complexes of UO_2^{2+}, $[UO_2F_2].3H_2O$ and $(NH_4)_4[UO_2F_6]$

Compound	Conductance ($\Omega^{-1}cm^2mol^{-1}$)	Element	Found (%)	Calcd. (%)
$UO_2(acac)_2.2H_2O$	–	U	47.08	47.20
		C	23.63	23.82
		H	3.74	3.61
$[UO_2(acac)F(H_2O)_2].3H_2O$	5	U	49.5	49.8
		F	4.1	4.0
		C	12.6	12.6
		H	3.6	3.6
$K_2[UO_2(acac)F_3]$	175	U	46.8	47.2
		F	11.5	11.3
		C	11.4	11.9
		H	1.7	1.4
		K	15.6	15.5
$[UO_2F_2].3H_2O$	7	U	65.9	65.7
		F	10.3	10.5
		H	1.8	1.7

Table 5.1 contd.

Compound	Conductance ($\Omega^{-1}cm^2mol^{-1}$)	Element	Found (%)	Calcd. (%)
$(NH_4)_4[UO_2F_6]$	495	U	51.87	52.17
		F	24.81	24.99
		N	12.25	12.28
		H	3.66	3.54

$acac^-$ = acetylacetonate ($C_5H_7O_2^-$)

Table 5.2: Analytical Data and Solution Electrical Conductance Values of $A[UO_2(CH_3COO)_2F].3H_2O$ (A = K, Na or NH_4) and $[UO_2(CH_3COO)F(H_2O)_2]$

Compound	Conductance ($\Omega^{-1}cm^2mol^{-1}$)	Element	Found (%)	Calcd. (%)
$K[UO_2(CH_3COO)_2F].3H_2O$	125	U	47.24	47.58
		F	3.56	3.8
		C	9.82	9.60
		H	2.18	2.42
		K	8.15	7.82
$Na[UO_2(CH_3COO)_2F].3H_2O$	130	U	49.54	49.16
		F	3.62	3.92
		C	10.15	9.92
		H	2.64	2.5
		Na	4.58	4.75
$NH_4[UO_2(CH_3COO)_2F].3H_2O$	128	U	50.12	49.67
		F	4.22	3.96
		C	10.33	10.02
		H	3.54	3.37
		N	2.66	2.92
$[UO_2(CH_3COO)F(H_2O)_2]$	6	U	60.8	62.0
		F	4.4	5.0
		C	5.8	6.3
		H	1.7	1.8

Table 5.3: Analytical Data and Solution Electrical Conductance Values of $A_3[UO_2(GlyH)_2F_5].3H_2O$ (A = K or NH_4), $K_3[UO_2(AlanH)_2F_5].2H_2O$, $(NH_4)_5[UO_2(CysH)_2F_5].2H_2O$ and $K_5[UO_2F_7].2H_2O$

Compound	Conductance ($\Omega^{-1}cm^2mol^{-1}$)	Element	Found (%)	Calcd. (%)
$K_3[UO_2(GlyH)_2F_5].3H_2O$	d	U	34.1	34.7
		F	13.6	13.8
		C	7.1	7.0
		H	2.4	2.4
		N	4.0	4.1
		K	17.3	17.1
$(NH_4)_3[UO_2(GlyH)_2F_5].3H_2O$	d	U	37.7	38.2
		F	15.4	15.2
		C	7.6	7.7
		H	4.7	4.5
		N	11.1	11.2
$K_3[UO_2(AlanH)_2F_5].2H_2O$	d	U	34.2	34.2
		F	13.5	13.6
		C	10.2	10.3
		H	2.8	2.6
		N	4.0	4.0
		K	16.8	16.8

Table 5.3 contd.

Compound	Conductance ($\Omega^{-1}cm^2mol^{-1}$)	Element	Found (%)	Calcd. (%)
$(NH_4)_5[UO_2(CysH)_2F_5].2H_2O$	d	U	32.3	32.5
		F	13.6	13.6
		C	9.6	9.9
		H	4.7	5.0
		N	13.3	13.4
$K_5[UO_2F_7].2H_2O$	590	U	37.4	37.5
		F	21.1	21.0
		K	30.6	30.8

d = decomposed in water, GlyH = glycine ($C_2H_5NO_2$), AlanH = L-alanine ($C_3H_7NO_2$), $CysH^-$ = cysteinate ($C_3H_6O_2NS^-$).

Table 5.4: IR and LR Spectral Data of Bis(acetylacetonato) and Mixed-fluoro(acetylacetonato) Complexes of UO_2^{2+}, $[UO_2F_2].3H_2O$ and $(NH_4)_4[UO_2F_6]$ with their Assignments

Compound	IR (cm^{-1})	LR (cm^{-1})	Assignment
$UO_2(acac)_2.2H_2O$	895s	-	ν(U=O)
	300m		ν(U-O)
	610m		ring def.+
			ν(U-O)
	1640m		δ(H-O-H)
	3460s		ν(O-H)
$[UO_2(acac)F(H_2O)_2].3H_2O$	369m	-	ν(U-F)
	890s		ν(U=O)
	612m		ring def.+
			ν(U-O)
	295m		ν(U-O)
	725m		$\rho_r(H_2O)$
	1635m		δ(H-O-H)
	3450s		ν(O-H)
$[UO_2F_2].3H_2O$	374m	425m	ν(U-F)
	946s		ν_{as}(U=O)ν_3
	857s	866s	δ(O-U-O)ν_1
	1625m		δ(H-O-H)
	3358s		ν(O-H)

Table 5.4 contd.

Compound	IR (cm^{-1})	LR (cm^{-1})	Assignment
$K_2[UO_2(acac)F_3]$	366m	438m	ν(U-F)
	900s	890s	ν(U=O)
	615m		ring def.+
			ν(U-O)
	290m		ν(U-O)
$(NH_4)_4[UO_2F_6]$	356m	340m	ν(U-F)
	-	853s	δ(O-U-O)ν_1
	913s	951m	ν(U=O)ν_3
	1418s	1379s	ν(N-H)ν_4
	3025s		ν(N-H)ν_1
	3160m		ν(N-H)ν_3

Table 5.5: Mass Spectrometric Data for $UO_2(C_5H_7O_2)_2$

Assignment	m/z	Intensity(%)
$[UO_2(C_5H_7O_2)_2]^+$	468	54
$[UO_2(C_5H_7O_2)(C_4H_4O_2)]^+$	453	10
$[UO_2(C_5H_7O_2)(C_3H_5O)]^+$	426	10
$[UO_2(C_5H_7O_2)]^+$	369	100
$[UO_2(C_4H_4O_2)]^+$	354	14
$[UO_2(C_5H_5O)]^+$	351	4
$[UO_2]^+$	270	47

Table 5.6: IR Spectral Data of $A[UO_2(CH_3COO)_2F].3H_2O$ (A = K, Na or NH_4) with their Assignments

Compound	IR (cm^{-1})	Assignment
$K[UO_2(CH_3COO)_2F].3H_2O$	388m	ν(U-F)
	924s	ν(U=O)
	1468s	ν_s(OCO)
	1553s	ν_{as}(OCO)
	679m	δ(OCO)
	1629m	δ(H-O-H)
	3462m	ν(O-H)
$Na[UO_2(CH_3COO)_2F].3H_2O$	389m	ν(U-F)
	934s	ν(U=O)
	1469s	ν_s(OCO)
	1565s	ν_{as}(OCO)
	678m	δ(OCO)
	1630m	δ(H-O-H)
	3447m	ν(O-H)
$NH_4[UO_2(CH_3COO)_2F].3H_2O$	382m	ν(U-F)
	925s	ν(U=O)
	1468s	ν_s(OCO)
	1550s	ν_{as}(OCO)
	680m	δ(OCO)
	1631m	δ(H-O-H)
	3462m	ν(O-H)
	1403s	ν(N-H)ν_4

Table 5.6 contd.

Compound	IR (cm^{-1})	Assignment
$[UO_2(CH_3COO)F(H_2O)_2]$	387m	ν(U-F)
	905s	ν(U=O)
	1468s	ν_s(OCO)
	1545s	ν_{as}(OCO)
	725m	$\rho_r(H_2O)$
	670m	δ(OCO)

Table 5.7: IR and LR Spectral Data of $A_3[UO_2(GlyH)_2F_5].3H_2O$ (A = K or NH_4), $K_3[UO_2(AlanH)_2F_5].2H_2O$, $(NH_4)_5[UO_2(CysH)_2F_5].2H_2O$ and $K_5[UO_2F_7].2H_2O$ with their Assignments

Compound	IR (cm^{-1})	LR (cm^{-1})	Assignment
$K_3[UO_2(GlyH)_2F_5].3H_2O$	377m	-	ν(U-F)
	900s		ν(U=O)
	1585s		$\nu_{as}(COO^-)$
	1400s		$\nu_s(COO^-)$
	1120m		$\rho_r(NH_3^+)$
	680m		$\rho_w(COO^-)$
	580m		$\delta(COO^-)$
	1645m		δ(H-O-H)
	3450m		ν(O-H)
$(NH_4)_3[UO_2(GlyH)_2F_5].3H_2O$	372m	-	ν(U-F)
	910s		ν(U=O)
	1590s		$\nu_{as}(COO^-)$
	1402s		$\nu_s(COO^-)$
	1115m		$\rho_r(NH_3^+)$
	680m		$\rho_w(COO^-)$
	585m		$\delta(COO^-)$
	1640m		δ(H-O-H)
	3445m		ν(O-H)
	1420s		ν(N-H)ν_4

Table 5.7 contd.

Compound	IR (cm^{-1})	LR (cm^{-1})	Assignment
$K_3[UO_2(AlanH)_2F_5].2H_2O$	374m	-	ν(U-F)
	905s		ν(U=O)
	1600s		$\nu_{as}(COO^-)$
	1395s		$\nu_s(COO^-)$
	1110m		$\rho_r(NH_3^+)$
	685m		$\rho_w(COO^-)$
	575m		$\delta(COO^-)$
	1630m		δ(H-O-H)
	3440m		ν(O-H)
$(NH_4)_5[UO_2(CysH)_2F_5].2H_2O$	372m	-	ν(U-F)
	902s		ν(U=O)
	1650s		$\nu_{as}(COO^-)$
	1385s		$\nu_s(COO^-)$
	451m		ν(U-O)
	2568m		ν(S-H)
	1418s		ν(N-H)ν_4
	1483m		NH_3^+ (symm.def.)
	1640m		δ(H-O-H)
	3440m		ν(O-H)
$K_5[UO_2F_7].2H_2O$	373m	314m	ν(U-F)
	866s	920s	ν(U=O)
	1640m		δ(H-O-H)
	3460m		ν(O-H)

anticipated that an interaction of basic uranium trioxide with weakly acidic acetylacetone ($C_5H_8O_2$) might provide a straight access to the desired compound. In accord with this, $UO_3.4H_2O$ was reacted with acacH under warming when uranium trioxide dissolved completly in a few minutes producing an orange yellow solution. The pH of the solution was found to be 5-5.5 providing a condition suitable for the chelation of $acac^-$ ($C_5H_7O_2^-$) with UO_2^{2+} centre. The coloured solution on being cooled to room temperature (*ca.* 20°C) afforded orange yellow crystalline $UO_2(acac)_2.2H_2O$ in a nearly quantitative yield.

$$UO_3 + 2C_5H_8O_2 \longrightarrow UO_2(C_5H_7O_2)_2.2H_2O + H_2O$$

The colour, appearance, solubility properties and the results of elemental analyses as well as those of IR spectral measurements conform to the identity of the product as bis(acetylacetonato)-dioxouranium(VI) dihydrate and agree very well with those reported in the literature[26,27] for a similar compound. The notable feature in the IR spectrum (Fig. 5.1) of $UO_2(acac)_2.2H_2O$ has been the observance of a medium intensity band at *ca.* 340 cm^{-1} owing its origin to ν(U-O) arising from the coordinated acetylacetonate, which is a characteristic feature for metal acetylacetonates.[38a] To adduce further support to its identity, mass spectrum (Fig.5.2) of the compound was recorded with the ion-source temperature being maintained at 100°C. The compound was held in the ion-source prior

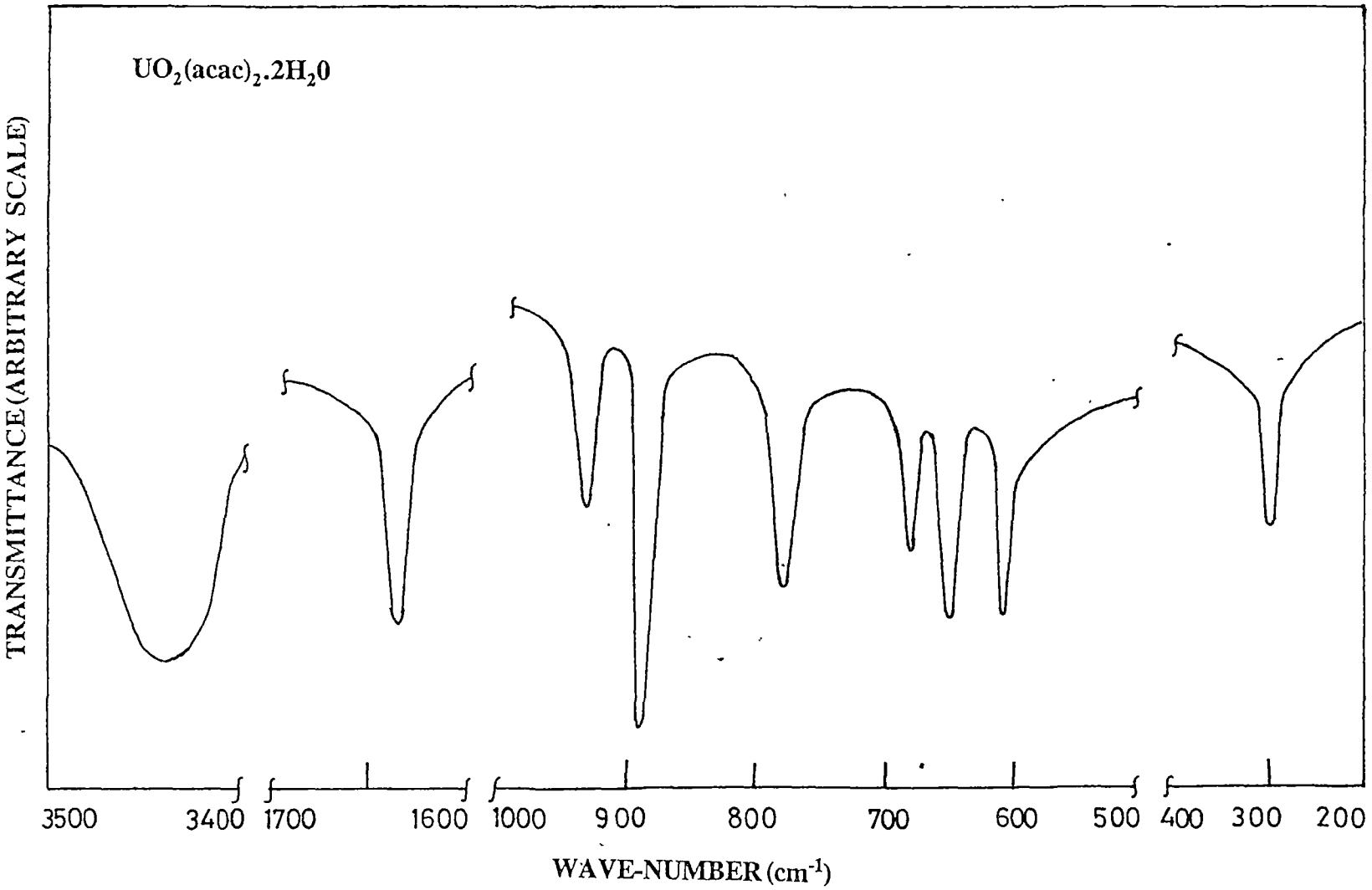


FIG. 5.1: IR SPECTRUM

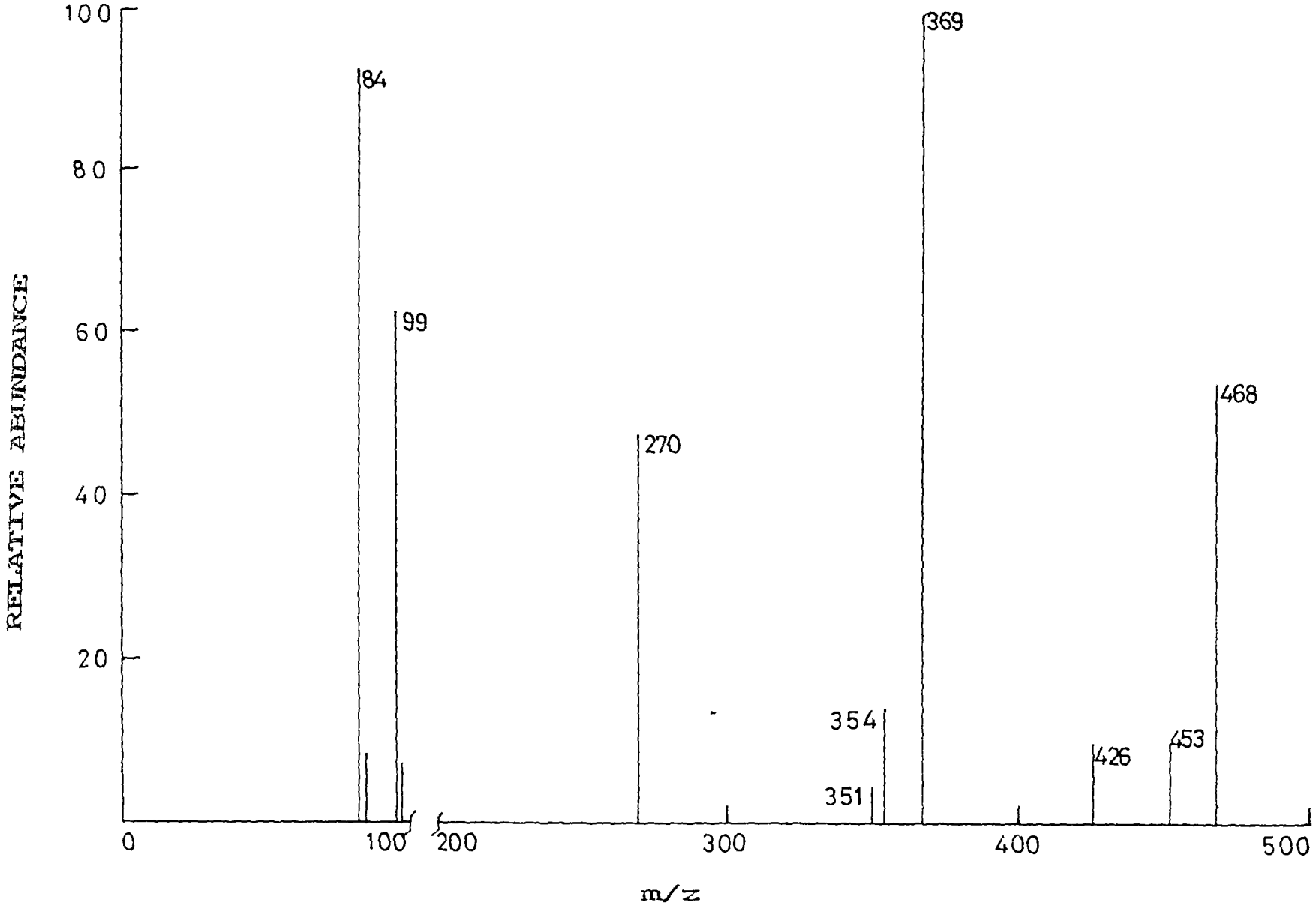


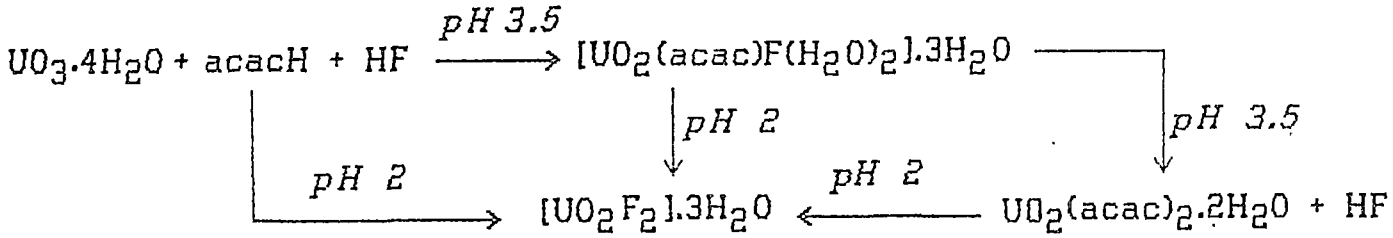
FIG. 5.2: MASS SPECTRUM OF $UO_2(C_5H_7O_2)_2$

to ionization by electron impact for *ca.* 20 min. in order to make the compound anhydrous. The salient features of the mass spectrum were a parent ion signal at m/z 468 (55%) owing to $[UO_2(C_5H_7O_2)_2]^+$, the most dominant signal at m/z 369 (100%) due to $[UO_2(C_5H_7O_2)]^+$ and a medium intensity signal at m/z 270 (45%) assigned to $[UO_2]^+$. The general pattern of the spectrum is similar to that reported in 1986.[27] The observed mass spectral features thus conform to the identity of the compound as $UO_2(C_5H_7O_2)_2.2H_2O$. The advantages of the new synthetic procedure are that it is a straight method for accessing $UO_2(acac)_2.2H_2O$ in a very high yield and it does not require any buffer to maintain the appropriate pH and accordingly no contamination is apprehended. In addition, the new method does not need any extra preparation and purification steps, thereby rendering this procedure superior to the existing ones.

Reactions of $UO_2(acac)_2.2H_2O$

An acetylacetonate ($C_5H_7O_2^-$) ligand generally binds the metal centre through two of its oxygen atoms. It was anticipated that the ligand would be detached in the presence of an acid to produce acetylacetone ($C_5H_8O_2$) and UO_2^{2+} *in situ.* The uranyl ion would then interact with the nucleophile, F^-, to afford fluoro compounds of the metal. Alternatively, the reaction might as well proceed

through the formation of intermediate fluoro(acetylacetonato)dioxouranate(VI) complex ions to finally produce oxofluorouranates(VI). With this being the strategy, two different reactions of $UO_2(acac)_2.2H_2O$ with NH_4F and aqueous HF were conducted separately. The reaction of $UO_2(acac)_2.2H_2O$ with NH_4F (molar stoichiometry of U:F as 1:4) in an acetylacetone medium containing a trace of water at pH 4 led to the first synthesis of yellow microcrystalline $(NH_4)_4[UO_2F_6]$, while the reaction of $UO_2(acac)_2.2H_2O$ produced *in situ* by interacting $UO_3.4H_2O$ with acacH and a controlled amount of aq. HF at pH 3.5 (attained spontaneously) afforded the molecular $[UO_2(acac)F(H_2O)_2].3H_2O$ complex. However, on lowering the pH to *ca.* 2 by further addition of aq. HF, a known fluoro compound $[UO_2F_2].3H_2O$ was obtained. It may be mentioned that in two separate reactions $UO_2(acac)_2.2H_2O$ and $[UO_2(acac)F(H_2O)_2].3H_2O$ were reacted with excess of aqueous HF to yield $[UO_2(acac)F(H_2O)_2].3H_2O$ and $[UO_2F_2].3H_2O$, respectively. An important implication of the observed sequential loss of coordinated acetylacetonate ligands from $UO_2(acac)_2.2H_2O$ at pH 3.5 and pH 2 is that an enhanced acidity appears to be detrimental to the formation of fluoro(acetylacetonato) complexes of the metal. In other words, $[UO_2(acac)F(H_2O)_2].3H_2O$ may be regarded as an isolable intermediate in the process $UO_2(acac)_2.2H_2O$ to $[UO_2F_2].3H_2O$.



Uranyl fluoride hydrate was synthesized as a precursor of UO_2F_2. Indeed, on being pyrolysed at 120-125^{o}C to constant weight, the yellow $[UO_2F_2].3H_2O$ suffered a weight loss of 14.6%. This corresponds to a loss of three molecules of water per formula weight (calculated loss 14.93%) of the compound.

On having ascertained a pH of 3.5 being suitable for the synthesis of $[UO_2(acac)F(H_2O)_2].3H_2O$, it was conjectured that this pH might as well conduce the formation of fluoro(acetylacetonato) compounds of the metal. Incidentally, the reaction of $K_2U_2O_7$ with KF and acacH gave rise to a natural pH of *ca.* 3.5, thereby affording $K_2[UO_2(acac)F_3]$ in support of our contention.

The complexes have been characterized by a combination of elemental analyses, solution electrical conductance measurements, IR and Laser Raman spectroscopic studies. Based upon the elemental

analyses, the molecular weights of each of the compounds was calculated and then their molar conductance in water was recorded. The solution electrical conductance values of 495, 5, 7 and 175 $\Omega^{-1}cm^2mol^{-1}$ favoured the occurrence of 4:1 electrolytic, two non-electrolytic and 2:1 electrolytic complexes, respetively. The complexes were therefore formulated as $(NH_4)_4[UO_2F_6]$, $[UO_2(acac)F(H_2O)_2].3H_2O$, $[UO_2F_2].3H_2O$ and $K_2[UO_2(acac)F_3]$, respectively.

The structural assessment of the compounds has been based upon the results of IR and laser Raman (LR) spectroscopic investigations. The common features in the IR spectra of the compounds were bands due to ν(U=O)[38b,39] [trans.linked O=U=O] and ν(U-F)[40] mode of coordinated fluoride in the region *ca.* 910 cm^{-1} and *ca.* 365 cm^{-1}, respectively. Typically in the IR spectrum (Fig.5.3) of $(NH_4)_4[UO_2F_6]$, the corresponding bands were observed at 913 and 356 cm^{-1}, respectively. In addition, IR features attributed to the NH_4^+ ion were observed at 3160m, 3025s and 1418s cm^{-1}. These correlate very well with those observed for the ammonium ion of fluorometallate systems and have been assigned to the ν_3, ν_1 and ν_4 modes of NH_4^+.[38c] The IR spectra (Figs. 5.4 and 5.5) of $[UO_2(acac)F(H_2O)_2].3H_2O$ and $K_2[UO_2(acac)F_3]$ displayed additional bands typical of chelated acetylacetonate[38a] in the region *ca.* 610 and *ca.* 295 cm^{-1} attributed to the ring def. + ν(U-O) and ν(U-O) modes, respectively.

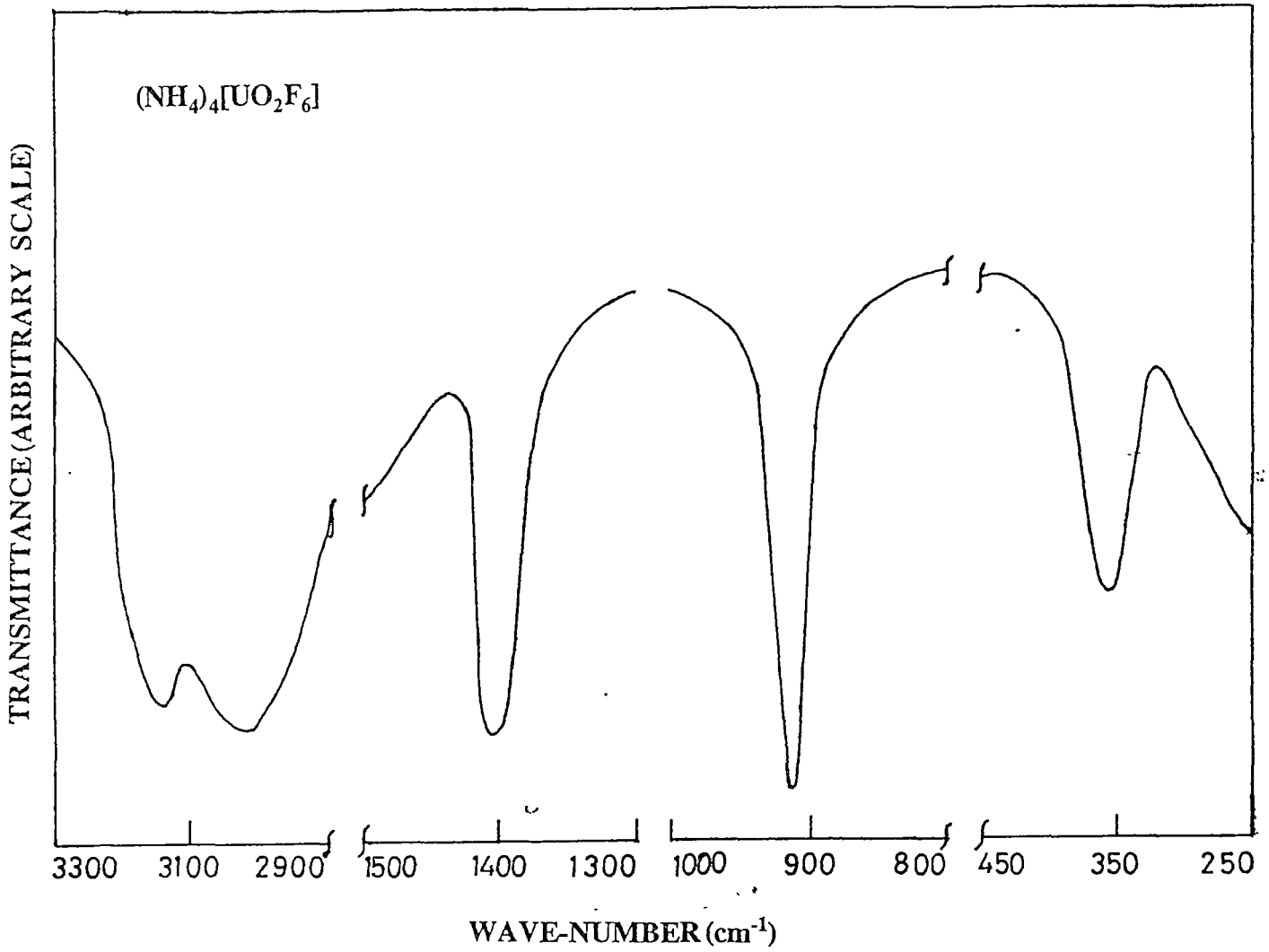


FIG. 5.3: IR SPECTRUM

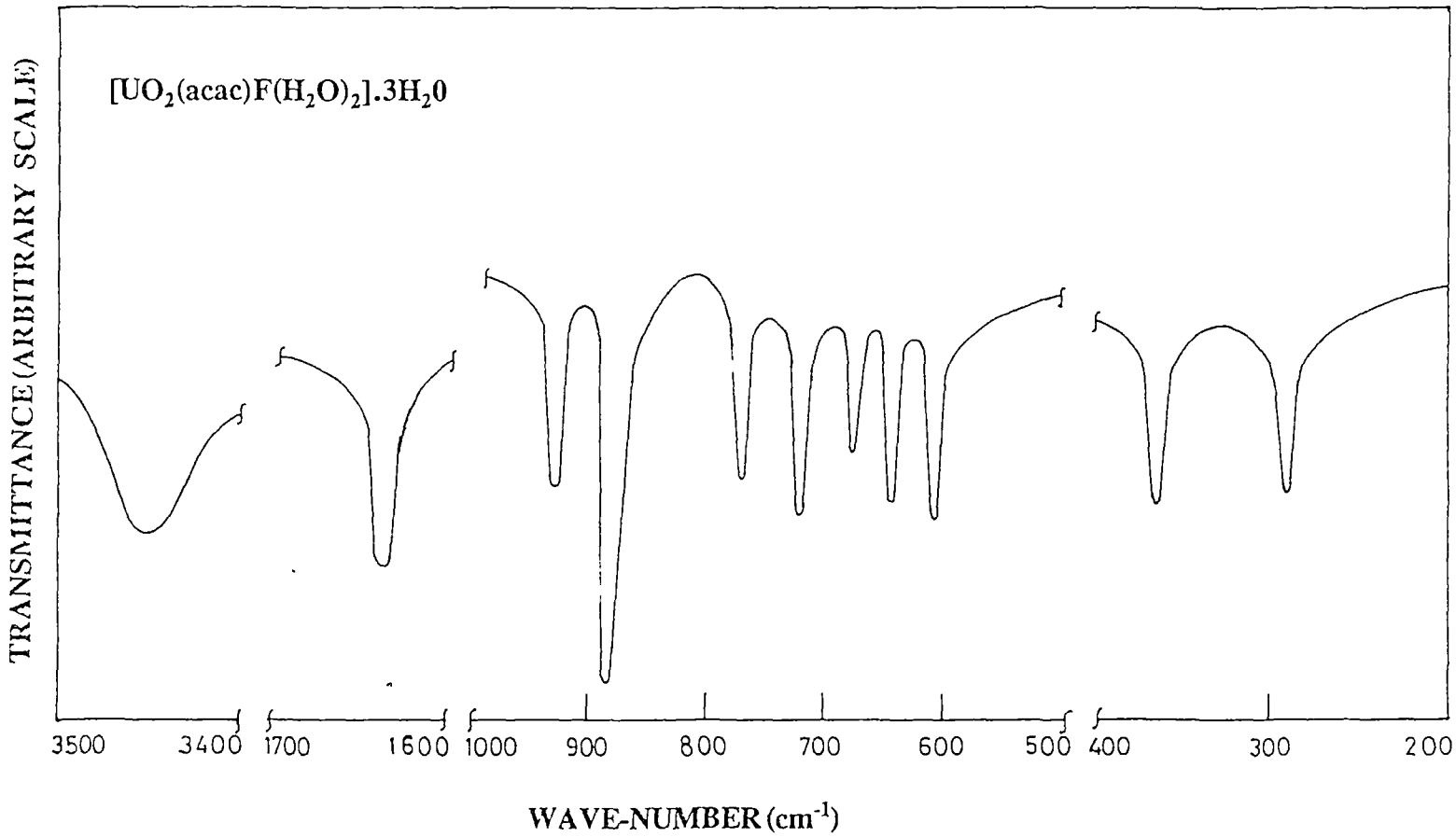


FIG. 5.4: IR SPECTRUM

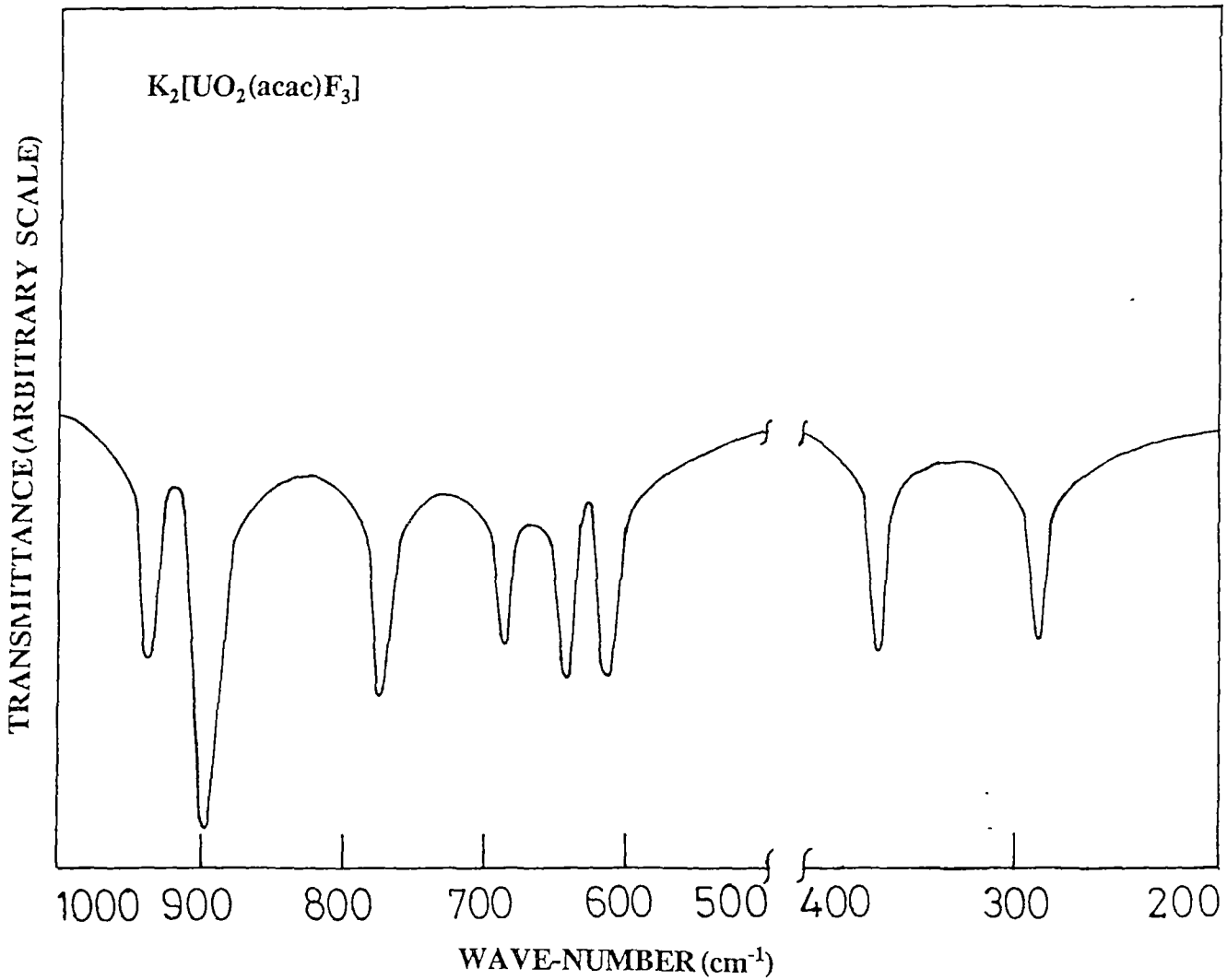


FIG. 5.5: IR SPECTRUM

The broad nature of the ν(U-F) band at 374 cm^{-1} in the IR spectrum (Fig.5.6) of $[UO_2F_2].3H_2O$ indicates the occurrence of -U-F-U-F-U-F- interactions in the crystal lattice. The spectrum also conforms to the presence of lattice water and the absorptions originating from δ(H-O-H) and ν(O-H) have been observed at 1625 and 3358 cm^{-1}, respectively. Broadening of the ν(O-H) band and its lowering in position in comparison to that of free water are clear indications of hydrogen bonding of H_2O with coordinated fluoride. It is relevant to mention at this stage that the pyrolysed product of $[UO_2F_2].3H_2O$ did not display any characteristics of lattice water in its IR spectrum.

In order to complement the IR spectroscopic results, laser Raman (LR) spectra of the compounds were recorded on the solids. Fortunately, the absorptions due to ν(U=O) and ν(U-F) in each of the compounds $(NH_4)_4[UO_2F_6]$ (Fig.5.7), $K_2[UO_2(acac)F_3$ (Fig.5.8) and $[UO_2F_2].3H_2O$ (Fig.5.9) were Raman active except for the complex $[UO_2(acac)F(H_2O)_2].3H_2O$ which did not display any pattern owing to extensive fluoroscence. For example, the Raman signals for the complex $(NH_4)_4[UO_2F_6]$ were observed at *ca.* 951, *ca.* 853, *ca.* 340 and *ca.* 1379 cm^{-1}, which have been assigned as the ν(U=O)ν_3, δ(O-U-O) [trans.linked O=U=O], ν(U-F) and ν(N-H)ν_4, respectively. The results of IR and LR spectroscopic studies, solution electrical conductance measurements and elemental analyses are thus in full agreement with the assigned formulae.

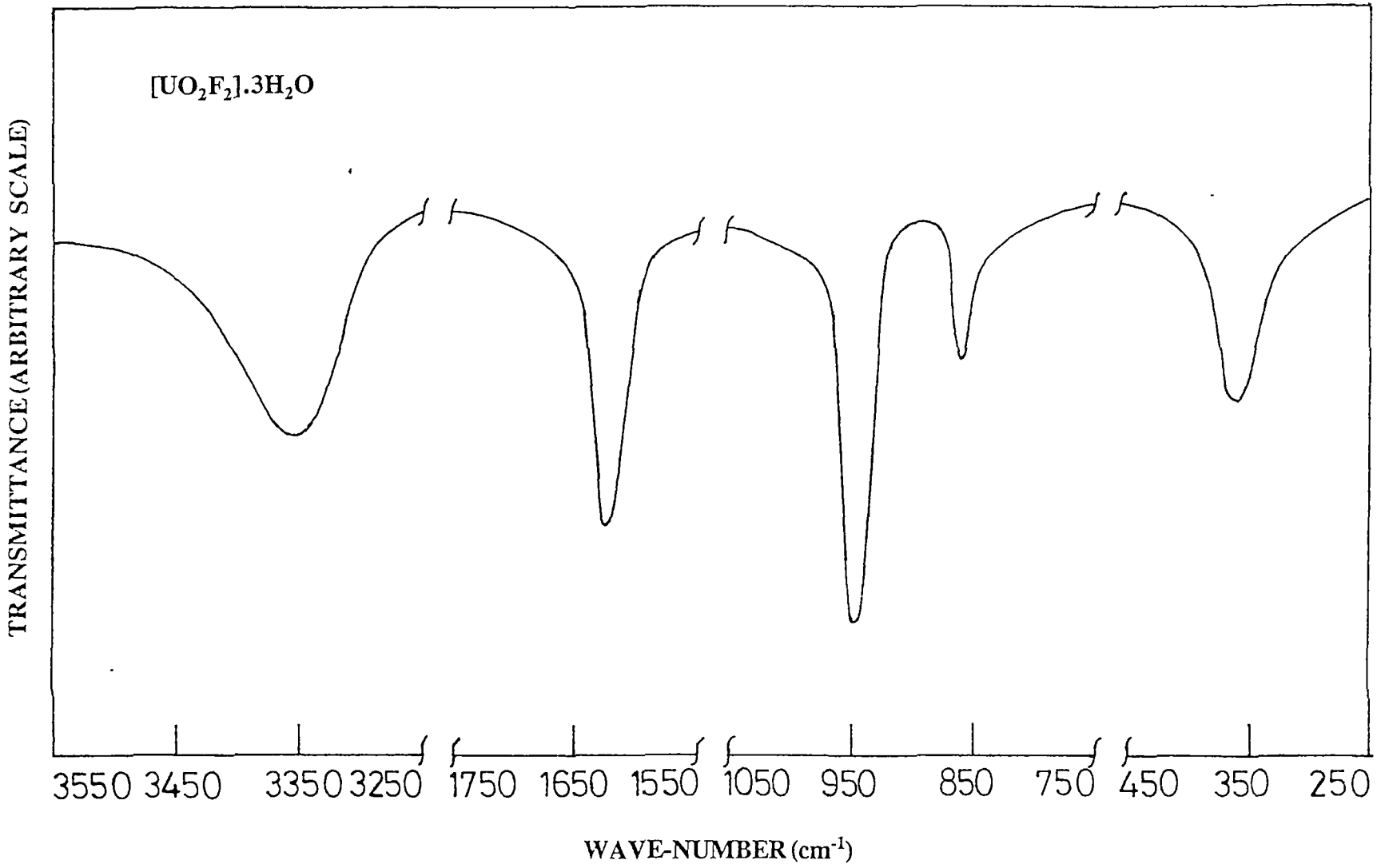


FIG. 5.6: IR SPECTRUM

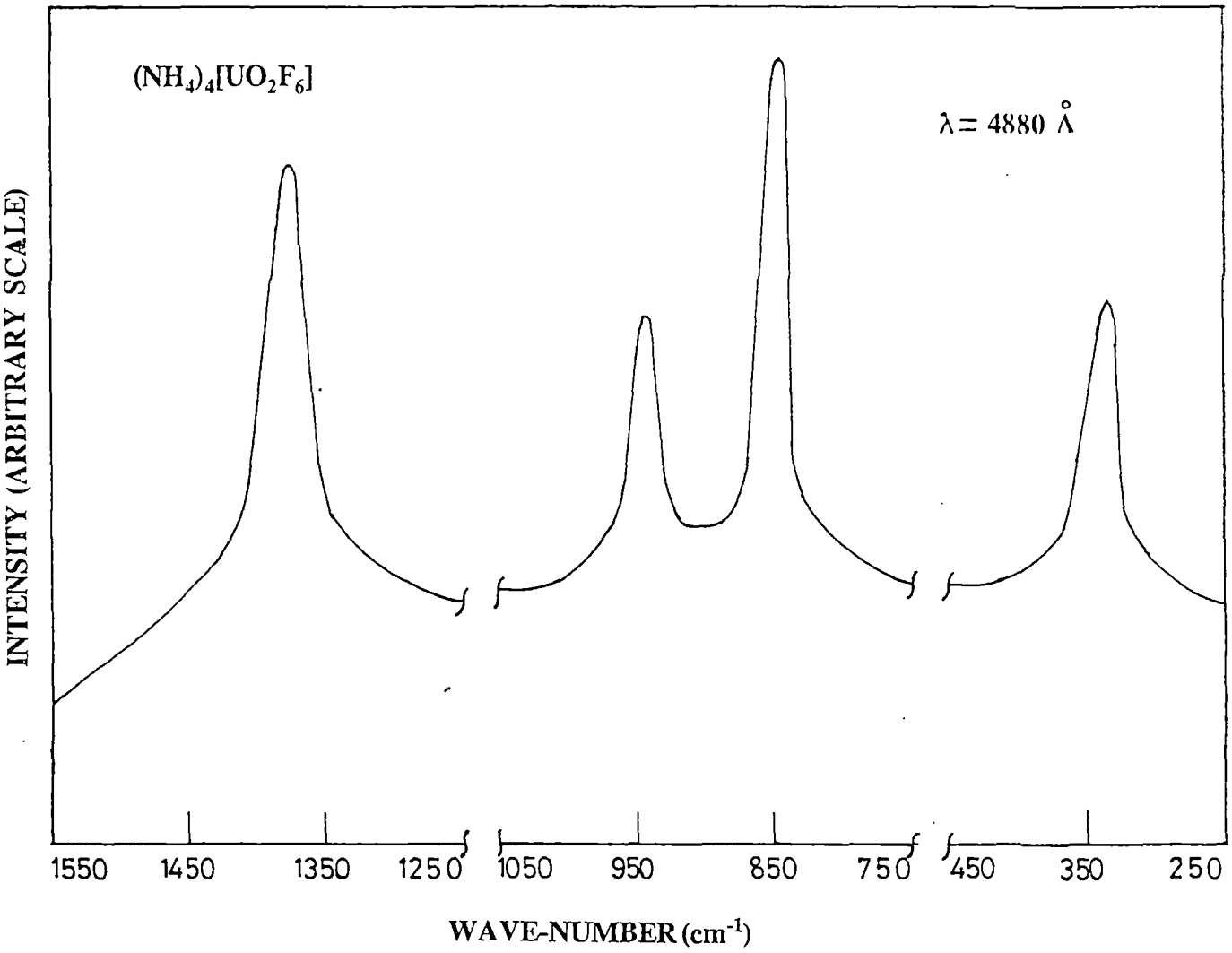


FIG. 5.7: RAMAN SPECTRUM

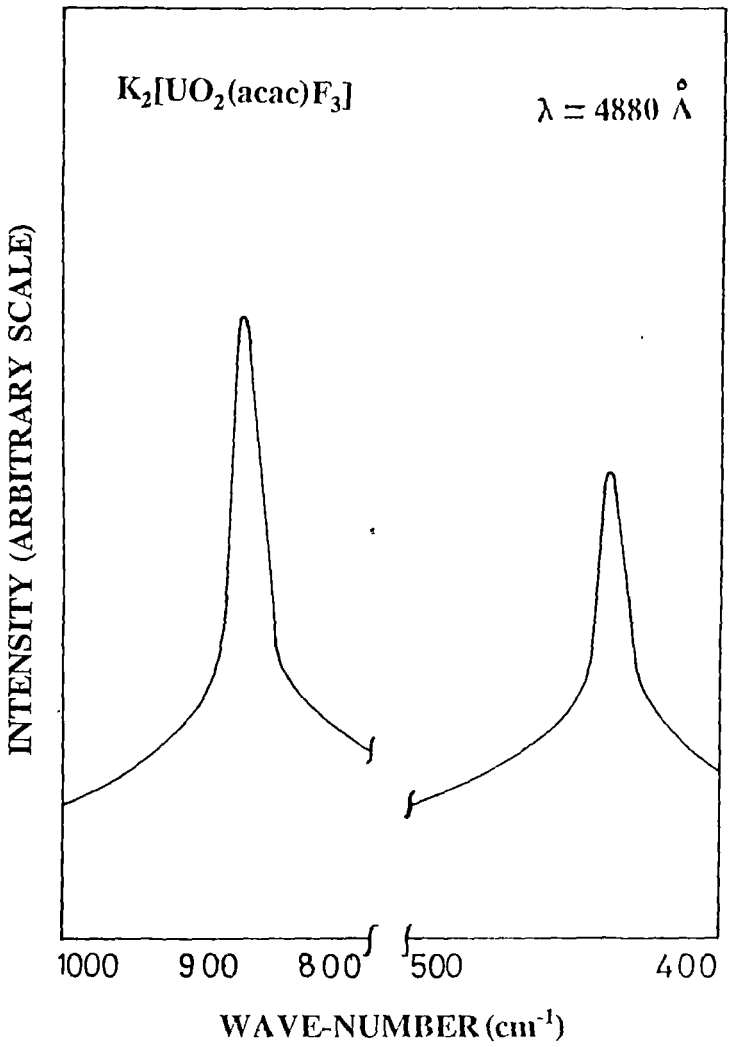


FIG. 5.8: RAMAN SPECTRUM

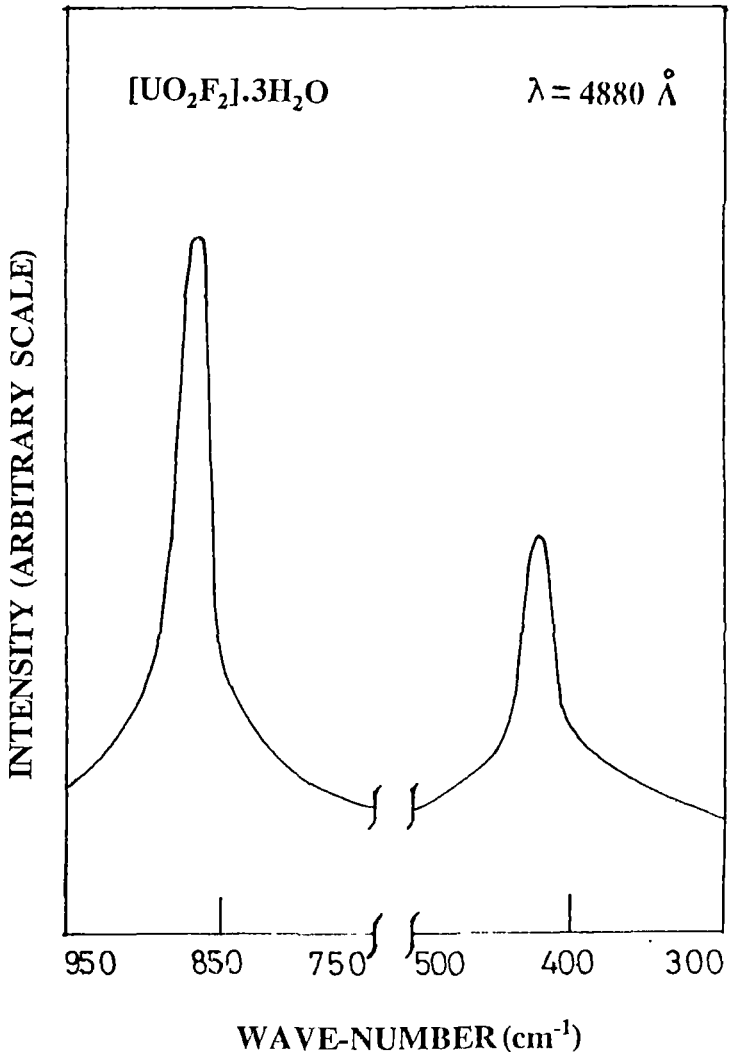
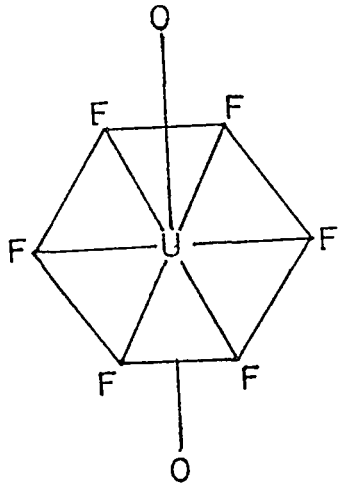


FIG. 5.9: RAMAN SPECTRUM



Tentative Structure of $[UO_2F_6]^{4-}$

Mixed-Ligand Fluoro(acetato)dioxouranates(VI)

The only report on fluoro(acetato) complexes of UO_2^{2+} was that involving the synthesis of the ammonium salt of the $[UO_2(CH_3COO)_2F]^-$ complex [41] ion obtained from the reaction of uranyl acetate with ammonium fluoride. Critically speaking, the chances of contamination of the end product by ammonium acetate in such a methodology cannot be ruled out. Surprisingly, there has been no mention of the corresponding Na and K salts in the literature. In view of this, it was proposed to provide access to the missing Na and K salts of the $[UO_2(CH_3COO)_2F]^-$ complex species. And accordingly, the reaction of $A_2U_2O_7$ (A = K, Na or NH_4) with HOAc in the presence of aq. HF afforded the desired fluoro(acetato) complexes $A_2[UO_2(CH_3COO)_2F].3H_2O$ (A = K, Na or

NH_4), thereby enabling us not only to provide the missing Na and K salts but also to develop a general synthetic methodology for the salts of the $[UO_2(CH_3COO)_2F]^-$ complex species.

Having successfully synthesized the $[UO_2(acac)F(H_2O)_2].3H_2O$ complex from the reaction of $UO_3.4H_2O$ with aq. HF in the presence of acacH, it was anticipated that by adapting a similar synthetic methodology, molecular mixed-ligand fluoro complexes of UO_2^{2+} could be accessed with the co-ligand drawn from a weak acid. Thus, $UO_3.4H_2O$ on being reacted with aqueous HF and glacial acetic acid afforded $[UO_2(CH_3COO)F(H_2O)_2]$.

The fluoro(acetato) complexes of uranyl are lemon yellow crystalline solids highly soluble in water. The solution electrical conductances for the ionic as well as the molecular complexes in water were in the range 105-110 and 8 $\Omega^{-1}cm^2mol^{-1}$, respectively, in conformity with their 1:1 electrolytic and non-electrolytic nature.

The IR spectra (Figs.5.10-5.13) of the fluoro(acetato)dioxo-uranates(VI) exhibited bands typical of uranyl moeity at *ca.* 920 cm^{-1} [ν(U=O)]; coordinated fluoride at *ca.* 385 cm^{-1} due to [ν(U-F)], bands due to lattice water[38d] in their usual positions and bands due to coordinated acetate. Of particular interest were the absorptions at *ca.* 1550s, *ca.* 1468s and *ca.* 675m cm^{-1} assigned as $\nu_{as}(COO^-)$, $\nu_s(COO^-)$ and $\delta(COO^-)$, which clearly indicates the

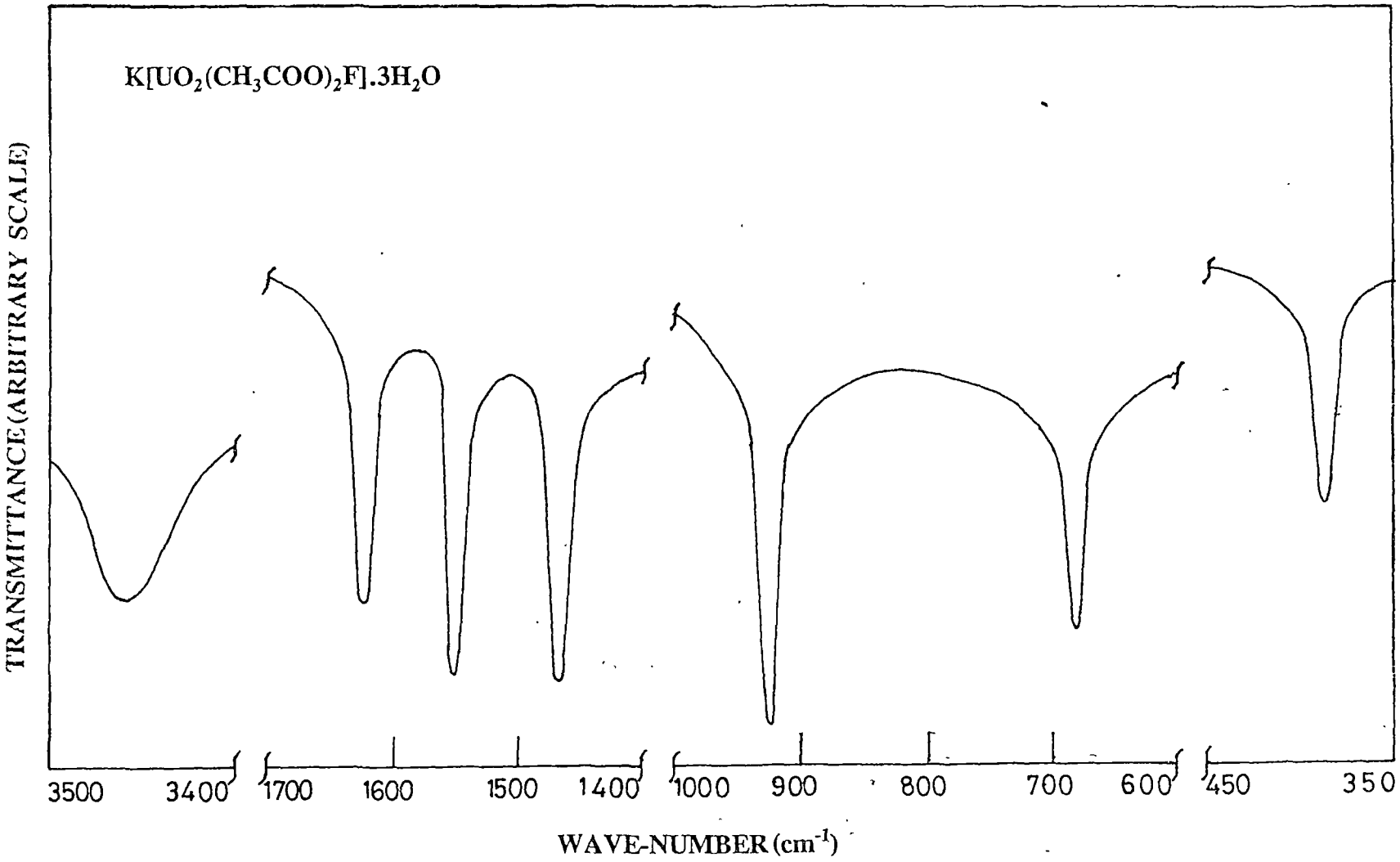


FIG. 5.10: IR SPECTRUM

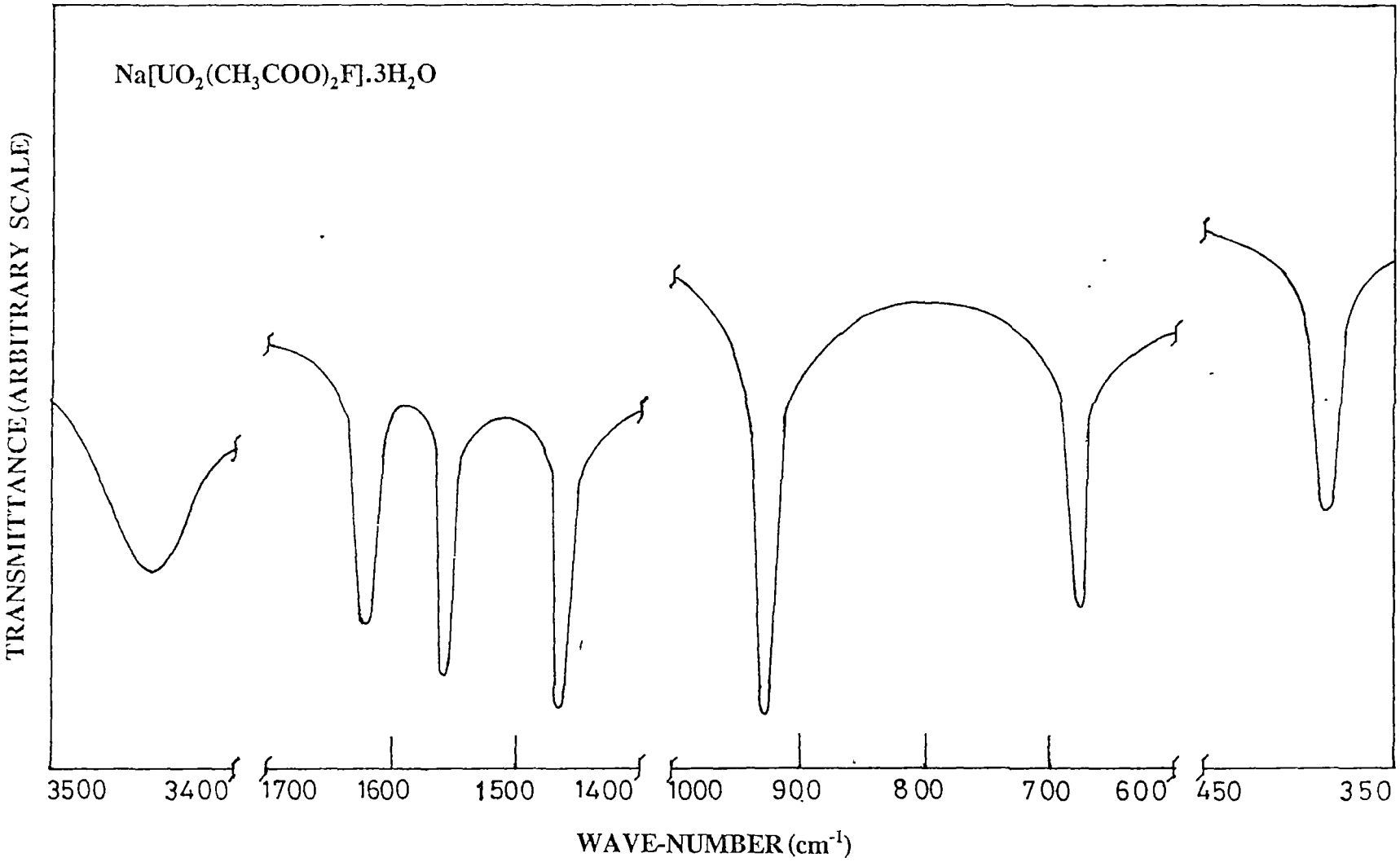


FIG. 5.11: IR SPECTRUM

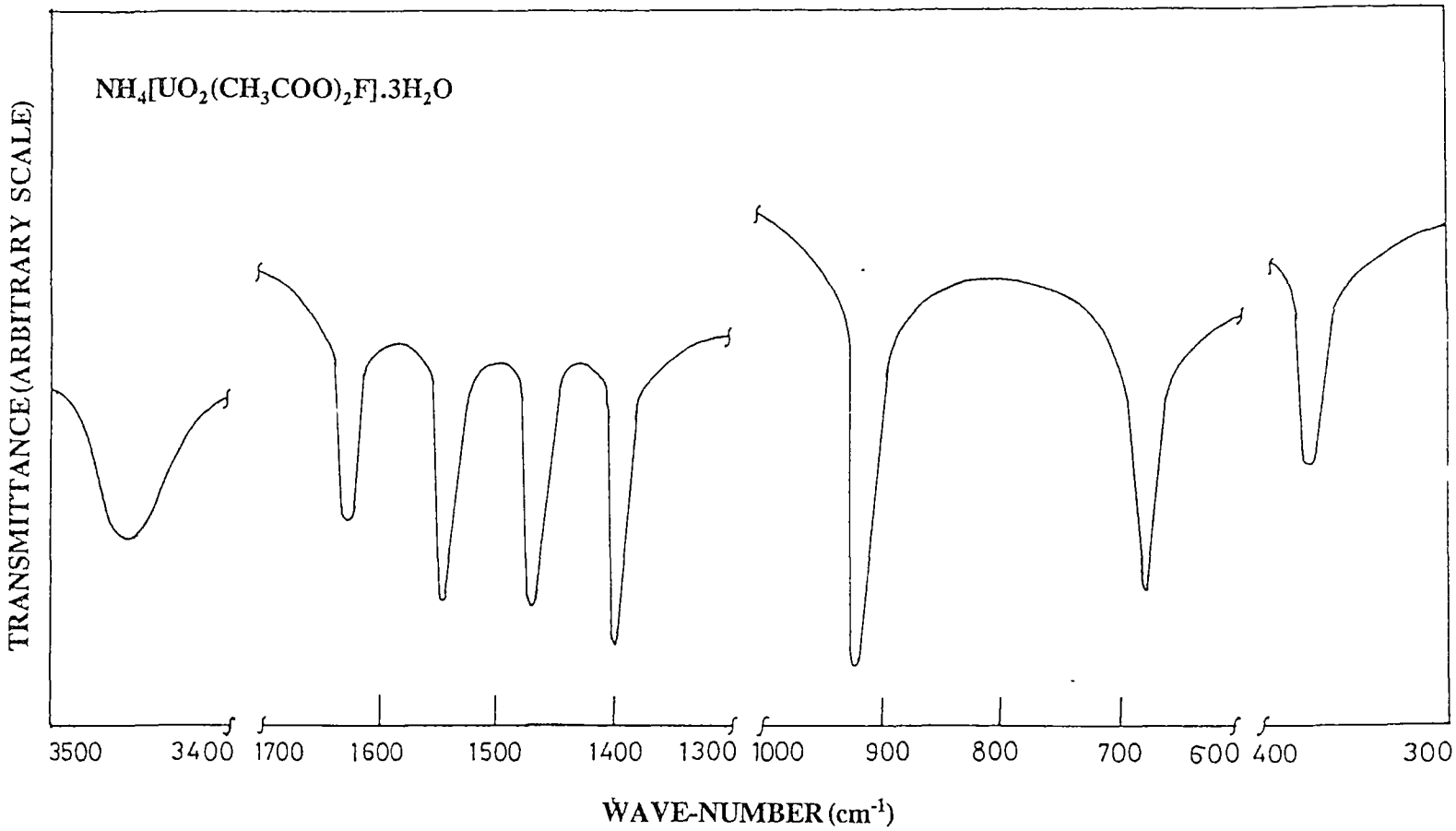


FIG. 5.12: IR SPECTRUM

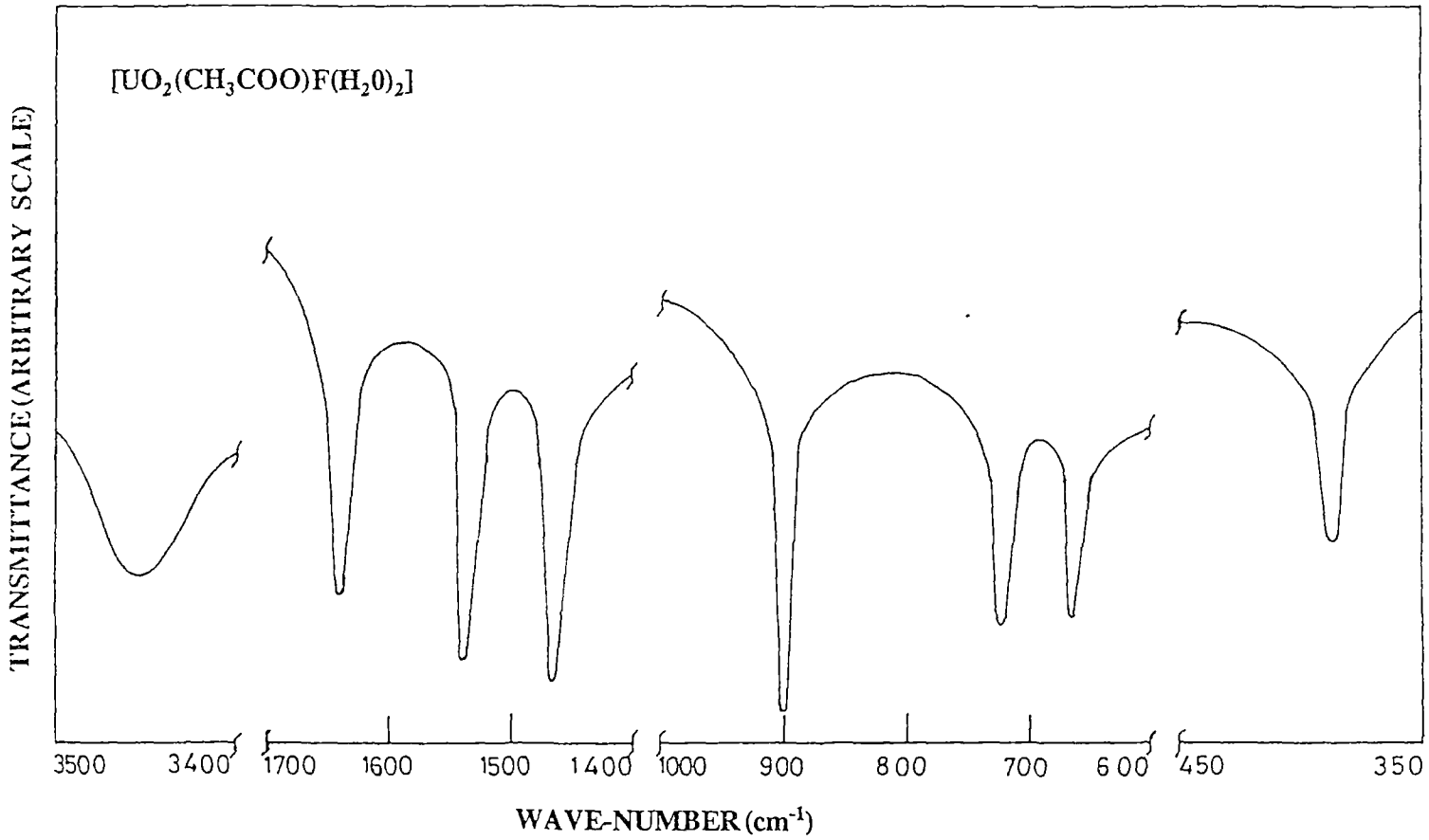


FIG. 5.13: IR SPECTRUM

coordination of acetate to the metal centre in a chelated manner.[38e]

Mixed-Ligand Fluorodioxouranates(VI) with Amino Acids as the Co-Ligands

Interestingly, UO_2^{2+} has the tendency to form complexes with amino acids as well. This and the well known history of fluorouranates(VI) caused us to perceive that under appropriate experimental conditions, interaction of amino acids and fluoride with UO_2^{2+} in an aqueous solution might be a very reasonable synthetic proposition to obtain the desired complex fluorouranates(VI). An important parameter for achieving the goal would be the pH of the reaction medium.

It is known[42] that amino acids do not coordinate with UO_2^{2+} below pH *ca*.1.8, while above pH 4-4.5 there exists a strong tendency for hydrolysis of the complexes. Further, pH titration and solvent extraction experiments described in an earlier study[43] provided evidence for the formation of binary uranyl-amino acid complexes at pH *ca.* 2. It was therefore anticipated that a pH range of 2-4.5 would be conducive for the coordination of an amino acid to UO_2^{2+} in the presence of F^-. The amino carboxylic acids chosen for the present study were glycine (GlyH), L-alanine (AlanH) and L-cysteine ($CysH_2$).

In line with the elicit strategy, $UO_3.4H_2O$ was reacted with AHF_2 (A = K or NH_4) in the case of L-alanine and L-cysteine or a combination of AF (A = K or NH_4) and HF in the case of glycine. The natural pH of the reaction medium was recorded to be *ca.* 2.5, a value which incidentally happens to fall in the range suitable for the coordination of the chosen co-ligands. The complexes thus were isolated as $A_3[UO_2(GlyH)_2F_5].3H_2O$ (A = K or NH_4); $K_3[UO_2(AlanH)_2F_5].2H_2O$ and $(NH_4)_5[UO_2(CysH)_2F_5].2H_2O$.

The mixed-fluoro(glycine) and fluoro(alanine) complexes of UO_2^{2+} are lemon-yellow in colour while the mixed-fluoro(cysteinate) complex of UO_2^{2+} is green. Owing to their instability in aqueous medium, solution electrical conductance measurements were not attempted at. The compounds have been subjected to vibrational spectroscopic studies in order to ascertain the mode of coordination of amino acids. The important IR spectral features (Figs.5.14-5.17) in each of the complexes were absorptions due to ν(U=O) at *ca.* 900 cm^{-1}, band due to coordinated fluoride at *ca.*375 cm^{-1} owing its origin to ν(U-F), bands due to lattice water at *ca.* 1640 [δ(H-O-H)] and at *ca.* 3450 cm^{-1} [ν(O-H)] and bands due to NH_4^+ ion at 1420s [ν(N-H)ν_4]. Besides the pattern originating from UO_2^{2+}, coordinated fluoride, lattice water and ammonium ion, the complexes exhibited bands due to coordinated amino acid as well.

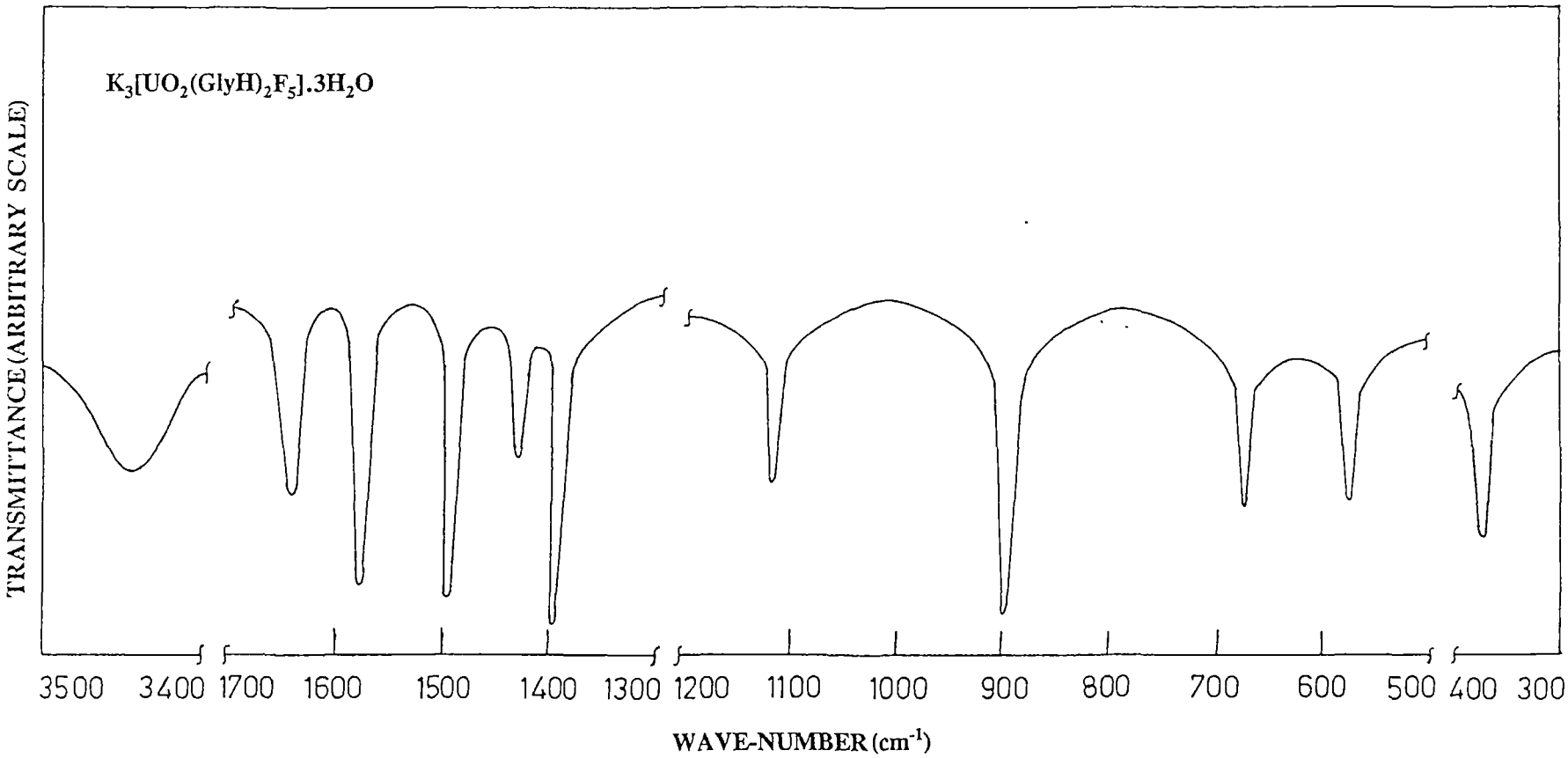


FIG. 5.14: IR SPECTRUM

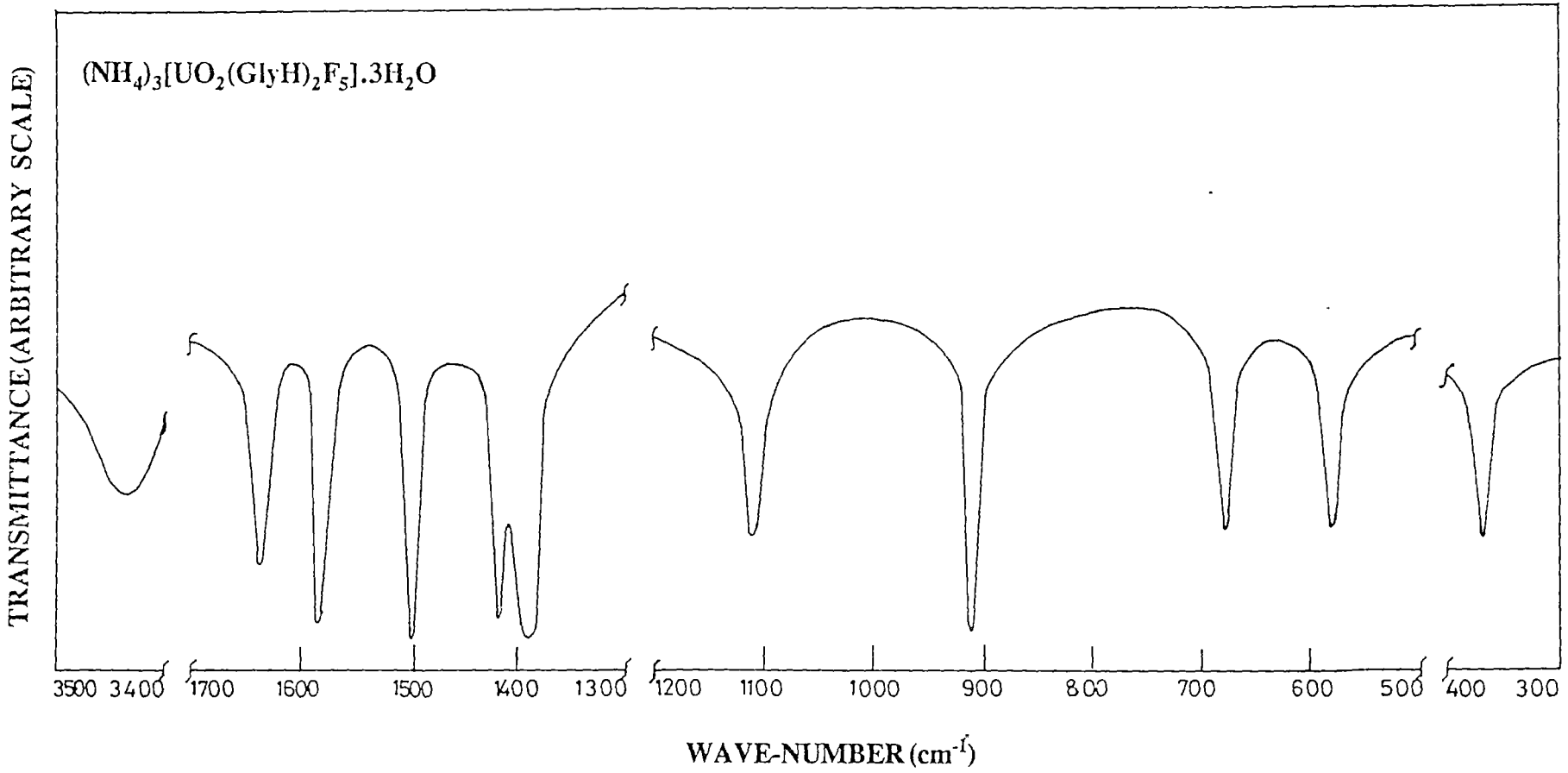


FIG. 5.15: IR SPECTRUM

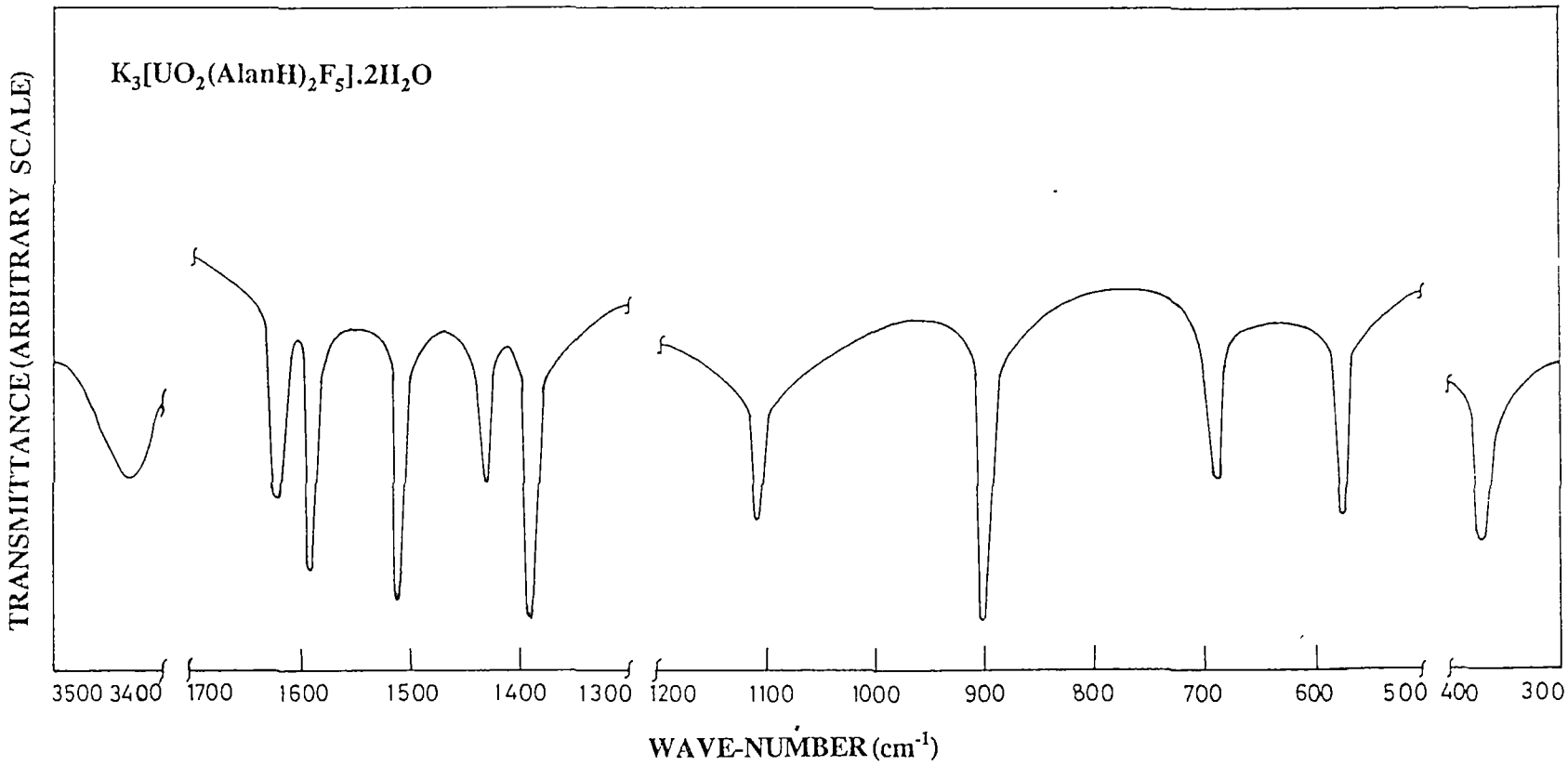


FIG. 5.16: IR SPECTRUM

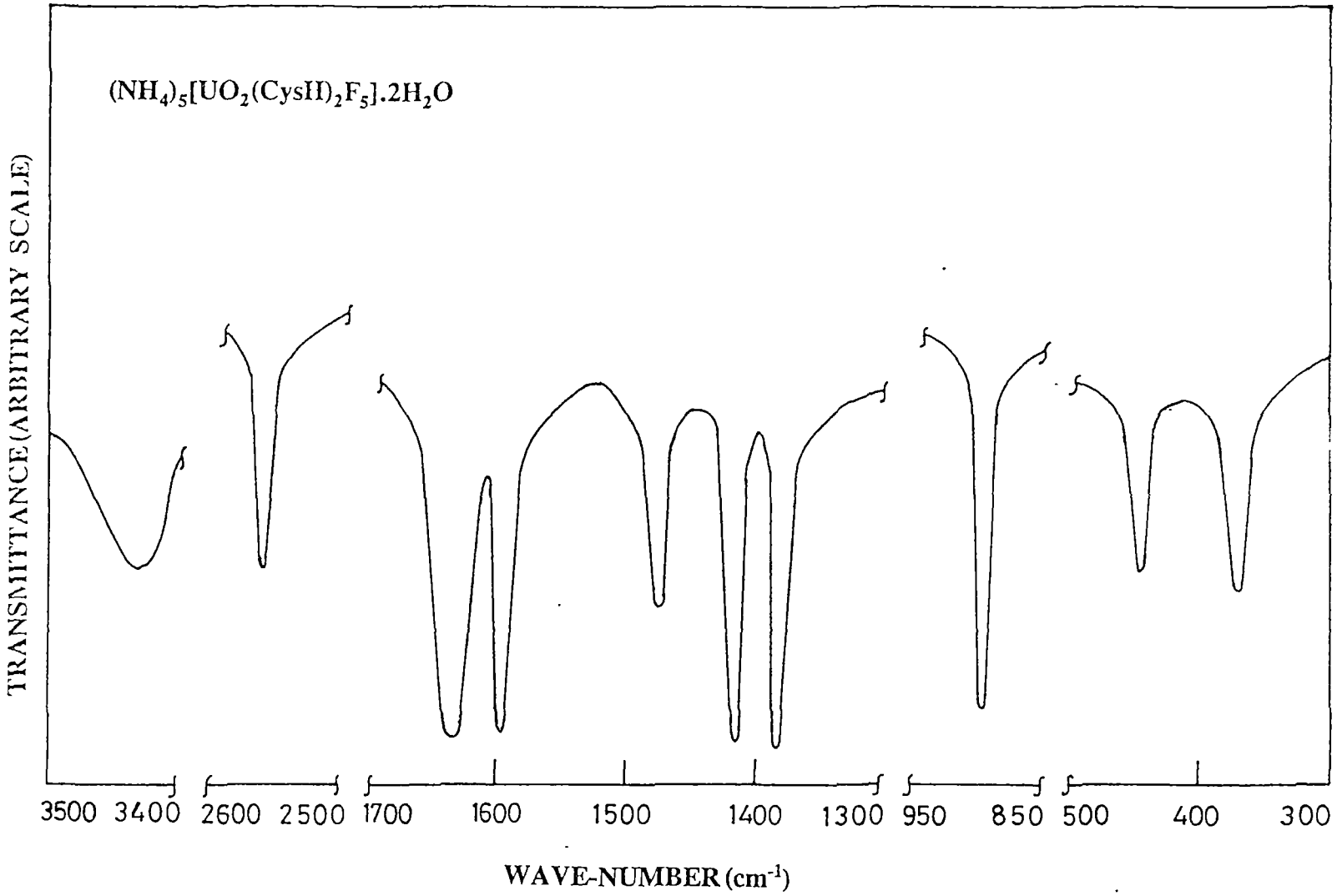


FIG. 5.17: IR SPECTRUM

Interestingly, the chosen amino acids are good IR spectral probes. While glycine and L-alanine form complexes with metals in either their zwitterionic or ionic forms[44-46] coordinating either through their N,O atoms in a bidentate manner or through their carboxylate oxygen atoms in a monodentate fashion, L-cysteine,[47] the other amino acid included in our present study, contained sulphhydryl group as an additional coordination site. The patterns due to coordinated glycine and coordinated alanine have been essentially similar. Notable were the bands at *ca.* 1600s [$\nu_{as}(COO^-)$], *ca.*1400s [$\nu_{s}(COO^-)$], *ca.* 1120m [$\rho_{r}(NH_3^+)$], *ca.*680m [$\rho_{w}(COO^-)$] and *ca.* 580m [$\delta(COO^-)$]. The presence of $\nu_{as}(COO^-)$, $\nu_{s}(COO^-)$ and unaltered positions of N-H stretching frequencies, with respect to free glycine and alanine, suggests the occurrence of the two ligands in their zwitterionic[38f,47] forms being coordinated through their carboxylate oxygen atoms in a monodentate fashion. This is a very interesting structural feature of these complexes. But unlike in the case of glycine and alanine, cysteine occurs in its cysteinate form ($CysH^-$) in the complex. The IR spectral (Fig.5.17) bands at 1650s and 1385s owe their origin to $\nu_{as}(COO^-)$ and $\nu_{s}(COO^-)$ modes, respectively. Notable in this context is the observed shifts of $\nu_{as}(COO^-)$ to higher and $\nu_{s}(COO^-)$ to lower wave numbers compared to the corresponding values of free cysteine,[47] which therefore offers evidence for the coordination

of $CysH^-$ through its carboxylate oxygen in a monodentate fashion. The complimentary ν(U-O) has been observed at 451m cm^{-1}. The appearance of a band at 2565 cm^{-1} due to S-H stretch comparable to that of free cysteine suggests that the sulphur atom does not participate in coordination. Further, the unaltered NH_3^+ deformation[47] band observed at 1483 cm^{-1} indicates that the N-atom has also not involved itself in coordination. Thus, based upon the IR results highlighted above, it may be stated that the amino acid in each of the complexes has acted as a monodentate ligand being coordinated to the metal centre through the carboxylate oxygen atom.

Heptafluorodioxouranate(VI) Complex Species, $[UO_2F_7]^{5-}$

As mentioned earlier in this section, the mixed-ligand (amino acid) fluoro complexes are unstable in aqueous solution. Each of the complexes decomposed in aqueous solution forming intractable products, except for $K_3[UO_2(GlyH)_2F_5].3H_2O$, which underwent hydrolysis affording a well-defined hitherto unknown binary fluoro complex $K_5[UO_2F_7].2H_2O$. It is rather difficult to comment on the formation of $[UO_2F_7]^{5-}$ from the fluoro(glycine) complex, but most probably there must have been hydrolysis of the $[UO_2(GlyH)_2F_5]^{3-}$ complex and a reorganization of the coordination sphere of UO_2^{2+} resulting into the formation of the complex species. The solution pH recorded at the stage of precipitation of $[UO_2F_7]^{5-}$ was found

to be 1.7 which might have facilitated the dissociation of the co-ligand GlyH. This therefore enabled us to make the first report on the heptafluorodioxouranate(VI) complex.

The complex $K_5[UO_2F_7].2H_2O$ is lemon-yellow in colour and stable in the solid state. It's solubility in water permitted us to record its solution electrical conductance. The solution (10^{-3} M) electrical conductance of $K_5[UO_2F_7].2H_2O$ was measured to be 590 $\Omega^{-1}cm^2mol^{-1}$ in conformity to its 5:1 electrolytic nature. The unaltered electrical conductance over a period of three days attests to its stability in water under the present experimental conditions.

The IR spectrum (Fig. 5.18) of $K_5[UO_2F_7].2H_2O$ exhibited only a few bands at 866s [ν(U=O)] [trans.linked O=U=O] and 373m ν(U-F) in addition to the ν(O-H) and δ(H-O-H) modes of lattice water at 1640 and 3455 cm^{-1}, respectively. In order to complement the IR spectroscopic results, laser Raman (LR) spectroscopic experiment was conducted on the complex. The Raman signals (Fig.5.19) were observed at 920s [ν(U=O)] [trans.linked O=U=O] and 314m [ν(U-F)]. These also augment our assumptions on the characteristic spectral features of the complex $[UO_2F_7]^{5-}$ species. The stability of the complex in water enabled recording the solution Raman spectrum of the heptafluorodioxouranate(VI) complex. The principal features of the solution Raman spectrum are the appearance of ν(U=O) and

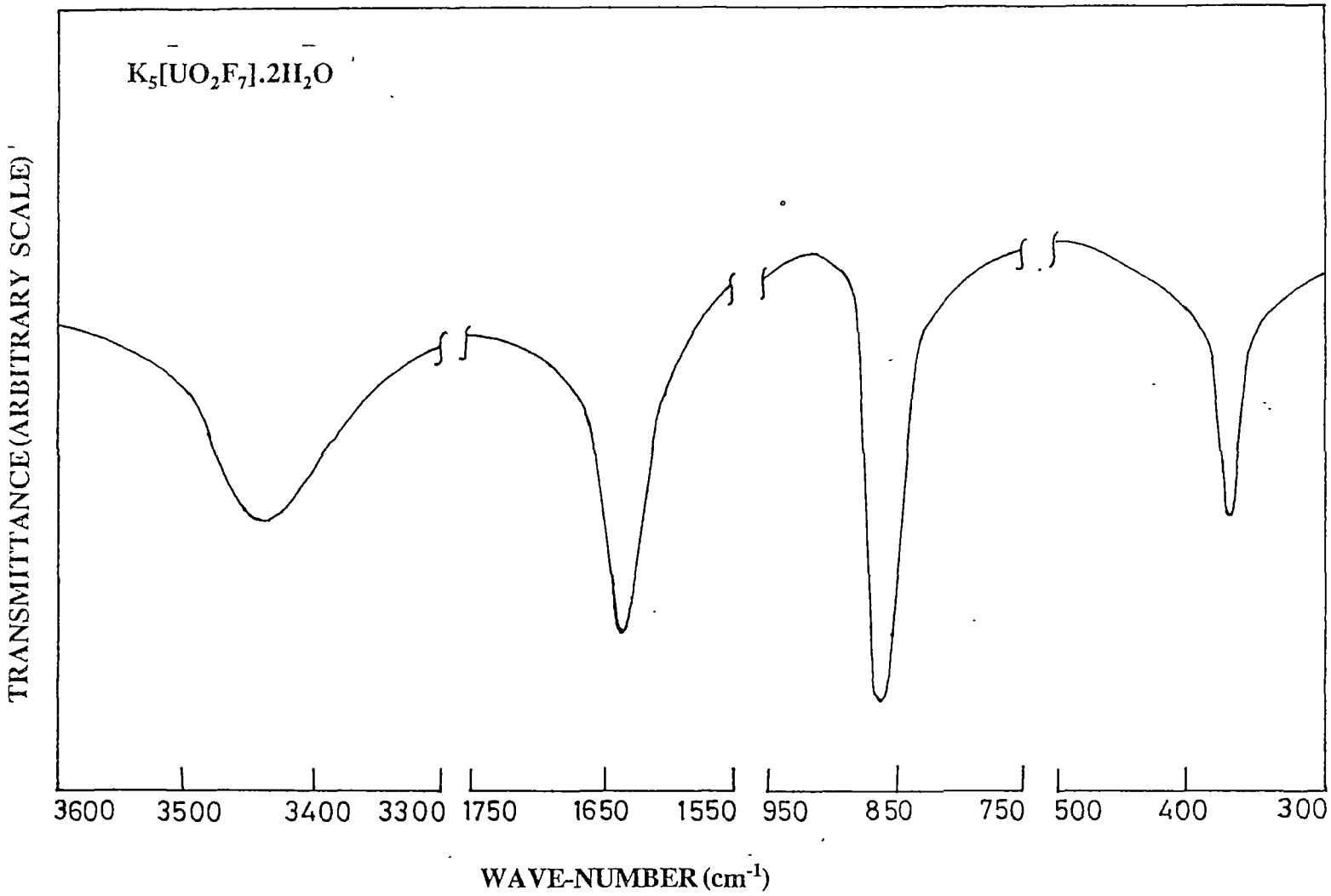


FIG. 5.18: IR SPECTRUM

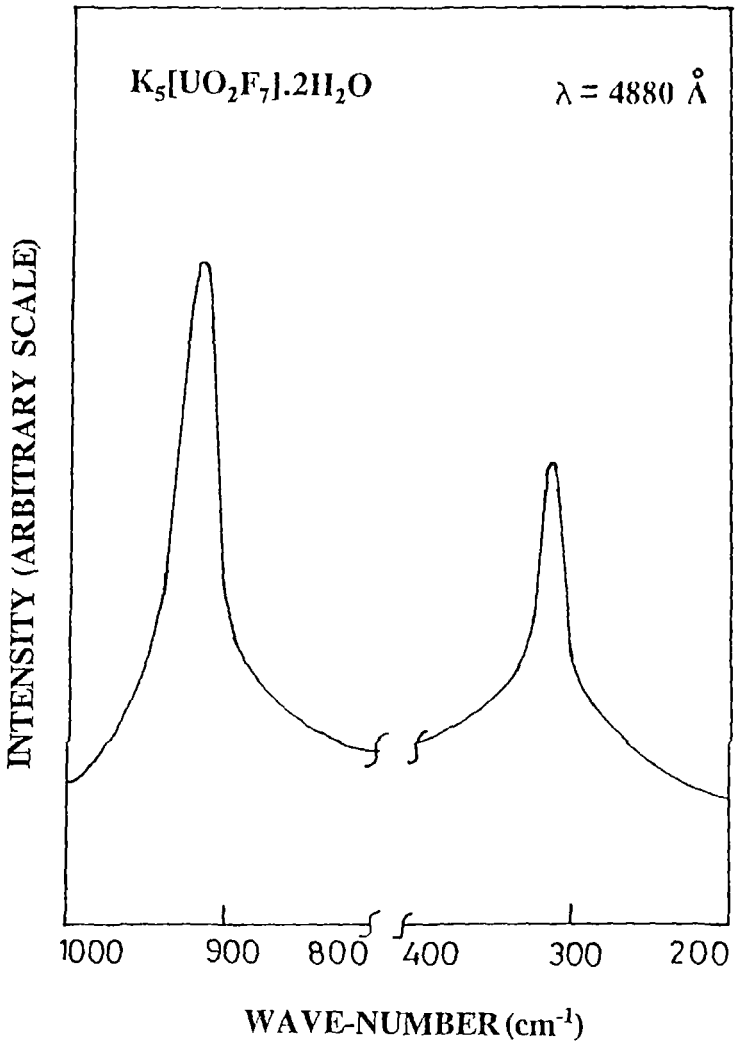


FIG. 5.19: RAMAN SPECTRUM

ν(U-F) signals at 915 and 325 cm^{-1}. The pattern resembles that of the corresponding solid, thus indicating that the structure of the complex $[UO_2F_7]^{5-}$ ion in aqueous solution is same as the solid.

In order to probe into the homogeneity and the crystalline character of the hitherto unreported binary fluoro complexes $(NH_4)_4[UO_2F_6]$ and $K_5[UO_2F_7].2H_2O$, they were subjected to Scanning Electron Microscopy (SEM). The SE-micrographs (Figs.5.20 and 5.21) attest to their homogeneity and crystalline nature. The SEM pictures provide evidence for their occurrence as single phase species.

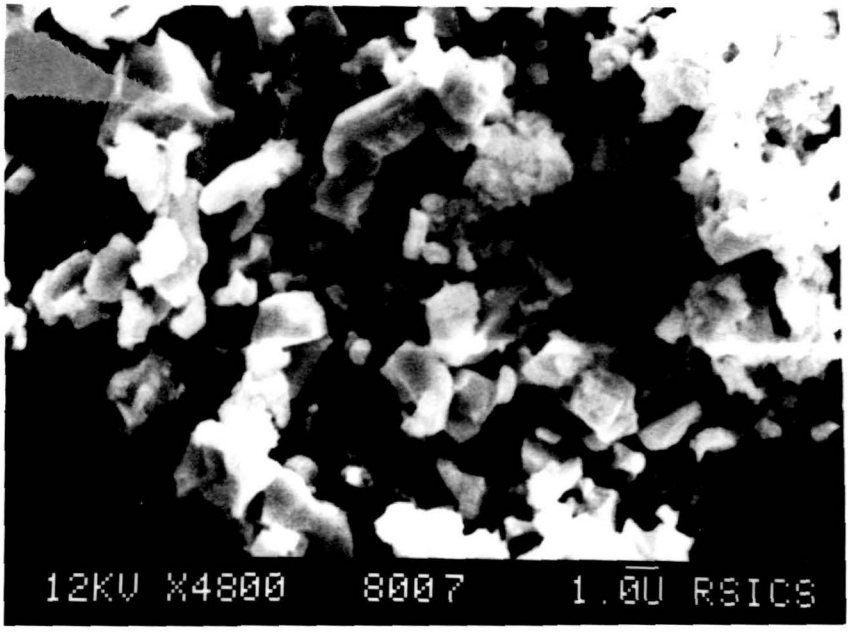


FIG. 5.20: SE MICROGRAPH OF $(NH_4)_4[UO_2F_6]$

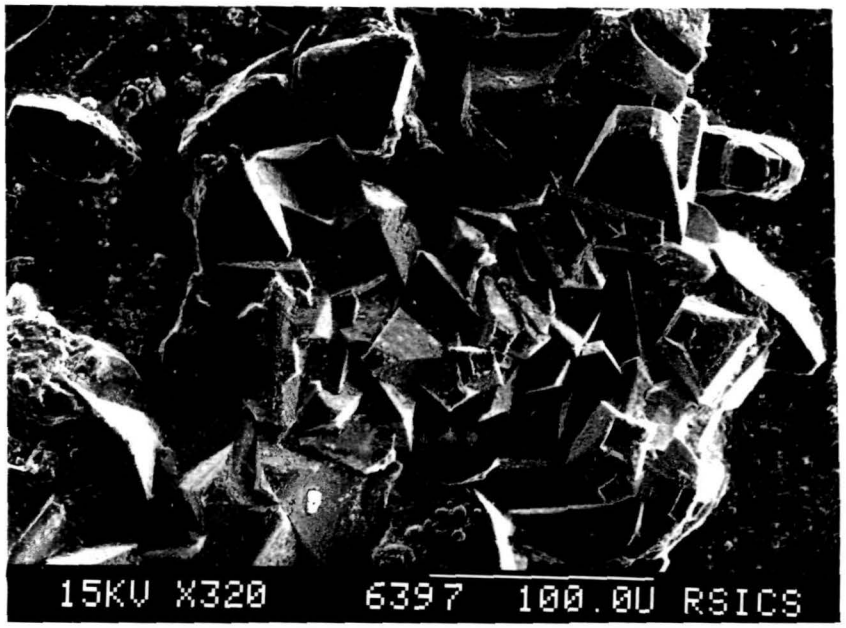


FIG. 5.21: SE MICROGRAPH OF $K_5[UO_2F_7].2H_2O$

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CHAPTER VI

COMPLEX FLUOROURANATES(VI). SYNTHESIS, CHARACTERIZATION AND STRUCTURAL ASSESSMENT OF NEW MIXED-FLUORO COMPLEXES OF UO_2^{2+} CONTAINING PHOSPHATE, NITRATE OR HYDRAZINE AS THE CO-LIGANDS AND IMPROVED SYNTHESIS OF $A_2[UO_2F_4].3H_2O$ (A = K, Na or NH_4)*

In continuation to our endeavour in the field of binary fluoro and mixed-fluorouranates(VI) as highlighted in Chapter V of

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* A major portion of the work described herein has been accepted for publication in *Polyhedron* (in press) [Manuscript No. 905478].

the thesis, we decided to embark on the study of hetero-ligand fluoro complexes of UO_2^{2+} containing inorganic co-ligands as well. Our chief concern here is to develop appropriate synthetic methodologies that would not only be operationally simple but also capable of affording pure products in high yields. The only inorganic co-ligand that was dealt with in our previous studies[1] on mixed-fluorouranates was peroxide (O_2^{2-}), wherein the complex $[UO_2(O_2)F_2]^{2-}$ was synthesized.

The co-ligands chosen for the present work include phosphate, nitrate and hydrazine. These ligands besides being good probes easily amenable to spectroscopic characterization are known to interact with UO_2^{2+} to form compounds of varying compositions and stability.[2] Moreover, both phosphato and nitrato-uranyl complexes are technologically important.[3,4] For instance, the formation of insoluble and slightly soluble uranyl phosphates is important in the technology of uranium production especially for low-grade uranium phosphate ores and in fuel reprocessing.[3] However, there appears to be some synthetic problem related to phosphato complexes of UO_2^{2+} specifically owing to the gelatinous nature of the products,[5a] while the uranyl-nitrato complexes are generally very weak.[5b] It was expected that the presence of fluoride might assist in bringing about stability to the nitrato complexes and improve upon the crystallinity of the phosphato ones. The complexes of coordinated hydrazine in general find considerable

interest owing to their tendency to act as possible intermediates[6] in the chemistry of coordinated dinitrogen and its reduction to NH_3 catalyzed by nitrogenases. Besides, the coordination chemistry of hydrazine and substituted hydrazines is of special interest because of the variety of ways in which it can be bonded to the metal ion. Interestingly, there have been only a few reports on hydrazine complexes of UO_2^{2+} and all of them are hetero-ligand complexes[5c] with SO_4^{2-}, NCS^-, NO_3^-, $C_2O_4^{2-}$ or a heavier halide like Cl^-, Br^- or I^- as the co-ligand. Surprisingly, there has been no mention of the corresponding fluoro(hydrazine) complex of UO_2^{2+} for which we were unable to discern any reason. Hence, we considered it important to include this aspect in our agenda.

Having achieved the syntheses of difluoro, hexafluoro and heptafluorodioxouranates(VI) as described in Chapter V of the thesis, we were interested in the synthesis of dioxotetrafluoro-uranate(VI) complex, $[UO_2F_4]^{2-}$. It may be recalled that a number of salts of the complex species $[UO_2F_4]^{2-}$ with the general formulae $A_2[UO_2F_4].nH_2O$[7] (A = K, Na or NH_4) were prepared from metathesis reactions of $[Ni(py)_4][UO_2F_4].H_2O$ and $NaClO_4$ or AI (A = K or NH_4). Further $[Ni(py)_4][UO_2F_4].H_2O$ was prepared from UO_2F_2, which for itself requires an extra preparation step. In view of these as well as our interest in fluorouranates(VI) in particular, it was incumbent on us to develop a rather simple and direct synthetic route for $A_2[UO_2F_4].nH_2O$ (A = K, Na or NH_4).

Accordingly the work that has been identified above was undertaken and a detailed account of the results are incorporated in this Chapter.

Experimental

The reagents used in these studies were reagent-grade or better (E.Merck (India) Ltd., S.d-Fine Chem., Qualigens Fine Chemicals). The details of the instruments/equipment used for characterization of the complexes are given in Chapter II.

Synthesis of $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ [A = K, Na or NH_4]

An amount of 1.0g (2.79 mmol) of $UO_3.4H_2O$ was dissolved in an aqueous solution (5 cm^3) of AHF_2 (8.37 mmol). This was followed by the addition of H_3PO_4 (0.3 cm^3, 5.37 mmol). The pH of the resultant clear solution was measured to be *ca.*2. The reaction solution was then concentrated on a steam-bath while lemon-yellow crystals began to appear. Addition of cold ethanol (7 cm^3) at this stage facilitated precipitation of the lemon-yellow crystalline $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ [A = K, Na or NH_4]. The product was isolated by centrifugation, washed three or four times with ethanol, and finally dried *in vacuo* over conc. H_2SO_4. The yields of $K_2[UO_2(PO_4)F(H_2O)_3].3H_2O$, $Na_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ and $(NH_4)_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ were 1.1g (69%), 1g (67%) and 1g (67.5%), respectively.

Synthesis of $A_2[UO_2(NO_3)_3F].3H_2O$ [A = K, Na or NH_4]

Uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, (1.0g, 1.99 mmol) was dissolved in water (15 cm^3) followed by a slow addition of 20% AOH solution or aqueous ammonia (sp.gr. 0.91) until the precipitation of the yellow product was complete. This was filtered and washed free from alkali and nitrate, and then dissolved in 10 cm^3 (20.8 mmol) of 2.08 M HNO_3. To the clear solution, 48% HF (3 cm^3, 72 mmol) was added and stirred at an ambient temperature for *ca.* 10 min. The reaction solution was then concentrated on a steam-bath to nearly half of its volume to afford a lemon-yellow solid. The whole was cooled to room temperature. The compound thus obtained was isolated by filtration, washed thrice with acetone, and finally dried *in vacuo* over conc. H_2SO_4. The yields of $K_2[UO_2(NO_3)_3F].3H_2O$, $Na_2[UO_2(NO_3)_3F].3H_2O$ and $(NH_4)_2[UO_2(NO_3)_3F].3H_2O$ were 0.98g (74%), 0.8g (69.6%) and 0.8g (70.8%), respectively.

Synthesis of $[UO_2(N_2H_4)_2F_2].2H_2O$

To an aqueous solution (10 cm^3) of an intimate mixture of 1.0g (2.37 mmol) of $UO_3.4H_2O$ and 8.37 mmol of AHF_2 (A = K or NH_4) was added an excess (0.6 cm^3, 12 mmol) of hydrazine hydrate, $N_2H_4.H_2O$. At this stage, a yellow solid appeared. This reaction mixture was heated on a steam-bath for *ca.* 30 min. whereupon the

colour of the solid changed from yellow to brown. The brown solid thus formed was isolated by filtration. The compound was purified by washing two or three times with acetone and finally dried *in vacuo* over conc.H_2SO_4. The yield of $[UO_2(N_2H_4)_2F_2].2H_2O$ was 0.9g (79%). Anal. Calcd. for $[UO_2(N_2H_4)_2F_2].2H_2O$: U, 58.31; F, 9.31; N, 13.73; H, 2.97. Found: U, 59.11; F, 9.56; N, 13.32; H, 2.72.

Synthesis of $A_2[UO_2F_4].3H_2O$ (A = K, Na or NH_4)

(a) Uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, (1.0g, 1.99 mmol) was dissolved in water (15 cm^3) followed by a slow addition of 20% AOH solution or aqueous ammonia (sp.gr. 0.91) until the precipitation of the yellow product was complete. This was filtered and washed free from alkali and nitrate. The product thus obtained was dissolved in 48% HF (1 cm^3, 24 mmol).To the resultant solution 3.96 mmol of A_2CO_3 (A = K, Na or NH_4) was added. The whole was then concentrated on a steam-bath to afford a lemon-yellow crystalline solid. This was then isolated by filtration and dried *in vacuo* over conc. H_2SO_4. The compound was identified to be $A_2[UO_2F_4].3H_2O$. The yields of $K_2[UO_2F_4].3H_2O$, $Na_2[UO_2F_4].3H_2O$ and $(NH_4)_2[UO_2F_4].3H_2O$ were 0.57g (60%), 0.55g (62%) and 0.54g (62%), respectively.

(b) Alternatively, an amount of (1.0g, 1.99 mmol) of uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$ was dissolved in 15 cm^3 of water and 0.1 cm^3 of conc. HNO_3 was added to it. After heating the

resulting solution to about 70°C, 0.5 cm^3 of 30% H_2O_2 was added washed thoroughly with water. This was then dissolved in 48% HF (1 cm^3, 24 mmol). To the resulting solution 12 mmol of AF (A = K, Na or NH_4) was added. The whole upon concentration over a steam-bath afforded a lemon-yellow crystalline solid which was isolated by filtration and dried *in vacuo* over conc. H_2SO_4. The compound was analysed as $A_2[UO_2F_4].3H_2O$ (A = K, Na or NH_4). The yields of $K_2[UO_2F_4].3H_2O$, $Na_2[UO_2F_4].3H_2O$ and $(NH_4)_2[UO_2F_4].3H_2O$ were 0.53g (56%), 0.48g (54%) and 0.5g (57.5%), respectively.

Elemental Analyses

Quantitative determinations of uranium, fluoride, nitrogen, hydrogen, phosphate, sodium and potassium were made by the methods described in Chapter II.

The analytical and characterization data (except the analytical data of $[UO_2(N_2H_4)_2F_2].2H_2O$) are summarised in Tables 6.1-6.8.

Results and Discussion

From the experience gathered by our group in dealing with uranyl systems, especially fluoro complexes of UO_2^{2+} as described in Chapter V, it was conjectured that complexation of PO_4^{3-}, NO_3^- or N_2H_4 with UO_2^{2+} in the presence of fluoride would be feasible

Table 6.1: Analytical Data of the Complexes $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ (A = K, Na or NH_4)

Compound	Element	Found (%)	Calcd. (%)
$K_2[UO_2(PO_4)F(H_2O)_3].3H_2O$	U	40.88	41.75
	F	3.23	3.33
	PO_4^{3-}	15.95	16.66
	H	2.24	2.13
	K	12.95	13.68
$Na_2[UO_2(PO_4)F(H_2O)_3].3H_2O$	U	44.11	44.24
	F	3.33	3.53
	PO_4^{3-}	17.42	17.65
	H	2.28	2.25
	Na	8.87	8.54
$(NH_4)_2[UO_2(PO_4)F(H_2O)_3].3H_2O$	U	44.25	45.06
	F	3.48	3.60
	PO_4^{3-}	17.85	17.98
	H	3.48	3.82
	N	5.22	5.30

Table 6.2: Analytical Data and Solution Electrical Conductance Values of $A_2[UO_2(NO_3)_3F].3H_2O$ (A = K, Na or NH_4)

Compound	Conductance ($\Omega^{-1}cm^2mol^{-1}$)	Element	Found (%)	Calcd. (%)
$K_2[UO_2(NO_3)_3F].3H_2O$	244	U	39.42	39.21
		F	3.24	3.13
		N	6.78	6.92
		K	13.11	12.85
$Na_2[UO_2(NO_3)_3F].3H_2O$	242	U	40.31	41.39
		F	3.36	3.30
		N	7.52	7.31
		Na	7.89	7.99
$(NH_4)_2[UO_2(NO_3)_3F].3H_2O$	244	U	42.32	42.11
		F	3.24	3.36
		N	12.41	12.39
		H	2.55	2.50

Table 6.3: Analytical Data and Solution Electrical Conductance Values of $A_2[UO_2F_4].3H_2O$ (A = K, Na or NH_4)

Compound	Conductance ($\Omega^{-1}cm^2mol^{-1}$)	Element	Found (%)	Calcd. (%)
$K_2[UO_2F_4].3H_2O$	245	U	50.12	49.77
		F	16.23	15.89
		H	1.33	1.27
		K	15.96	16.35
$Na_2[UO_2F_4].3H_2O$	238	U	53.21	53.26
		F	16.85	17.04
		H	1.52	1.30
		Na	10.43	10.31
$(NH_4)_2[UO_2F_4].3H_2O$	242	U	54.84	54.57
		F	17.13	17.42
		H	3.36	3.24
		N	6.63	6.42

Table 6.4: IR and LR Spectral Data of the Complexes $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ (A = K, Na or NH_4) with their Assignments

Compound	IR (cm^{-1})	LR (cm^{-1})	Assignment
$K_2[UO_2(PO_4)F(H_2O)_3].3H_2O$	920s	903s	ν(U=O)
	382m		ν(U-F)
	903m		$\nu_1(PO_4)$
	1002s, 1069s, 1130s		$\nu_3(PO_4)$
	742m		$\rho_r(H_2O)$
	1657m		δ(H-O-H)
	3477m		ν(O-H)
$Na_2[UO_2(PO_4)F(H_2O)_3].3H_2O$	926s	900s	ν(U=O)
	415m		ν(U-F)
	908m		$\nu_1(PO_4)$
	1004s, 1085s, 1120s		$\nu_3(PO_4)$
	737m		$\rho_r(H_2O)$
	1654m		δ(H-O-H)
	3418m		ν(O-H)

Table 6.4 contd.

Compound	IR (cm^{-1})	LR (cm^{-1})	Assignment
$(NH_4)_2[UO_2(PO_4)F(H_2O)_3].3H_2O$	925s	905s	ν(U=O)
	408m		ν(U-F)
	905m		$\nu_1(PO_4)$
	1008s, 1068s, 1120s		$\nu_3(PO_4)$
	735m		$\rho_r(H_2O)$
	1630m		δ(H-O-H)
	3467m		ν(O-H)
	1428s		ν(N-H)ν_4
	3089s		ν(N-H)ν_1
	3169m		ν(N-H)ν_3

Table 6.5: IR and LR Spectral Data of the Complexes $A_2[UO_2(NO_3)_3F].3H_2O$ (A = K, Na or NH_4) with their Assignments

Compounds	IR (cm^{-1})	LR (cm^{-1})	Assignment
$K_2[UO_2(NO_3)_3F].3H_2O$	950s	890s	ν(U=O)
	403m		ν(U-F)
	1503s		$\nu_1(NO_3)$
	1026m		$\nu_2(NO_3)$
	744m		$\nu_3(NO_3)$
	1283s		$\nu_4(NO_3)$
	705w		$\nu_5(NO_3)$
	808m		$\nu_6(NO_3)$
	1657m		δ(H-O-H)
	3442m		ν(O-H)
$Na_2[UO_2(NO_3)_3F].3H_2O$	948s	894s	ν(U=O)
	396m		ν(U-F)
	1503s		$\nu_1(NO_3)$
	1026m		$\nu_2(NO_3)$
	743m		$\nu_3(NO_3)$
	1290s		$\nu_4(NO_3)$
	708w		$\nu_5(NO_3)$
	805m		$\nu_6(NO_3)$
	1621m		δ(H-O-H)
	3440m		ν(O-H)

Table 6.5 contd.

Compounds	IR (cm^{-1})	LR (cm^{-1})	Assignment
$(NH_4)_2[UO_2(NO_3)_3F].3H_2O$	939s	900s	ν(U=O)
	401m		ν(U-F)
	1505s		$\nu_1(NO_3)$
	1024m		$\nu_2(NO_3)$
	741m		$\nu_3(NO_3)$
	1296s		$\nu_4(NO_3)$
	707w		$\nu_5(NO_3)$
	811m		$\nu_6(NO_3)$
	1657m		δ(H-O-H)
	3446m		ν(O-H)
	1427s		ν(N-H)ν_4
	3094s		ν(N-H)ν_1
	3182m		ν(N-H)ν_3

Table 6.6: Electron Absorption Spectral Data of $A_2[UO_2(NO_3)_3F].3H_2O$ (A = K, Na or NH_4)

Compound	UV-VIS λ_{nm}	ε ($Lmol^{-1}cm^{-1}$)
$K_2[UO_2(NO_3)_3F].3H_2O$	415	52
	425	105
	435	102
	465	48
$Na_2[UO_2(NO_3)_3F].3H_2O$	415	50
	425	110
	435	108
	465	45
$(NH_4)_2[UO_2(NO_3)_3F].3H_2O$	410	55
	420	105
	440	108
	460	50

Table 6.7: IR and LR Spectral Data of $[UO_2(N_2H_4)_2F_2].2H_2O$ with their Assignments

Compound	IR (cm^{-1})	LR (cm^{-1})	Assignment
$[UO_2(N_2H_4)_2F_2].2H_2O$	924s	907s	ν(U=O)
	415m		ν(U-F)
	307m		ν(U-N)
	3265s, 3207m, 3131w		ν(N-H)
	1607m, 1555m		NH_2 bending
	1384w, 1336w, 1228w		NH_2 wagging
	1196m		NH_2 twisting
	955m		ν(N-N)
	1657m		δ(H-O-H)
	3438m		ν(O-H)

Table 6.8: IR and LR Spectral Data of $A_2[UO_2F_4].3H_2O$ (A = K, Na or NH_4) with their Assignments

Compound	IR (cm^{-1})	LR (cm^{-1})	Assignment
$K_2[UO_2F_4].3H_2O$	930s	-	ν(U=O)
	373m		ν(U-F)
	1630m		δ(H-O-H)
	3468m		ν(O-H)
$Na_2[UO_2F_4].3H_2O$	926s	-	ν(U=O)
	372m		ν(U-F)
	1624m		δ(H-O-H)
	3450m		ν(O-H)
$(NH_4)_2[UO_2F_4].3H_2O$	927s	910s	ν(U=O)
	376m	425m	ν(U-F)
	1626m		δ(H-O-H)
	3460m		ν(O-H)
	1433s		ν(N-H)ν_4
	3074s		ν(N-H)ν_1
	3198m		ν(N-H)ν_3

under appropriate experimental conditions. Thus, it was necessary to first ascertain the suitable experimental conditions and then work out the appropriate methodologies.

Fluoro(phosphato)uranates(VI)

It is known[8] that the interaction of phosphate with UO_2^{2+} is dependent on a number of parameters like concentrations of reactants, uranyl:phosphate concentration ratios, pH values of the reaction solutions and reaction temperatures. For instance,[8] a ratio of UO_3 to P_2O_5 < 1 seems to favour the precipitation of $(UO_2)_3(PO_4)_2$ from a concentrated solution of $UO_2(NO_3)_2$ and H_3PO_4 in the pH range 0.9–1.1, whereas a pH of 1.75–2.1 is required for the precipitation of a similar compound from dilute solutions. It was hence conjectured that the optimum conditions for the successful synthesis of fluoro(phosphato)uranates(VI) would be the UO_2^{2+}:phosphate:F^- concentration ratio of 1:2:6 in the pH range 1–2. The reaction of $UO_3.4H_2O$ with alkali hydrofluoride, AHF_2 and H_3PO_4 at a steam-bath temperature gave rise to a natural pH of *ca.* 2 thereby providing a condition conducive to the synthesis of lemon-yellow crystalline $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ (A = K, Na or NH_4) as obtained. The alkali hydrofluoride is believed to have played two major roles. For instance it has not only functioned as a fluorinating agent but also acted as a buffer to provide the appropriate pH of the reaction medium.

The compounds were insoluble in the commonly available polar or non-polar solvents and hence the question of solution electrical conductance measurement did not arise.

The IR spectra (Figs.6.1-6.3) of the complexes $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ (A = K, Na or NH_4) exhibited bands due to uranyl centre, coordinated fluoride, coordinated phosphate, coordinated and lattice water. The bands in the region of *ca.* 920-930 cm^{-1} and *ca.* 380-415 cm^{-1} have been assigned to the assymetric stretch $\nu_{as}(UO_2)$ of the trans.O=U=O group[9,10] and ν(U-F),[11] respectively. Phosphate is an important IR spectral probe for the determination of its mode of coordination to the metal centre. The range 850-1200 cm^{-1} involving the ν_1 and ν_3 fundamentals of coordinated phosphate is the most sensitive IR spectral region for ascertaining the local symmetry of a coordinated phosphato ligand. The observance of a medium intensity band at *ca.*900 cm^{-1} [$\nu_1(PO_4)$] and the splitting of the ν_3 mode of PO_4 into three strong bands at *ca.*1000, *ca.*1070 and *ca.*1120 cm^{-1} clearly shows the C_{2v} symmetry of phosphate ligand. Of particular significance was the absence of an absorption at *ca.*2700 cm^{-1} discernable to ν(P-O-H),[12] excluding the possibility of formation of hydrophosphate. The observed IR spectral pattern thus lends support to the presence of phosphate as PO_4^{3-} coordinated to the uranyl centre in a bidentate[13] fashion. In addition, the bands at *ca.*740 [$\rho_r(H_2O)$], *ca.*1645 [δ(H-O-H)] and *ca.*3450 [ν(O-H)] provide evidence for the presence

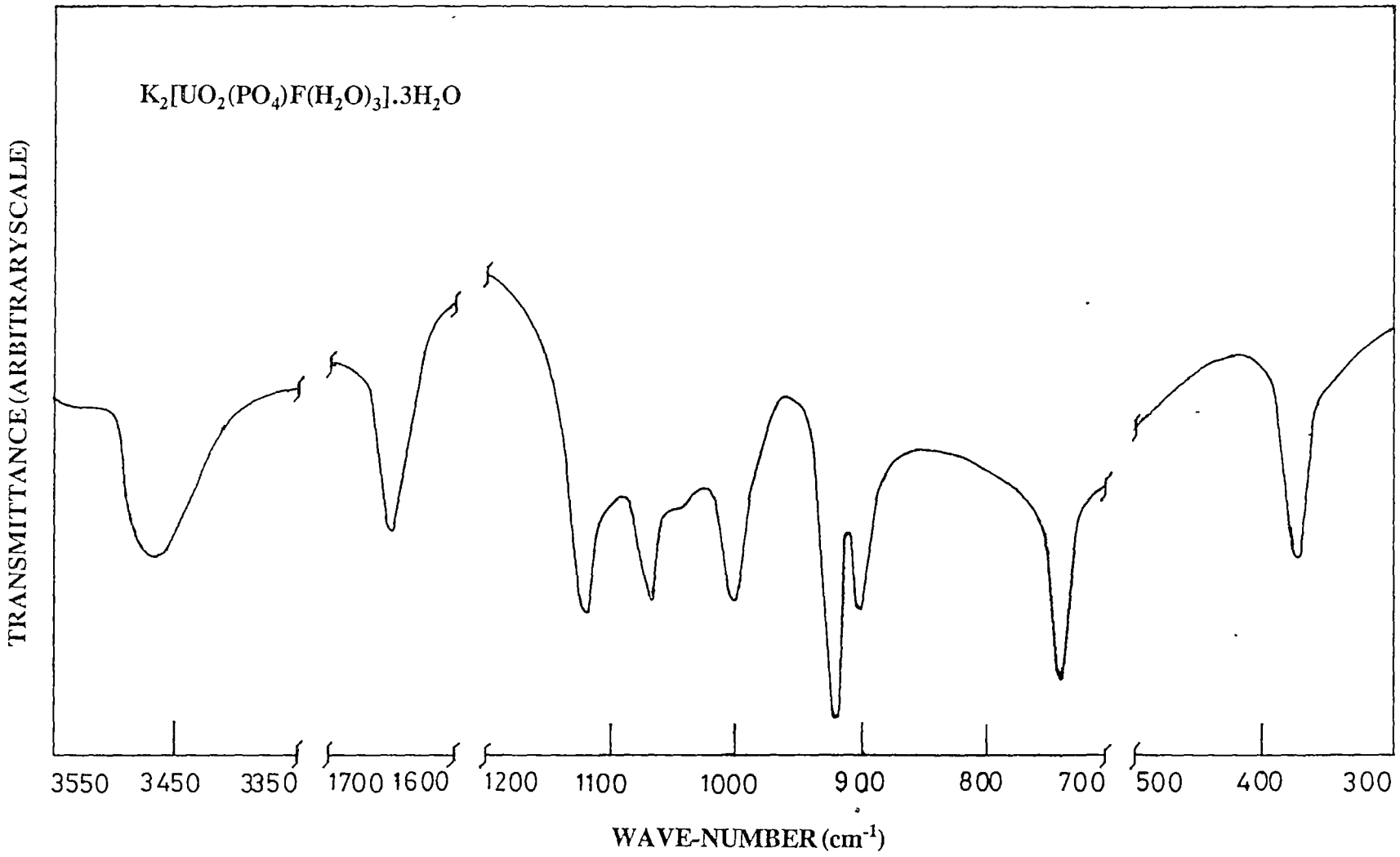

FIG. 6.1: IR SPECTRUM

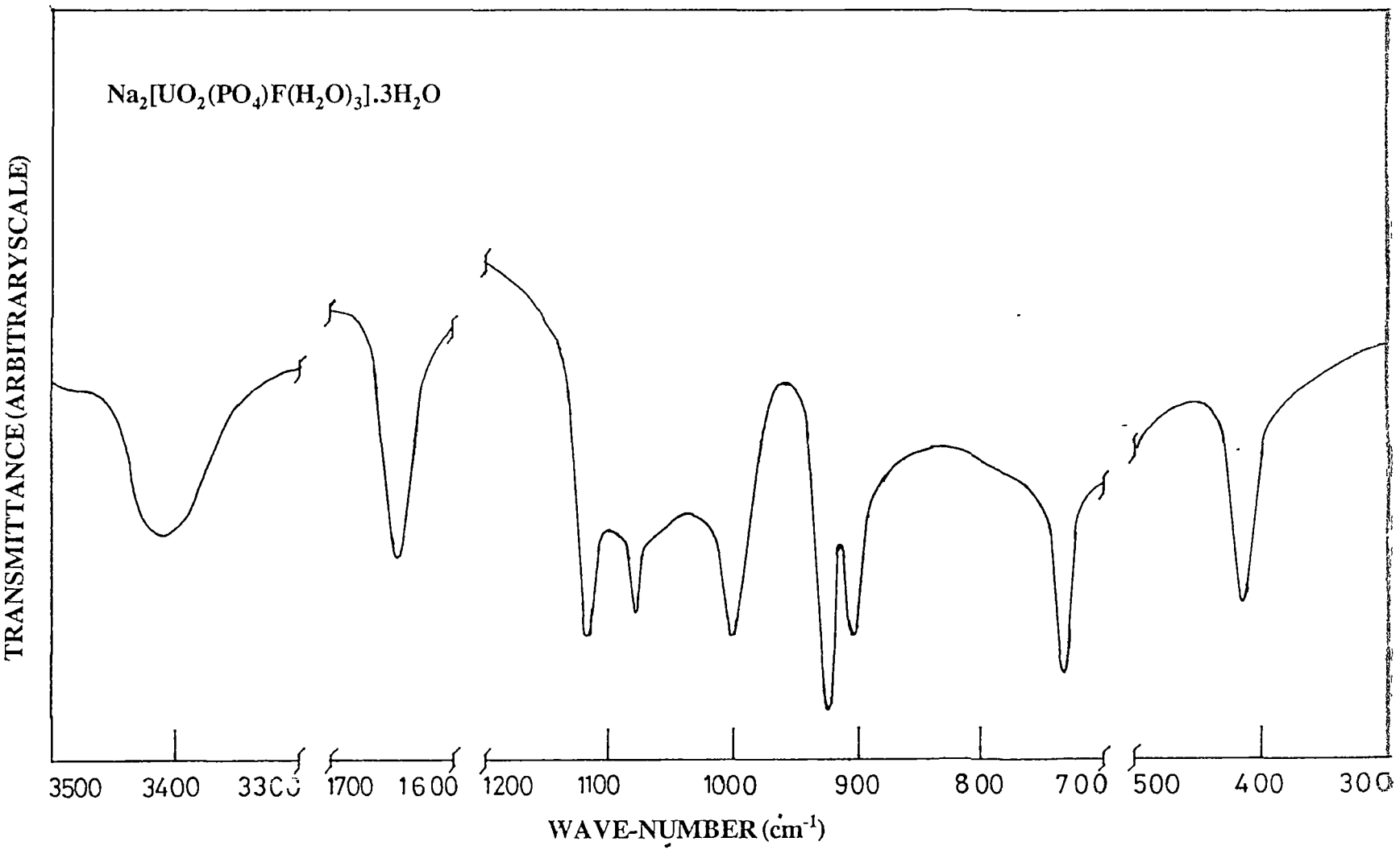

FIG. 6.2: IR SPECTRUM

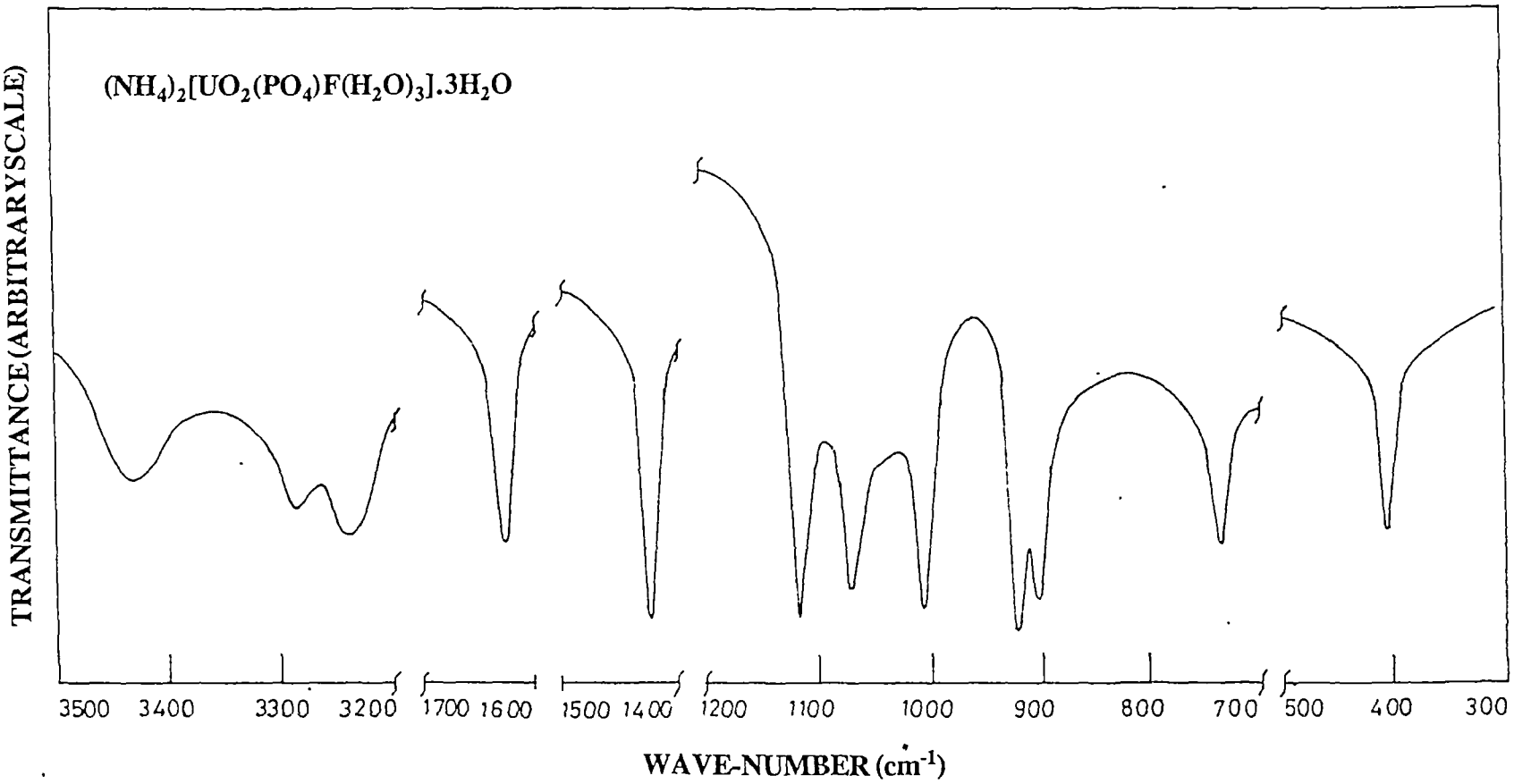

FIG. 6.3: IR SPECTRUM

of both coordinated as well as lattice water molecules in the complexes.

Phosphato complexes of UO_2^{2+} generally obtained from precipitation reactions are gelatinous in nature. Thus in the present case it was imperative to make use of Scanning Electron Microscopy to get an idea of the homogeneity and crystallinity of the newly synthesized fluoro(phosphato)complexes. As a typical case, micrographs of $Na_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ were recorded to expose two different stereo-views in Figs. 6.4 and 6.5. Fig.6.4 shows the symmetric hexagonal crystal morphology of the complex, whilst Fig.6.5 evidences for its cylindrical shape.

Fluoro(nitrato) complexes of UO_2^{2+}

Nitrate, one of the common inorganic anions is known to form binary complexes with uranyl ion. However, the complexes formed are very weak,[5c] the strength, in fact, comparable to the complexes formed by heavier halide ions.[5c,14] Moreover extensive complex formation appears to occur only at high nitrate ion concentration as observed by our group in an earlier occassion[15] and by others.[14] Significant in this context is that while 1-4 M nitric acid was shown[14] to favour tri- or tetranitrato complex formation, an acid concentration of < 1M facilitates the hydrolysis of UO_2^{2+}. It was hence anticipated that a concentration range of 1-4 M HNO_3 would be conducive to the complexation of NO_3^-

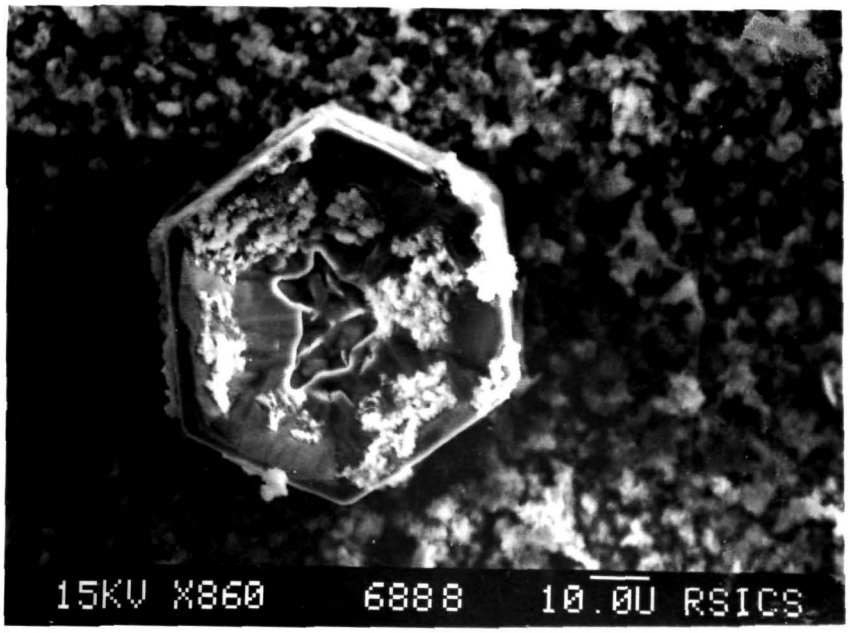

FIG. 6.4: SE MICROGRAPH OF $Na_2[UO_2(PO_4)F(H_2O)_3].3H_2O$

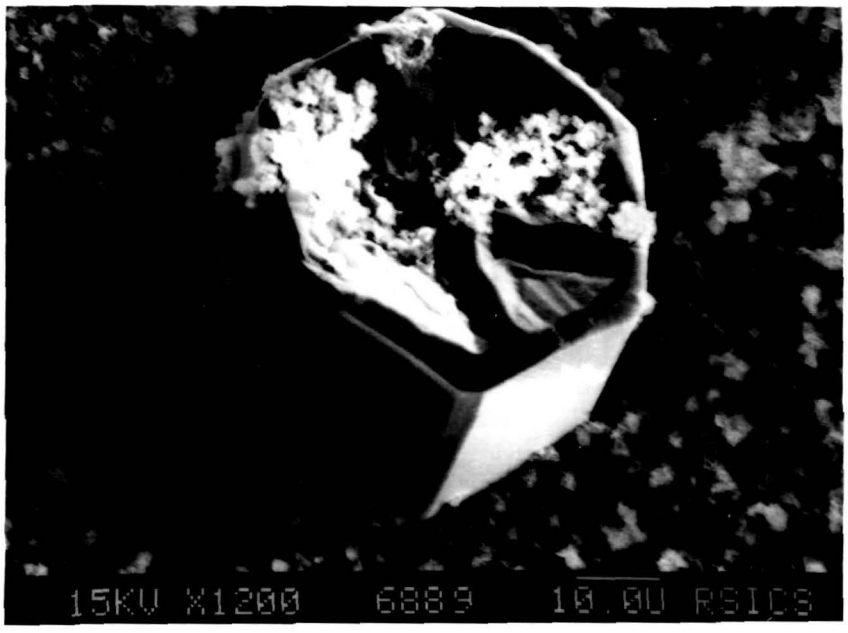

FIG. 6.5: SE MICROGRAPH OF $Na_2[UO_2(PO_4)F(H_2O)_3].3H_2O$

to UO_2^{2+} in the presence of F^-. Owing to the high concentrations of nitrate required for the syntheses as well as our goal being to access mixed-fluoro(nitrato) complexes of UO_2^{2+}, we were to also maintain an appreciably high F^- concentration. Accordingly, the reaction of $A_2U_2O_7$ (A = K, Na or NH_4) with 2.08 M HNO_3 and aqueous HF maintaining the concentration of UO_2^{2+}:NO_3^-:F^- as 1:*ca.*11:*ca.*36 afforded the complexes $A_2[UO_2(NO_3)_3F].3H_2O$ (A = K, Na or NH_4).

The fluoro(nitrato) complexes are lemon-yellow in colour and highly soluble in water. They are hygroscopic in nature and absorb moisture rather rapidly on exposure to air.

The IR spectral features (Figs.6.6-6.8) of all the three salts of the mixed-fluoro(nitrato) complexes were essentially similar bearing a close internal resemblance in respect of their patterns. The strong bands in the region *ca.*930-950 cm^{-1} and *ca.* 390-405 cm^{-1} owe their origins to the ν(U=O) [trans.linked O=U=O] and coordinated fluoride, respectively. The 700-1550 cm^{-1} region is important for coordinated nitrate group[16] and for the complexes under discussion, barring the absorption from ν(U=O) at 930-950 cm^{-1}, there is no interference from any other ligands. Incidentally, the coordinated nitrate does not exhibit any vibration in the ν(U=O) region. The symmetry of the free nitrate ion upon coordination changes from D_{3h} to C_{2v} and thereby six normal modes of vibration become IR active[10b,16] irrespective of

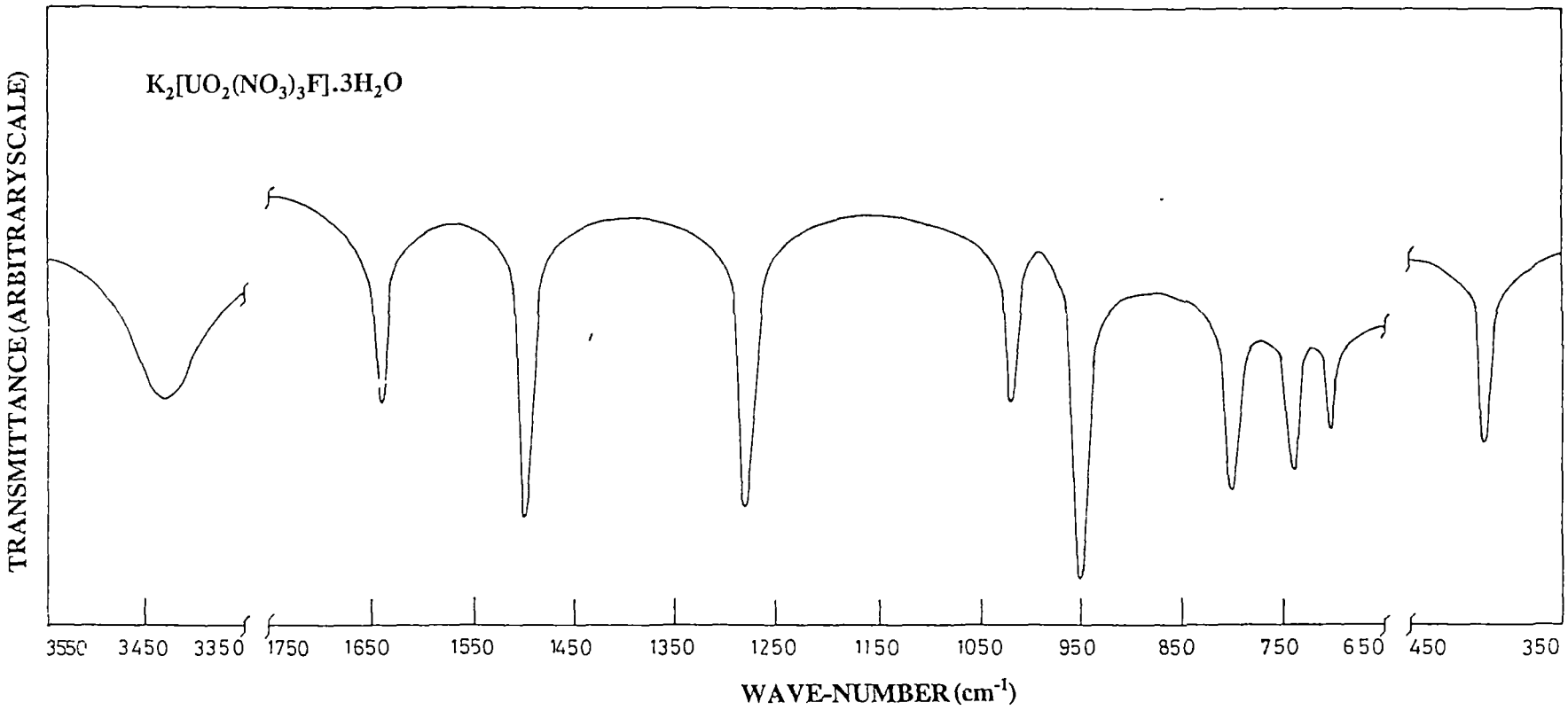

FIG. 6.6: IR SPECTRUM

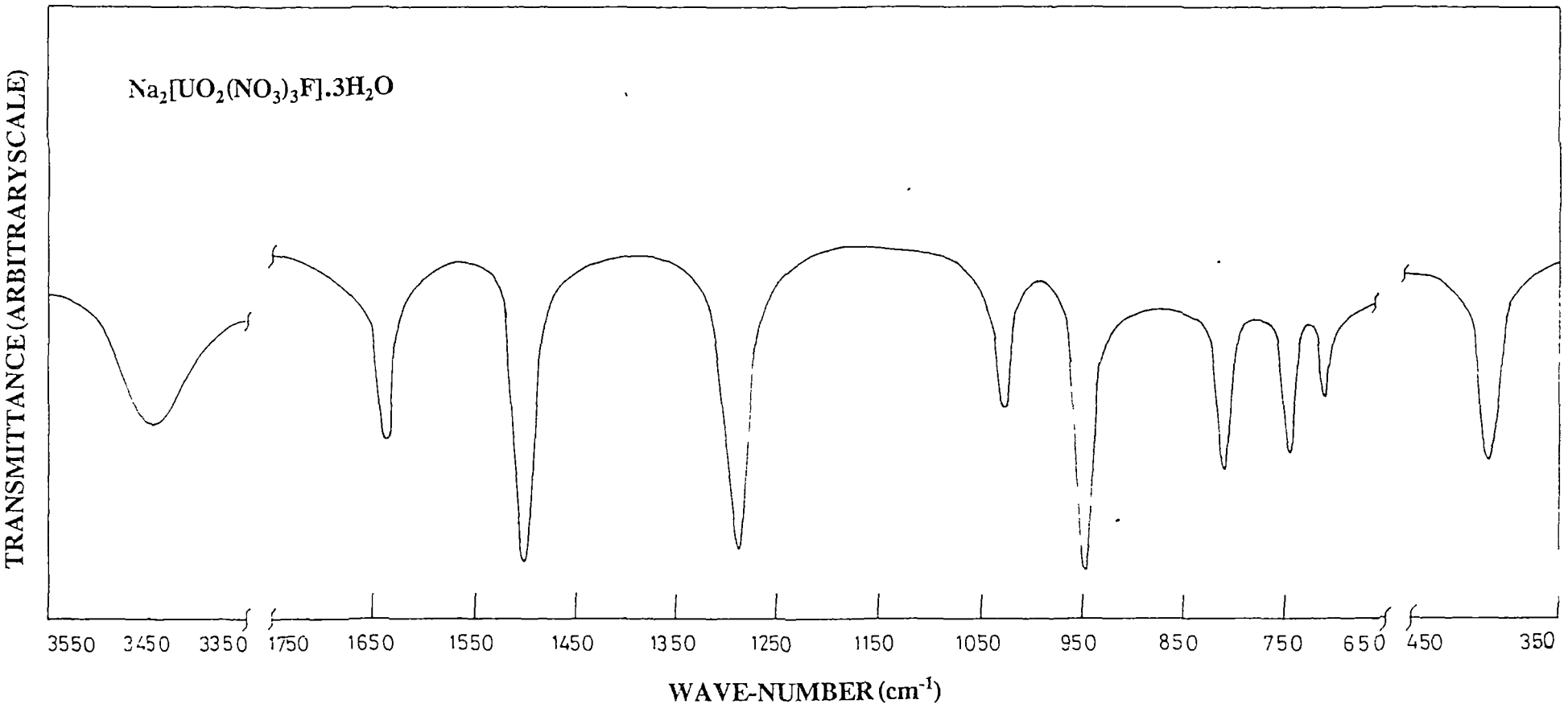

FIG. 6.7: IR SPECTRUM.

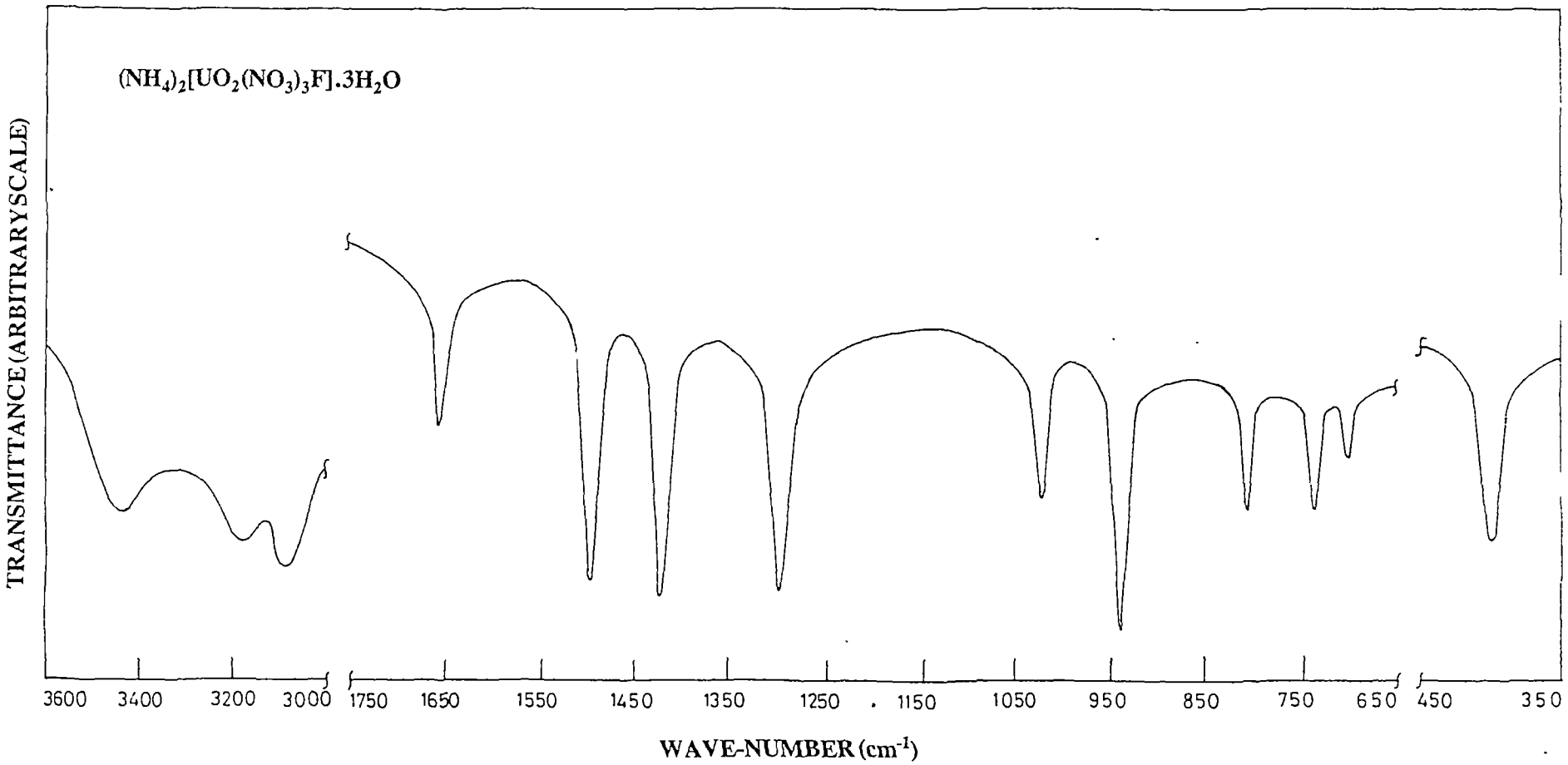

FIG. 6.8: IR SPECTRUM

its mono- or bidentate type of coordination. The complexes $A_2[UO_2(NO_3)_3F].3H_2O$ (A = K, Na or NH_4) displayed all the six modes with the ν_1 to ν_6 occurring at *ca.*1504s, *ca.*1025m, *ca.*742m, *ca.* 1290s, *ca.*707w and *ca.*805m cm^{-1}, respectively, thereby making it certain that the nitrates are coordinated to the metal centre.

In order to distinguish between mono- and bidentate coordination from IR data, a large separation of ν_1 and ν_4 (*ca.* 200 cm^{-1}) is used as an important criterion for bidentate[16] coordination of the ligand. This view is strongly supported by IR studies on crystallographically confirmed bidentate nitrates.[17,18] The (ν_1-ν_4) values in the present complexes was found to be *ca.*215 cm^{-1}, thereby making it logical to assume that the nitrates in the present complexes are coordinated to the metal centre in a bidentate fashion.

A high solubility of the fluoro(nitrato) complexes in water enabled us to carry out solution electrical conductivity measurements in order to know the mode of ionization of the complexes. Indeed, the recorded values of 244, 242 and 245 $\Omega^{-1}cm^2mol^{-1}$ respectively for the K, Na and NH_4 salts of the complex $[UO_2(NO_3)_3F]^{2-}$ ion conform to the 1:2 electrolytic nature befitting to their formulae. Moreover, the unaltered solution electrical conductivity values over a period of three or four days is a clean reflection of their stability in aqueous solution under the present experimental conditions.

The stability of the complexes in aqueous solution (as evidenced by solution electrical conductance experiments) prompted us to record their electron absorption spectra as well. The electronic absorptions were observed at *ca.*415, *ca.*425, *ca.*435 and *ca.*465 nm (Figs.6.9-6.11). These have been attributed to be the electron transfer bands of uranyl ion. The bathochromic shift observed as compared to that for the free uranyl ion[5e] can be explained in terms of coordination of the UO_2^{2+} ion. The nitrate ion that has got a high tendency to transfer electrons upon coordination must have most probably caused the electron-transfer bands to shift further into the visible region. The spectral pattern compares very well with those observed by others for uranyl-nitrato complexes.[19] This therefore provides credence to the contention that nitrates are coordinated to the metal centre in the respective complexes.

Hetero-ligand Fluoro(hydrazine) complex of UO_2^{2+}

Owing to the success in using alkali hydrofluoride as the fluorinating agent for the synthesis of a number of mixed-ligand fluorodioxouranates(VI) with a variety of co-ligands like amino acids (Chapter V), phosphate (present work), it was anticipated that a mixed-ligand fluoro complex of UO_2^{2+} with hydrazine as the co-ligand could be synthesized by adopting a similar methodology. In accordance with this, $UO_3.4H_2O$ on reaction with AHF_2 (A = K or

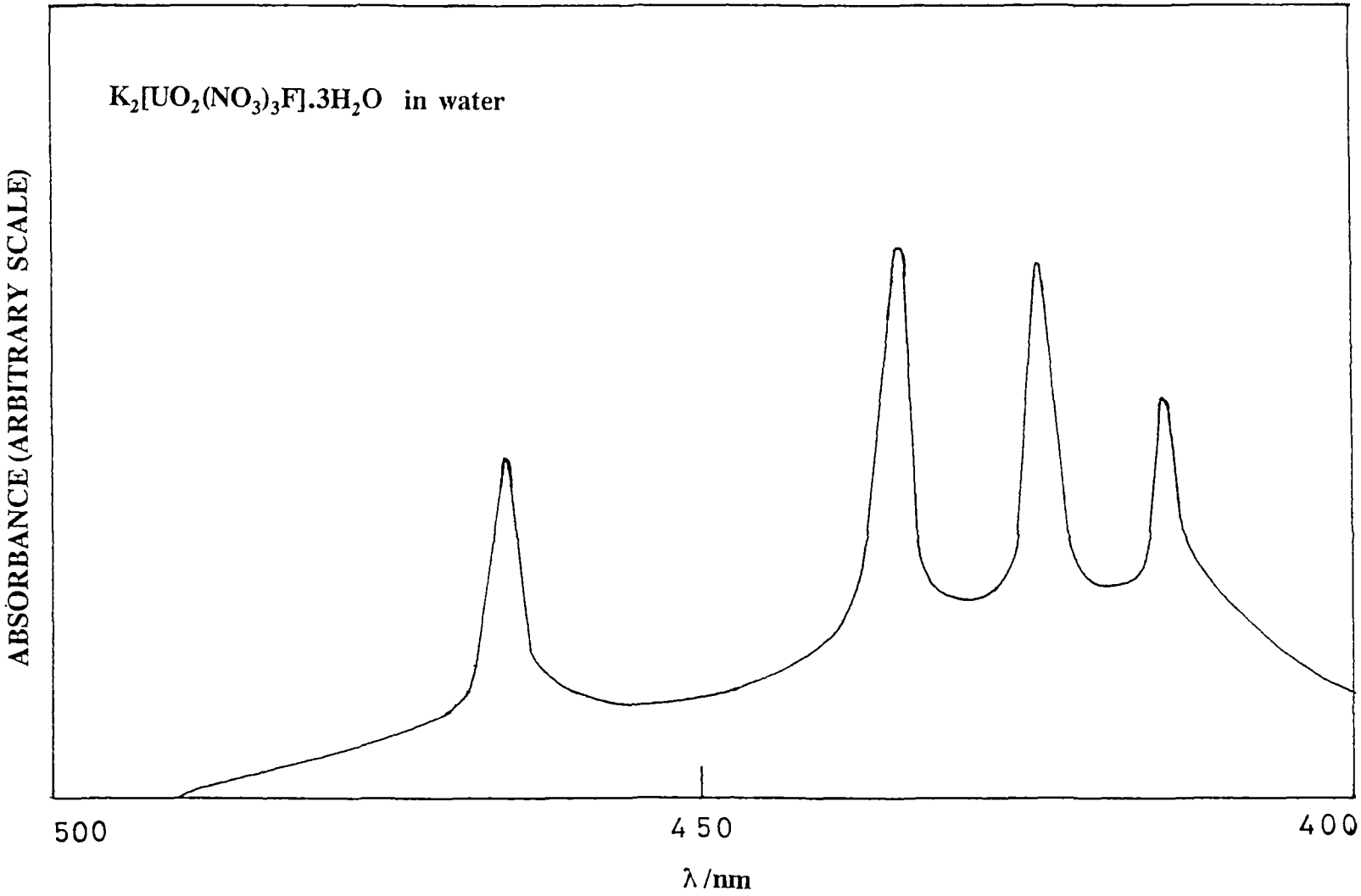

FIG. 6.9: ELECTRON ABSORPTION SPECTRUM

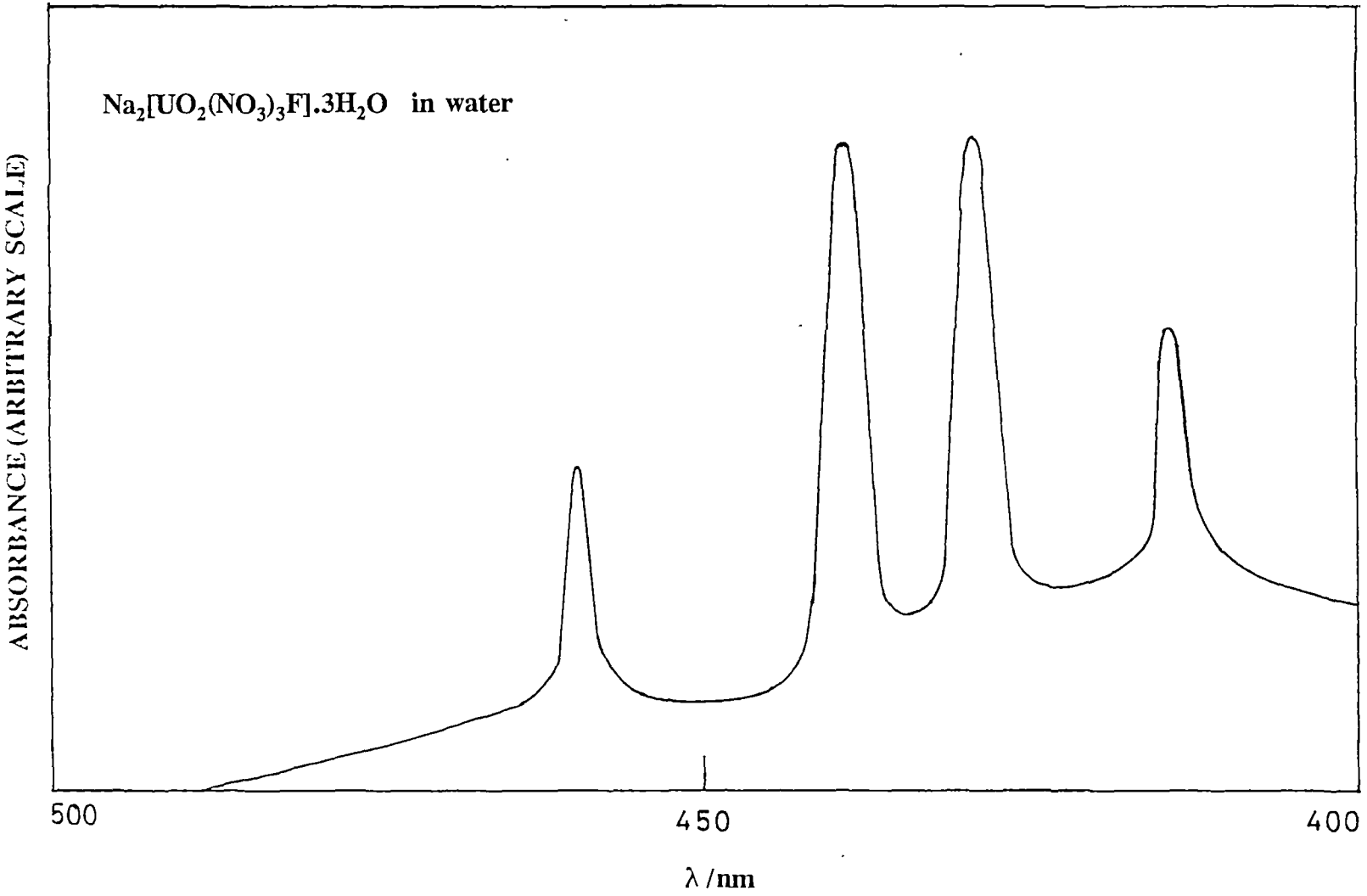

FIG. 6.10: ELECTRON ABSORPTION SPECTRUM

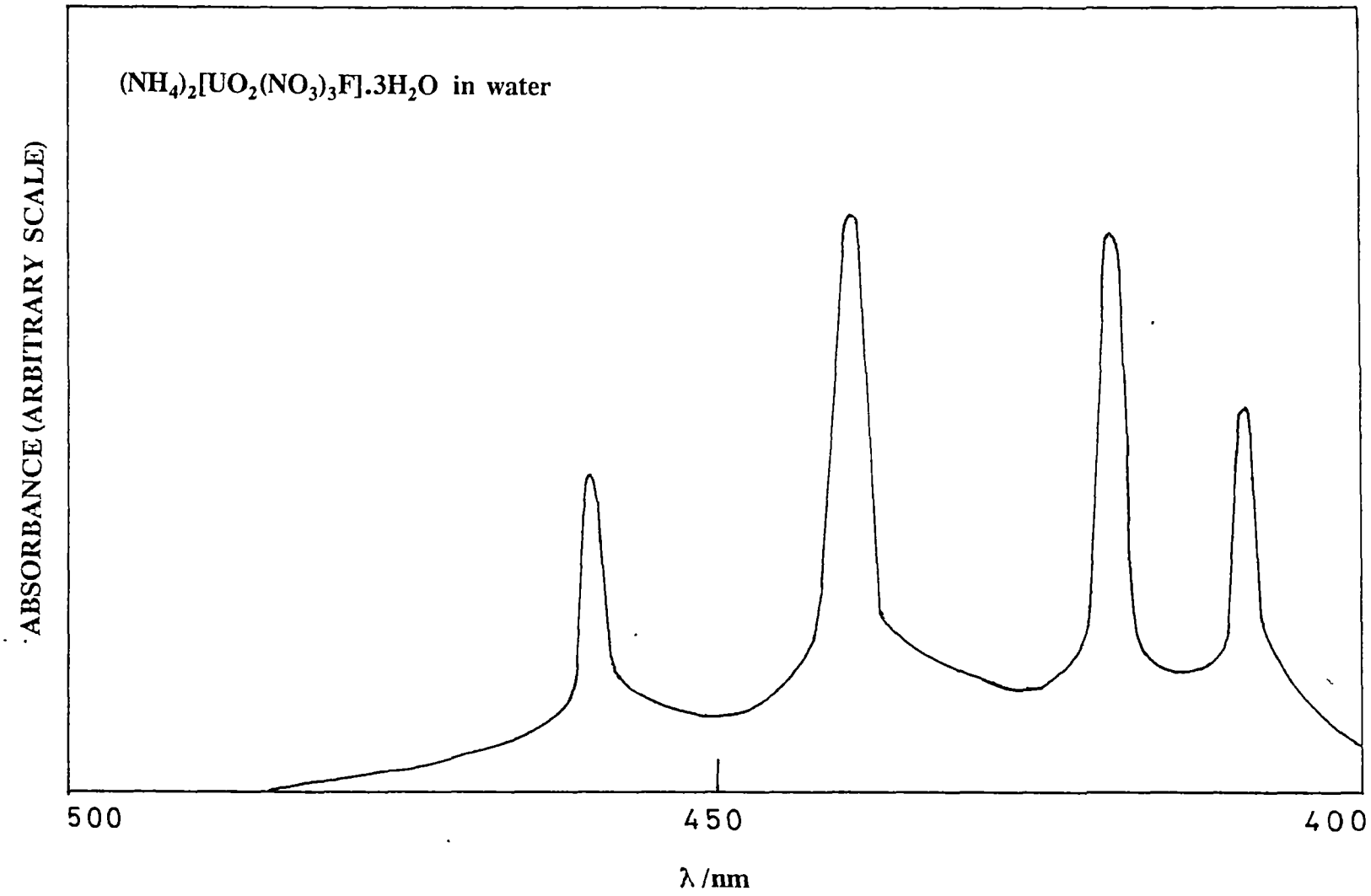

FIG. 6.11: ELECTRON ABSORPTION SPECTRUM

NH_4) and hydrazine hydrate, $N_2H_4.H_2O$ at steam-bath temperature afforded the hitherto unreported complex $[UO_2(N_2H_4)_2F_2].2H_2O$. The pH value of the reaction solution measured at the stage of precipitation of the compound was found to be *ca.*8.5 which has facilitated the coordination of N_2H_4 to the metal centre since in a basic medium the possibility of hydrazonium ion ($N_2H_5^+$) formation does not exist.

The compound is brownish in colour and insoluble in most of the commonly available polar and non-polar solvents. The scanning electron micrograph (Fig.6.12) is a reflection of the crystalline and homogenous nature of the complex $[UO_2(N_2H_4)_2F_2].2H_2O$. However, no definitive shape of the crystals could be discerned from the micrograph.

The IR spectrum (Fig.6.13) of $[UO_2(N_2H_4)_2F_2].2H_2O$ showed a few bands at 924s [ν(U=O), trans.linked O=U=O], 415m, [ν(U-F)] and bands typical of coordinated hydrazine. However, the absorptions of particular significance for coordinated hydrazine are those arising from N-N stretching vibrations.[20] In complexes containing unidentate hydrazine ligands ν(N-N) occurs around 930 cm^{-1} while in complexes containing bidentate hydrazine ν(N-N) appears at *ca.* 970 cm^{-1}. In the present case a medium intensity band was observed at 955 cm^{-1}. Further the appearance of NH_2 stretches at 3265s, 3207m and 3131w cm^{-1} and the similarity in spectral pattern with hydrazine and mixed-ligand hydrazine complexes of different metals

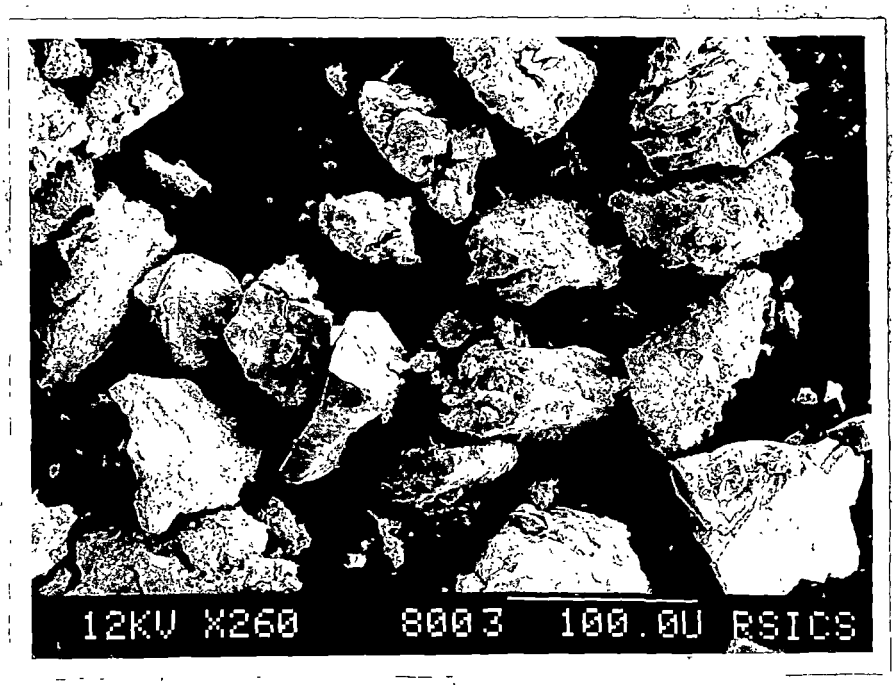

FIG. 6.12: SE MICROGRAPH OF $[UO_2(N_2H_4)_2F_2].2H_2O$

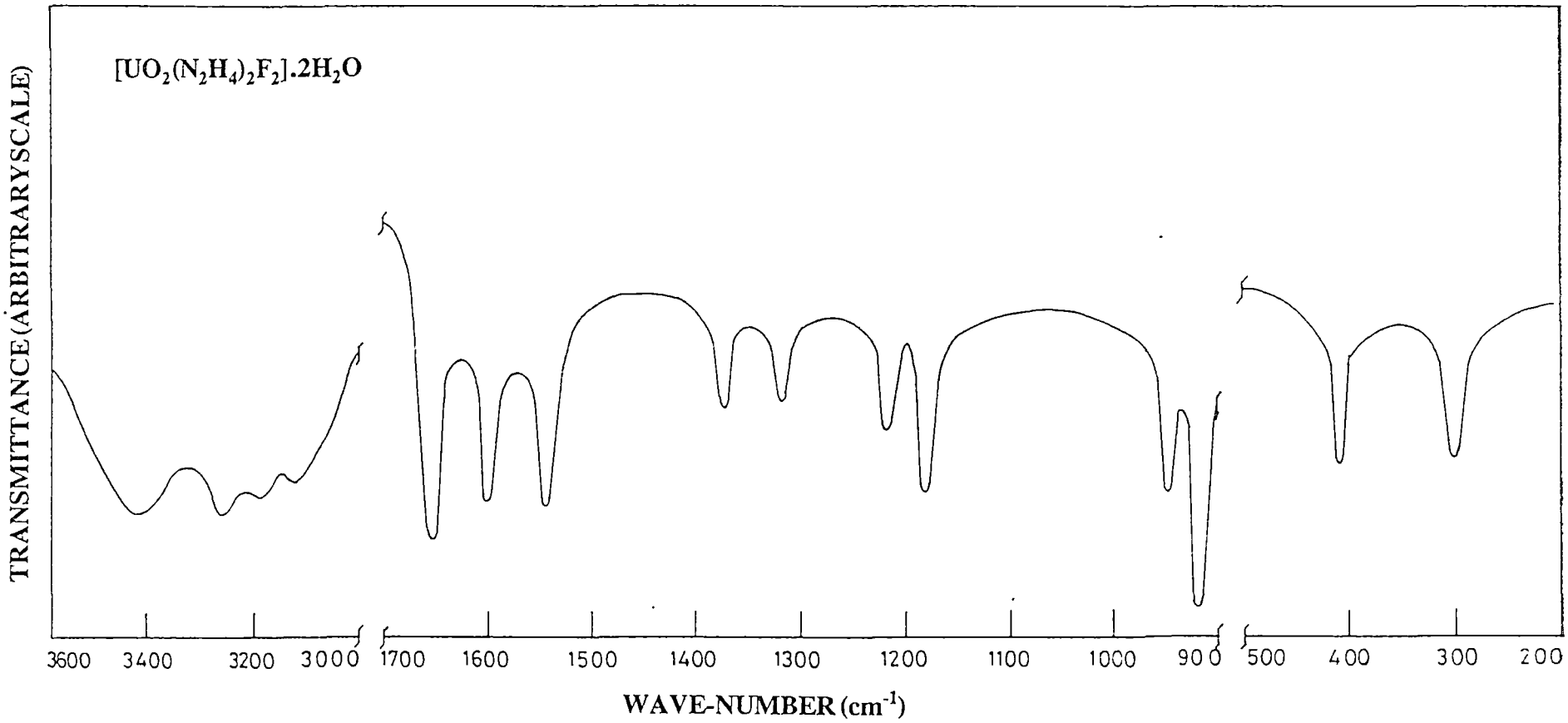

FIG. 6.13: IR SPECTRUM

synthesized earlier by others[20,21] and our group[22] cause us to state that the complex $[UO_2(N_2H_4)_2F_2].2H_2O$ contains only bidentate hydrazine ligands. Though the hydrazines in $[UO_2(N_2H_4)_2F_2].2H_2O$ might act as chelated ligands, the possibility of hydrazine bridges leading to a polymeric network in the crystal lattice cannot be ruled out. The insolubility of $[UO_2(N_2H_4)_2F_2].2H_2O$ might as well be an indication of polymeric nature of the complex. The metal-nitrogen stretching was observed at 307 cm^{-1} as a consequence of hydrazine coordination.

Pyrolysis studies were conducted on each of the mixed-fluoro (phosphato), fluoro(nitrato) and fluoro(hydrazine) complexes in order to ascertain the nature of water molecules present in the complexes. Pyrolyses of the compounds at *ca.*150^{o}C for nearly 2h gave products with weight losses corresponding to the loss of three molecules of water for each of the fluoro(phosphato) and fluoro(nitrato) complexes and product corresponding to the loss of two molecules of water in the case of fluoro(hydrazine) complex. This therefore enables us to state that each of the fluoro(phosphato) and fluoro(nitrato) complexes contains three molecules of lattice water whereas the fluoro(hydrazine) complex contains two such water molecules. Significant to note here is that each of the pyrolysed product of fluoro(hydrazine) and fluoro (nitrato) complexes did not show the characteristics of any kind of water in its IR spectra, but those of fluoro(phosphato)

complexes displayed the features of bonded water at *ca.*740 cm^{-1} attributed to the rocking mode of coordinated water [$\rho_r(H_2O)$].

In this way a number of mixed-ligand fluoro complexes of UO_2^{2+} containing inorganic co-ligands could be obtained in high isolated yields. A notable general point in the context of the present synthetic study is the avoidance of an excess of fluoride ion concentration to inhibit preponderance of binary fluoro complex formation.

Raman Spectroscopic Studies on Hetero-Ligand Fluoro(phosphato), Fluoro(nitrato) and Fluoro(hydrazine) complexes of UO_2^{2+}

One of the most important and powerful techniques useful for the characterization of coordination compounds of uranyl ion is Raman spectroscopy. The $\nu_s(U{=}O)$ is believed to be an important laser Raman (LR) probe. In the Raman, only the symmetric stretching mode, $\nu_s(UO_2)(\nu_1)$ is active [$\nu_{as}(UO_2)(\nu_3)$ is not active] and this has generally been observed at *ca.*900 cm^{-1} in the solids.[1,23] In solutions, however, $\nu_s(UO_2)(\nu_1)$ of UO_2^{2+} ions appears at 870 cm^{-1}. This generally decreases on complex formation with a variety of inorganic and organic ligands. A good correlation between the shift in the ν_1 frequency and the number of ligands coordinated to the metal centre has been discussed in a recent paper.[24]

In the present study, the laser Raman spectra (Figs.6.14-6.19) of the reaction solutions were recorded in the following manner. A small amount of the solution was drawn out from the reaction vessel and the spectra were recorded in each of the cases of fluoro(phosphato) and fluoro(nitrato) complexes before precipitating out the compounds. In each case the ν_1 frequency was observed to occur at *ca.*840 cm^{-1}. The observed shift in frequency by 30 cm^{-1} (*cf.* 870 cm^{-1} for aqueous uranyl ion) is a clear reflection of complex formation by uranyl ion and most probably also of the increase in stability upon complexation as compared to that of hydrated uranyl ion. Significant to note here is that though the $\nu_s(UO_2)(\nu_1)$ mode of UO_2^{2+} is insensitive to the coordination of NO_3^- (Refs. 24,25) to the uranyl centre, the observed lowering in frequency of fluoro(nitrato) complexes indicates that the presence of fluoride ligands must have been responsible for the increase in stability of mixed-fluoro(nitrato) complexes of the metal. Such an exercise could not be conducted for the complex $[UO_2(N_2H_4)_2F_2].2H_2O$ since a solid product precipitated out of the solution instantaneously on the addition of hydrazine.

On the contrary, each of the mixed-fluoro(phosphato), fluoro(nitrato) and fluoro(hydrazine) complexes of UO_2^{2+} displayed a strong Raman signal at *ca.* 900 cm^{-1} in the solid state and this has been attributed to the $\nu_s(UO_2)(\nu_1)$ mode of UO_2^{2+} ion. The

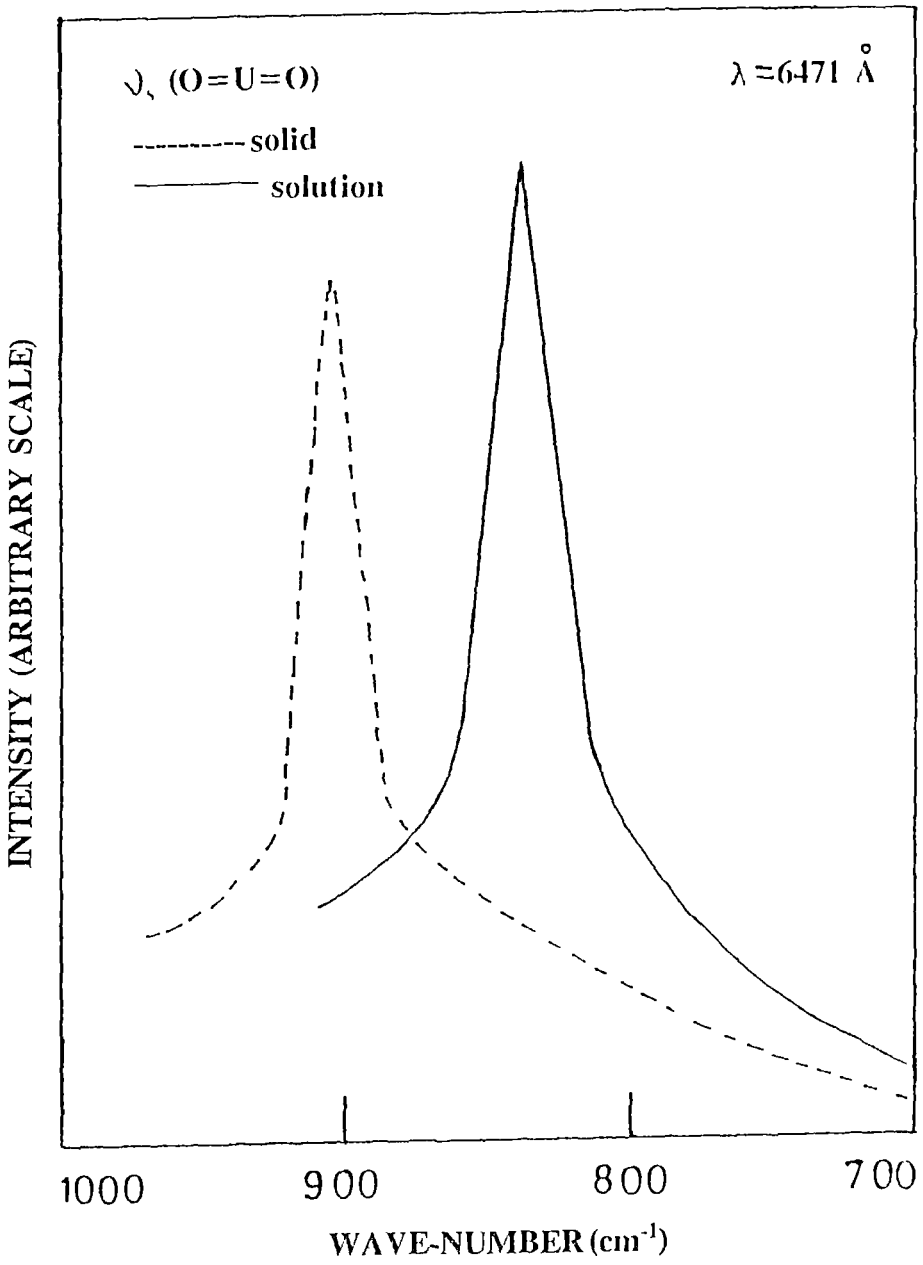

FIG. 6.14: RAMAN SPECTRUM OF $K_2[UO_2(PO_4)F(H_2O)_3].3H_2O$

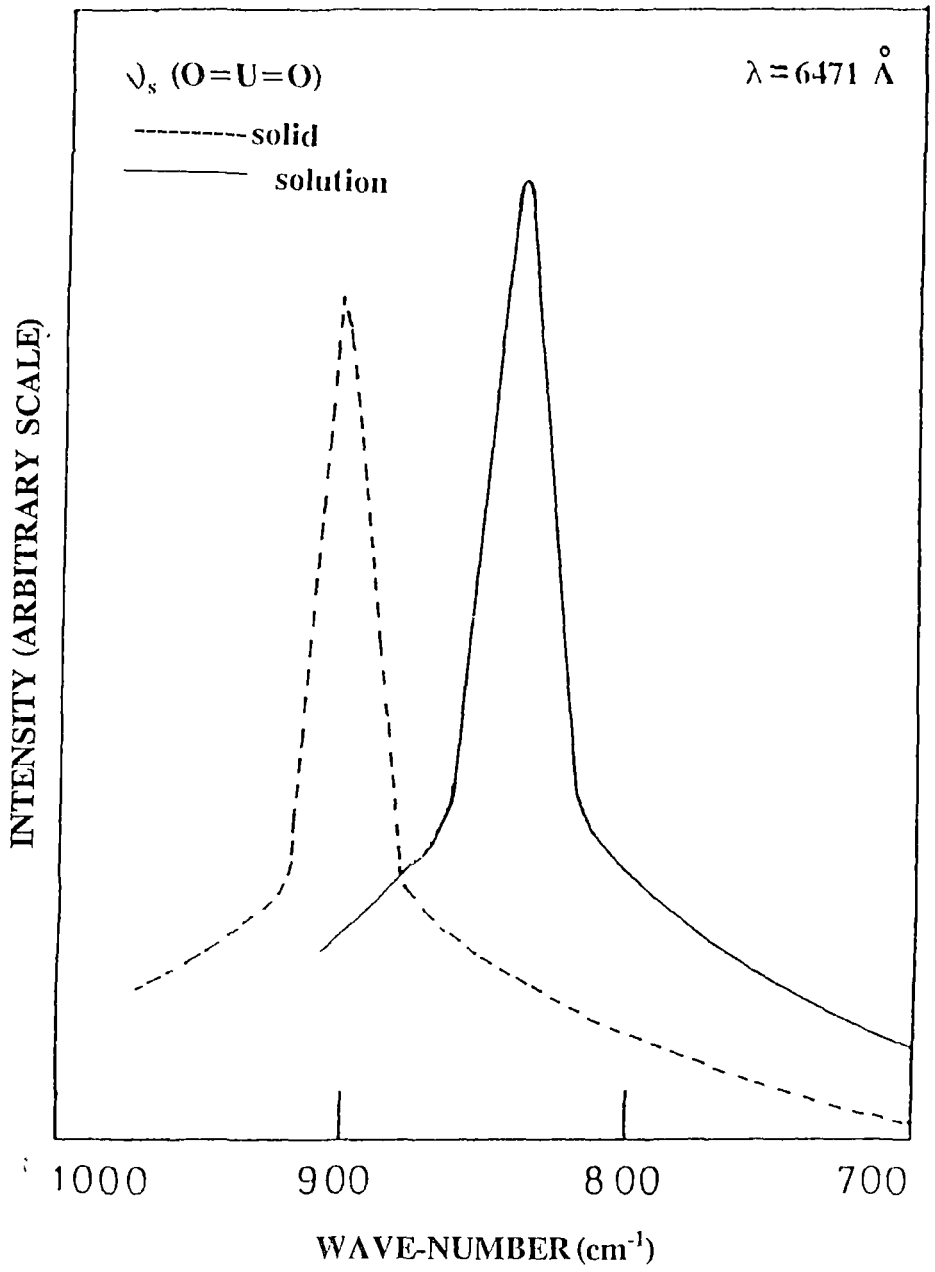

FIG. 6.15: RAMAN SPECTRUM OF $Na_2[UO_2(PO_4)F(H_2O)_3].3H_2O$

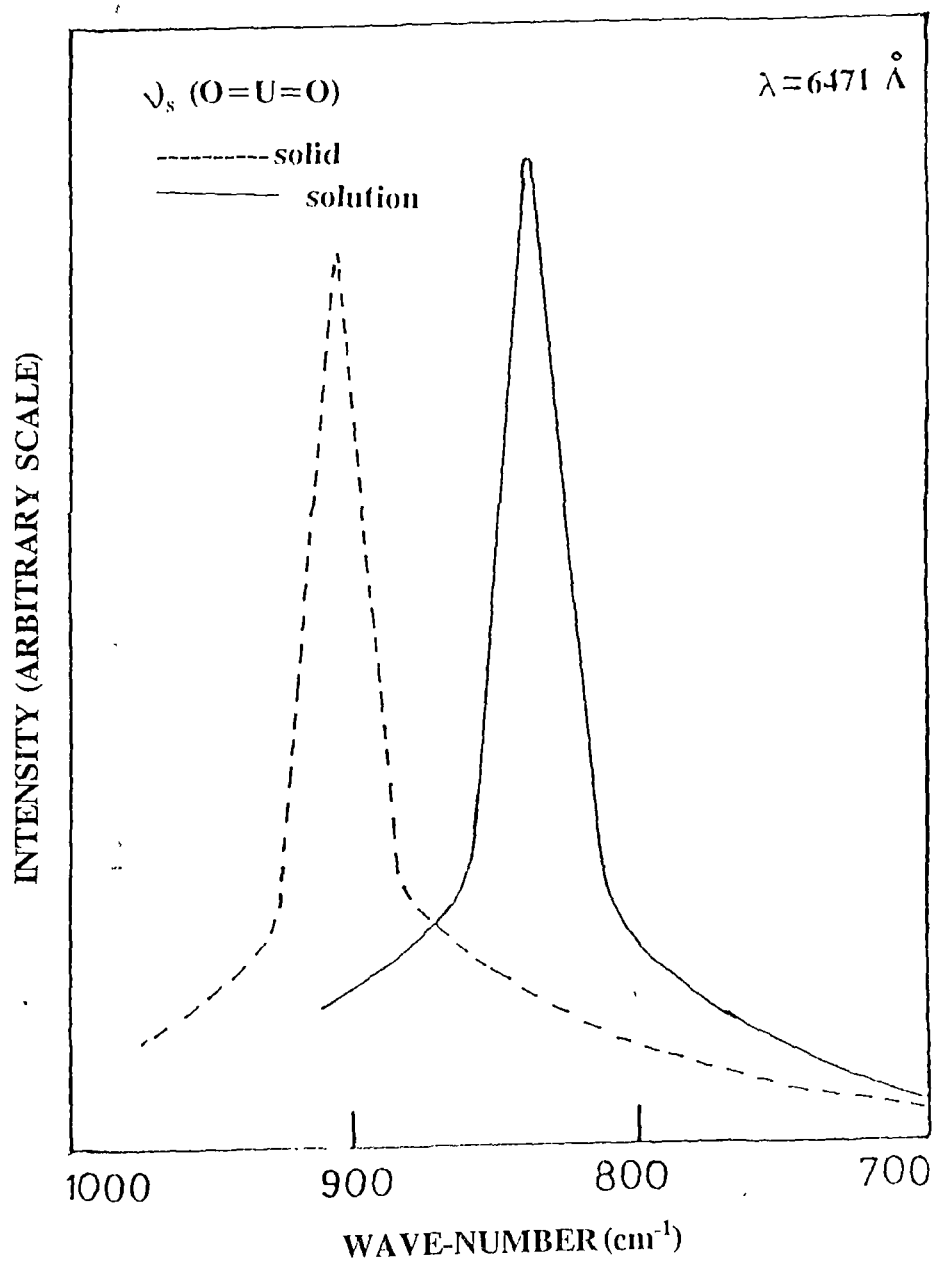

FIG. 6.16: RAMAN SPECTRUM OF

$(NH_4)_2[UO_2(PO_4)F(H_2O)_3].3H_2O$

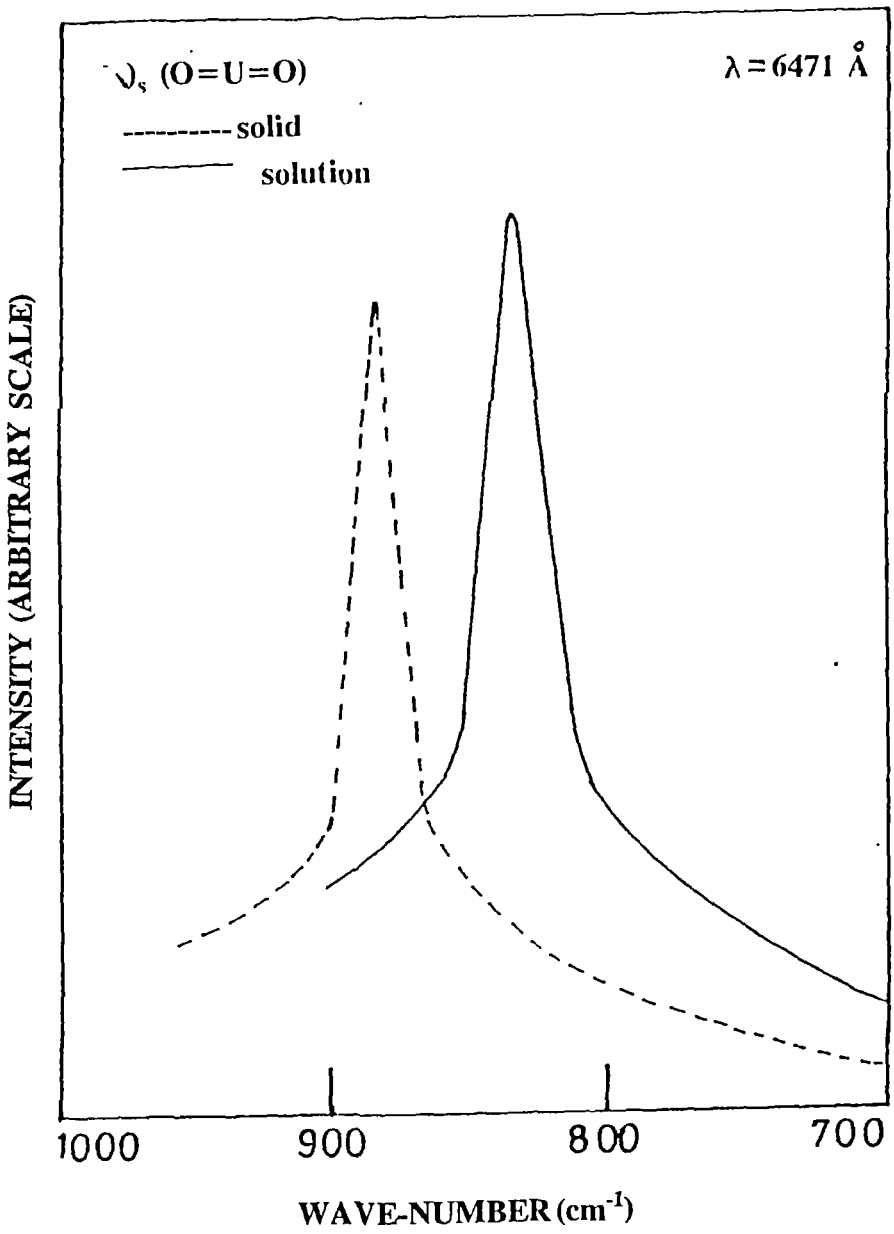

FIG. 6.17: RAMAN SPECTRUM OF

$K_2[UO_2(NO_3)_3F].3H_2O$

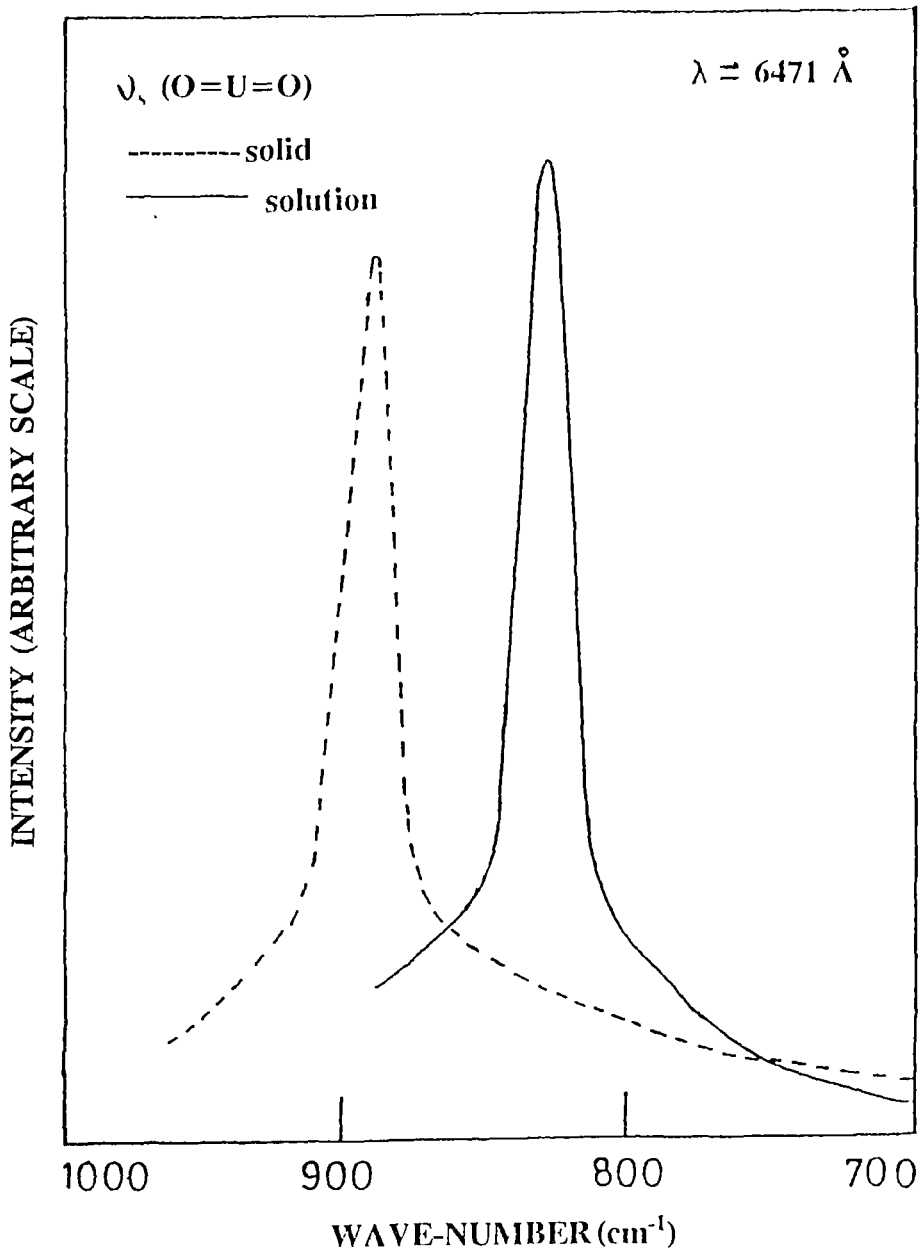

FIG. 6.18: RAMAN SPECTRUM OF

$Na_2[UO_2(NO_3)_3F].3H_2O$

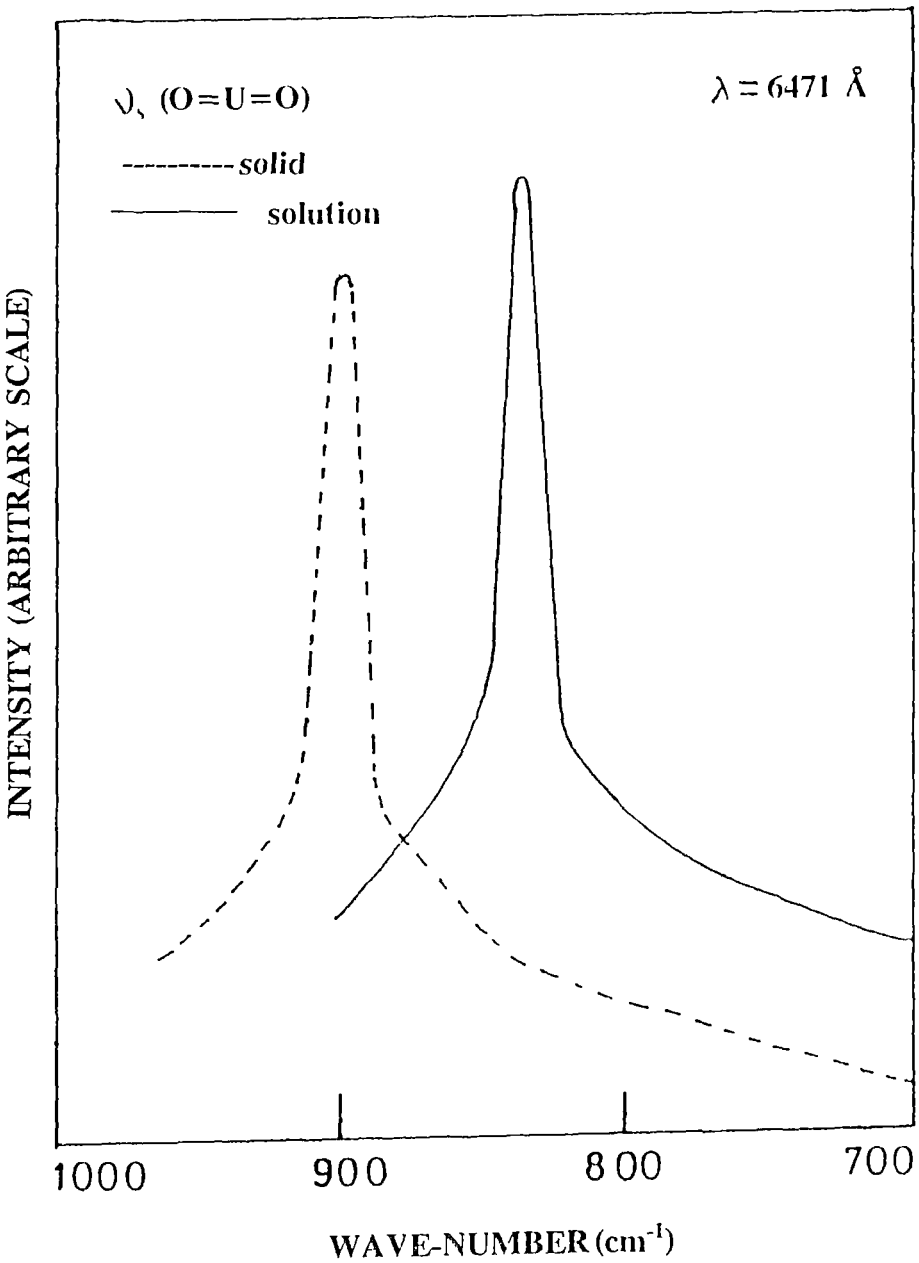

FIG. 6.19: RAMAN SPECTRUM OF $(NH_4)_2[UO_2(NO_3)_3F].3H_2O$

observed increase in ν_1 frequency in going from the solution to the solid state is most probably due to the decrease in number of aqua ligands in the UO_2^{2+} coordination shell of the solid complexes. A similar trend is occassionally encountered in highly ligand concentrated solutions of UO_2^{2+}.[26]

Alkali tetrafluorodioxouranates(VI) trihydrates $A_2[UO_2F_4].3H_2O$ (A = K, Na or NH_4)

Having been encouraged by the successful synthesis of a number of binary and mixed-ligand oxofluorouranates(VI) as described in Chapter V of the thesis as well as those set out in the present Chapter, our attention was drawn to the dioxotetrafluorouranate, $[UO_2F_4]^{2-}$ species as well. The complex species has been known and there is more than one method available for its preparation but the procedures are all circuitous. This point has been emphasized in the introduction section. Our goal in this context was to improvise direct synthetic routes to the complex $[UO_2F_4]^{2-}$ species. To this end we have been able to improvise two methodologies the strategies of which are highlighted below.

One of the methodologies is based upon the reaction of a yellow product, obtained by treating uranyl nitrate, $UO_2(NO_3)_2.6H_2O$, solution with an aqueous alkali, AOH (A = K or

Na), or aqueous ammonia (sp.gr.0.91), with 48% aqueous hydrofluoric acid and A_2CO_3 (A = K, Na or NH_4). The presence of alkali carbonate was apparently essential for it not only provided an appropriate concentration of the counter cation, A^+, but also presumably controlled the reaction pH ($4H^+ + CO_3^{2-} \longrightarrow CO_2 + 2H_2O$) to a level required for the success.

The basis of the other method has been a sort of nucleophilic substitution reaction. What was done in this case was that a well known[27] peroxouranium(VI) species, $UO_2(O_2).2H_2O$, was reacted with aqueous HF (48%) in the presence of alkali fluoride, AF (A = K, Na or NH_4) to afford $A_2[UO_2F_4].3H_2O$ in very high yields. The mechanism of the reaction presumably involved a concerted process wherein the hydrofluoric acid interacted with the bonded peroxide to liberate H_2O_2 quantitatively and F^- ions present in the reaction medium occupied the sites made available to provide the complex as obtained. Although one might tend to presume the formation of an aquated uranyl viz., $[UO_2(H_2O)_n]^{2+}$ ion resulting from the reaction of $UO_2(O_2)$ with aq. HF followed by its interaction with F^- ions already available in the solution. We wish to subscribe to the former pathway preferred to the latter because of the presence of a good amount of fluoride at a stage when $UO_2(O_2)$— HF reaction was to take place. Since fluoride is certainly a superior ligand as compared to aqua ligands (H_2O) our proposition seems to be rather rational.

The alkali dioxotetrafluorouranates(VI), $A_2[UO_2F_4].3H_2O$ (A = K, Na or NH_4) are lemon-yellow crystalline solids highly soluble in water. The solution electrical conductances of the compounds in water were found to lie in the range 230-240 $\Omega^{-1}cm^2mol^{-1}$ which conform to their 2:1 electrolytic nature. The favourable experimental result attests to their stability in aqueous solution.

The significant features of IR spectra (Figs.6.20-6.22) of the complexes $A_2[UO_2F_4].3H_2O$ (A = K, Na or NH_4) were the bands at *ca.*928, *ca.*374, *ca.*1627 and *ca.*3460 cm^{-1}, which have been attributed to the absorptions originating from ν(U=O) [trans. linked O=U=O], ν(U-F), δ(H-O-H) and ν(O-H) modes, respectively.

In order to obtain further support to the structural motifs of the complexes $A_2[UO_2F_4].3H_2O$ (A = K, Na or NH_4), $(NH_4)_2[UO_2F_4].3H_2O$, as a typical example, was subjected to laser Raman (LR) spectroscopy. The Raman signals (Fig.6.23) observed at 425 and 910 cm^{-1} have been assigned as the ν(U-F) and ν(U=O) [trans.linked O=U=O) modes, repectively. Importantly the LR spectral features also complement the IR spectral results obtained on the complexes.

The results of the Infrared and laser Raman spectroscopic studies are thus in full agreement with the formulae $A_2[UO_2F_4].3H_2O$.

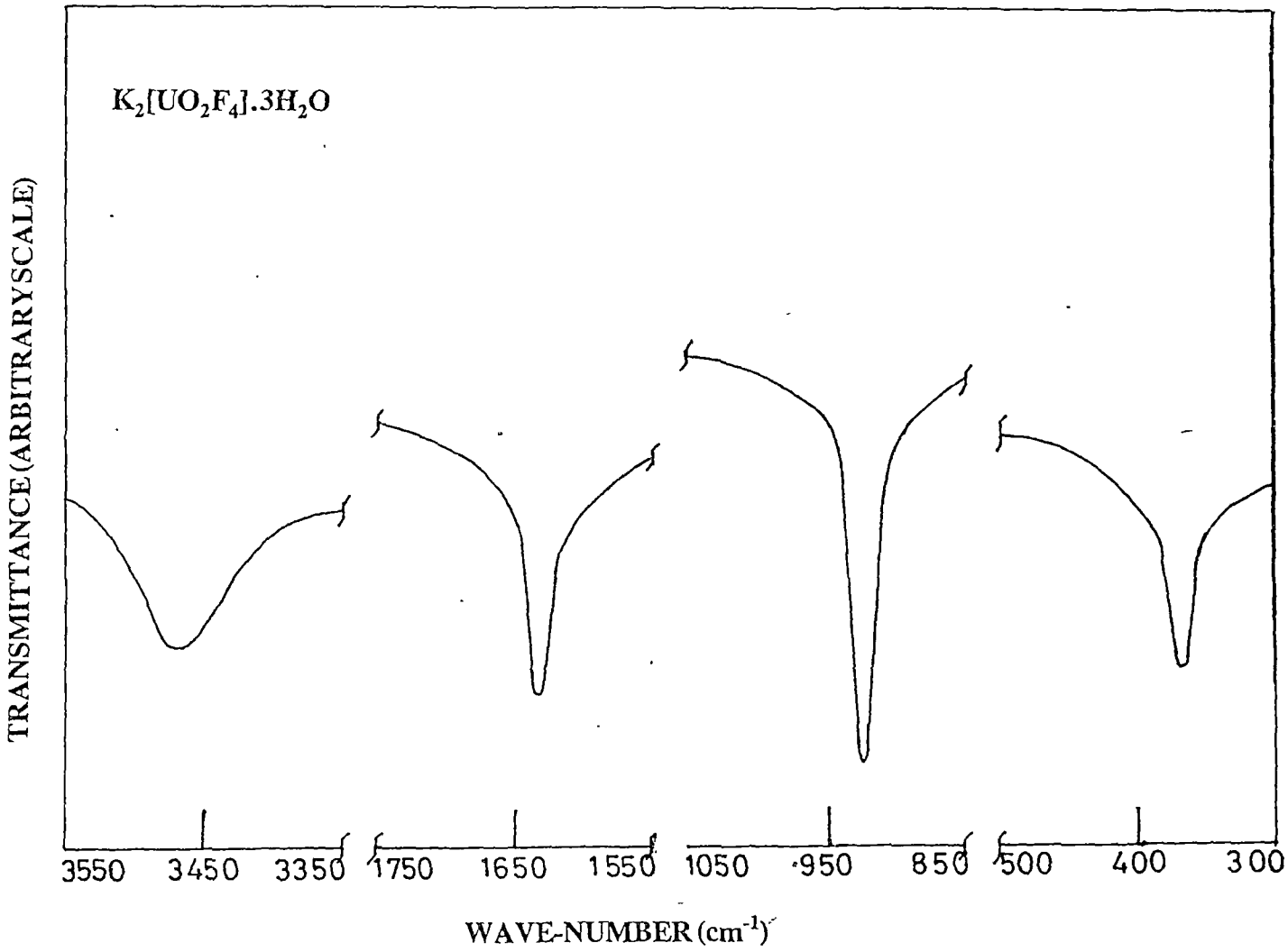

FIG. 6.20: IR SPECTRUM

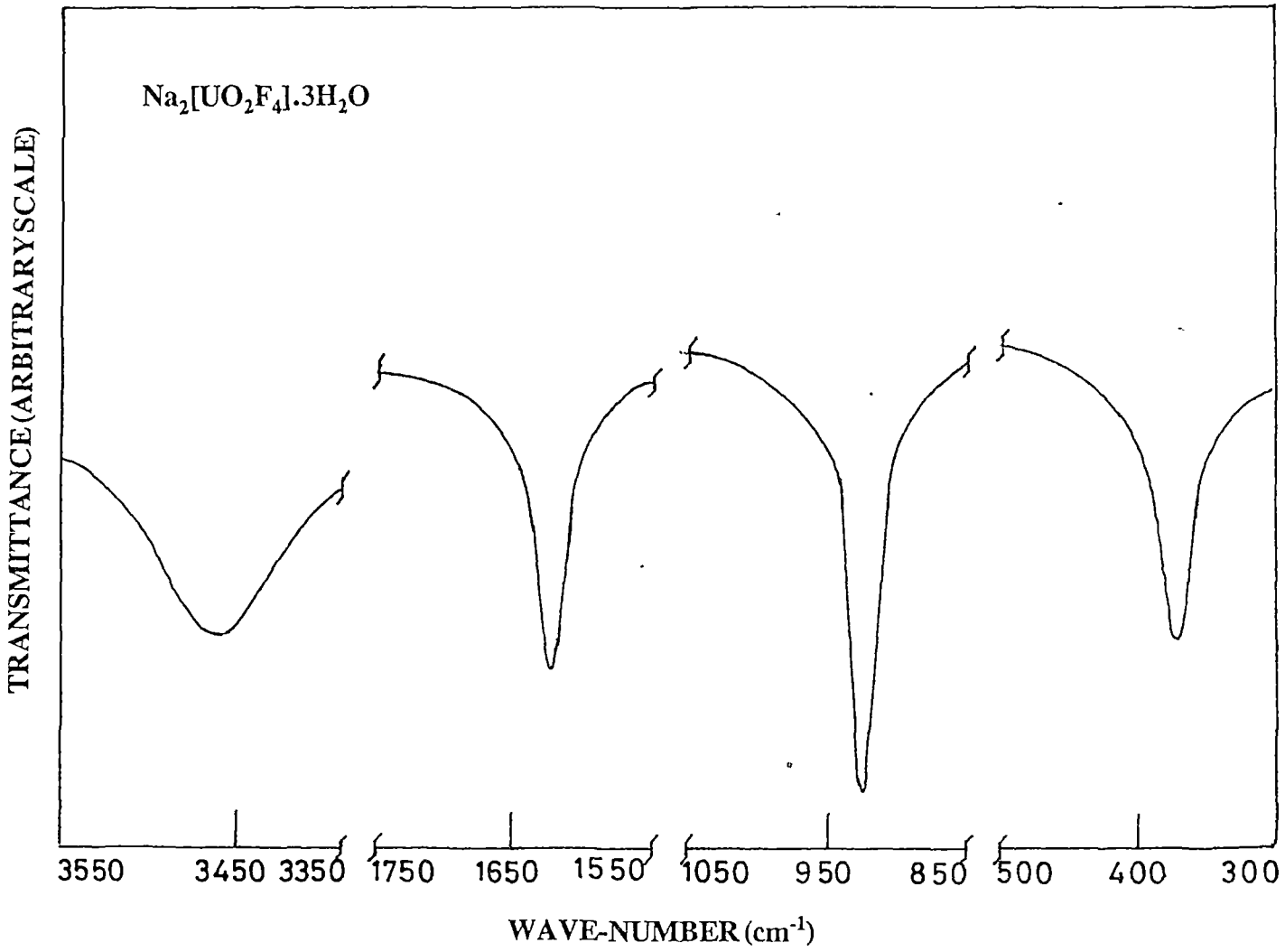

FIG. 6.21: IR SPECTRUM

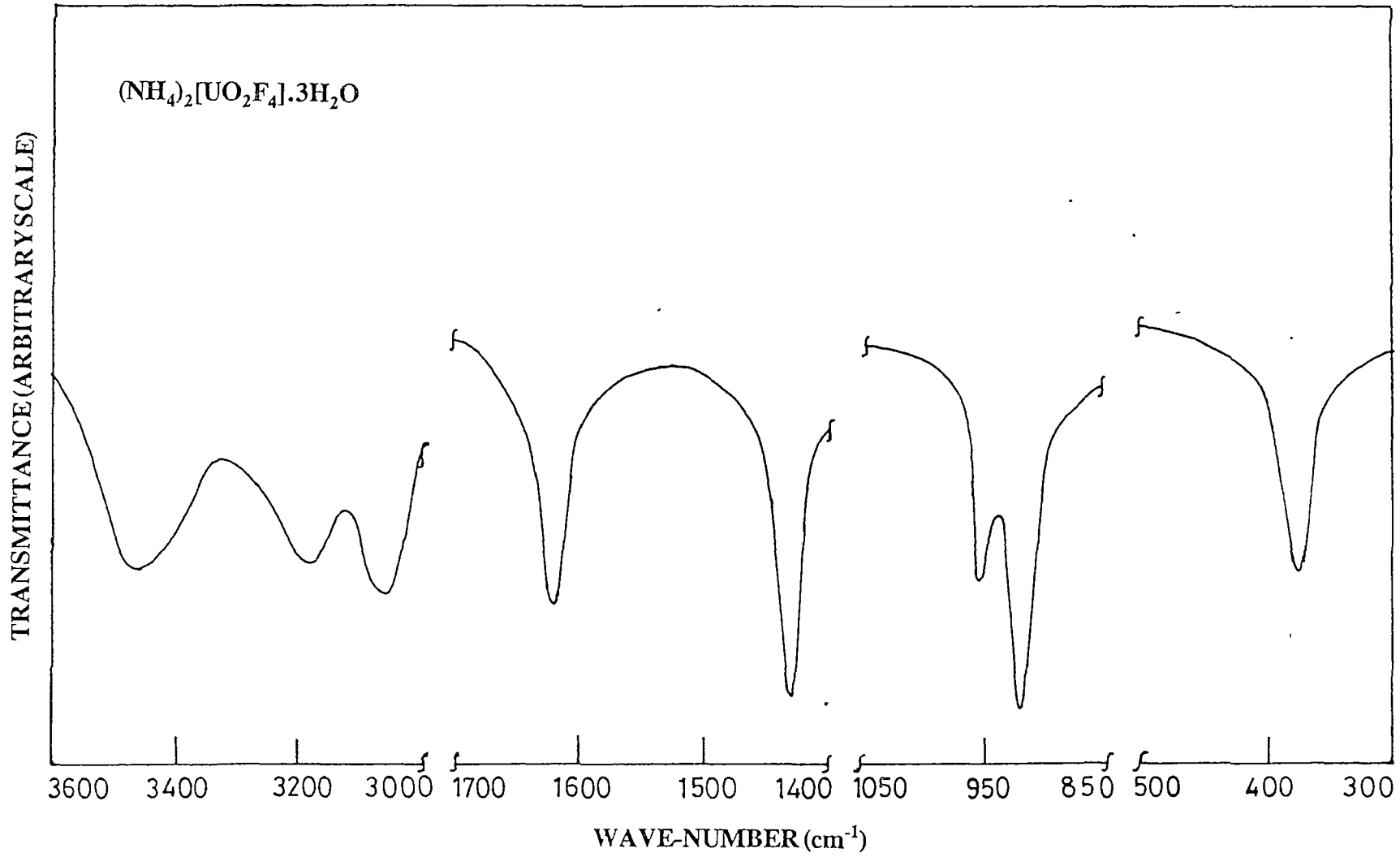

FIG. 6.22: IR SPECTRUM

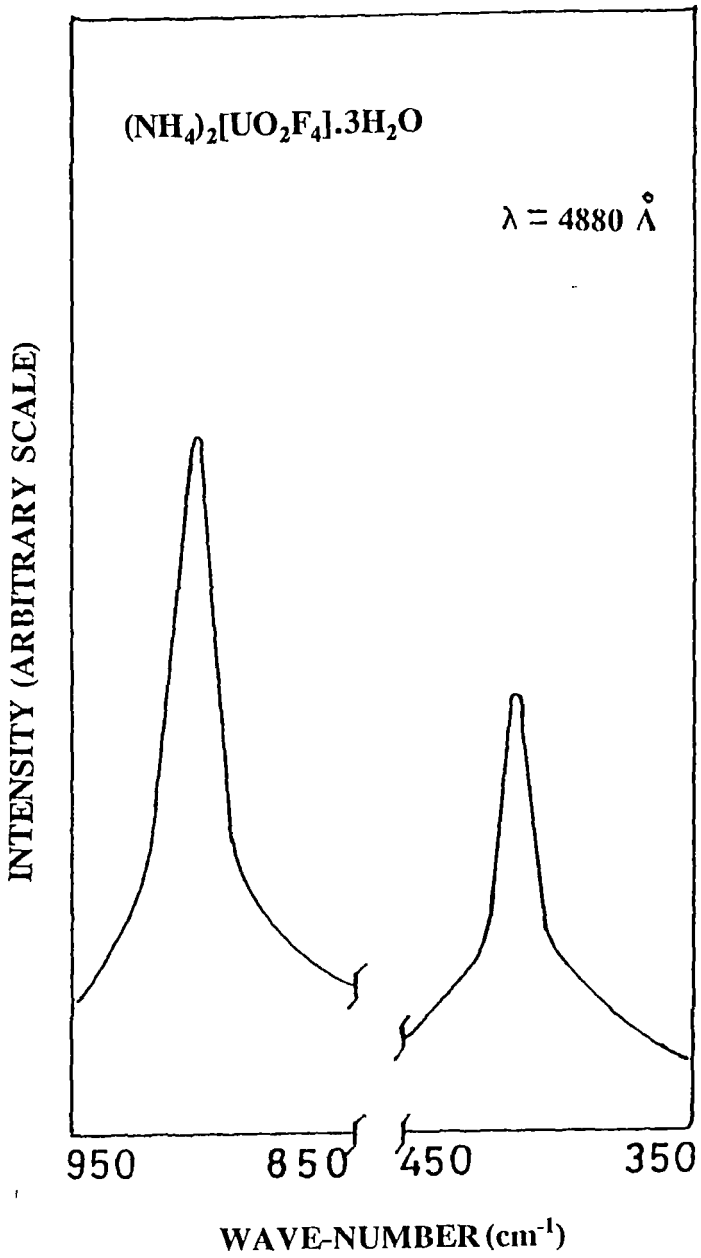

FIG. 6.23: RAMAN SPECTRUM

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APPENDIX

LIST OF PUBLICATIONS

1. Occurrence of a Manganese(III) Intermediate in the ($[MnO_4]^-$ —— SO_2) Redox Reaction

   C.Bhattacharjee, M.K.Chaudhuri, G.C.Mandal, P.C.Paul and P.Srinivas

   J.Chem.Soc.,Dalton Trans., 1993 (in press) Paper No. 3/03328/DAP.

2. A Simple Synthesis of bis(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2.2H_2O$

   M.K.Chaudhuri, P.C.Paul and P.Srinivas

   Proc.Indian Acad.Sci., 1992, 104, 479.

3. First Reported Synthesis of Ammonium Hexafluorodioxo-uranate(VI), $(NH_4)_4[UO_2F_6]$

   M.K.Chaudhuri, D.T.Khathing and P.Srinivas

   J.Fluorine Chem., 1992, 56, 305.

4. Synthesis and Spectroscopic Characterization of Mixed-Fluoro Complexes of UO_2^{2+} Containing Amino Acids, Acetylacetonate or Acetate as the Co-Ligands and the First Report on the Heptafluorodioxouranate(VI) Complex $[UO_2F_7]^{5-}$

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   Polyhedron, 1993, 12, 227.

5. Complex Fluorouranates(VI). Synthesis, Characterization and Structural Assessment of New Mixed-Fluoro Complexes of UO_2^{2+} Containing Phosphate, Nitrate or Hydrazine as the Co-Ligands

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Polyhedron (in press) Paper No. 905478.

Occurrence of a Manganese(III) Intermediate in the $[MnO_4]^-$–SO_2 Redox Reaction†

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Evidence for a manganese(III) intermediate, previously implicated in the $[MnO_4]^-$–SO_2 electron-transfer process, has been obtained by conducting the reaction in the presence of F^-. A combination of *in situ* EPR and electronic absorption spectroscopies was used to follow the reaction course and physico-chemical techniques were used to ascertain the identity of the isolated manganese(III) products. The evidence suggests that in the presence of F^- manganese(VII) is directly reduced to manganese(III) and thence to manganese(II).

It is a text book[1] story that manganese(VII) (*cf.* MnO_4^-) is reduced to manganese(II) by SO_2 in an aqueous medium. Owing to its high sensitivity the reaction serves as a very useful test for the two reagents. As manganese is capable of exhibiting a wide spectrum of oxidation states, there exists a finite possibility of involvement of an intermediate oxidation level in the $[MnO_4]^-$–SO_2 redox process. Indeed DeThomas and Purdy[2] conjectured the involvement of a manganese(III) intermediate in such a reaction more than three decades ago. However, no convincing evidence was available in this regard.

We have been interested in manganese(III) chemistry[3] for some time and it has been our argument that fluoride ion is an efficient stabilizer of this oxidation level of the metal. It is with this perception that we sought to demonstrate the involvement of manganese(III) in the $[MnO_4]^-$–SO_2 redox process. Our approach was to detect the reaction intermediate by *in situ* experimentation and also by product isolation and characterization. The *in situ* experiments were required in order to rule out the formation of divalent manganese prior to that of manganese(III). This was especially important because a rapid reduction of some of the $[MnO_4]^-$ to aquated Mn^{2+} followed by its reaction with $[MnO_4]^-$ leading to manganese(III) could be an alternative possibility.

The aim of this work is to provide evidence to support the view that in the presence of fluoride ions manganese(VII) is directly reduced to manganese(III) and thence to its divalent state.

Experimental

All the chemicals used were of reagent grade quality. Infrared spectra were recorded on a Perkin Elmer Model 983 spectrophotometer. Reflectance spectra were recorded against MgO using a Carl Zeiss Jena VSU 2-P instrument. Magnetic susceptibility measurements were made by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. EPR spectra were recorded using a Varian E 109 X-band spectrometer with 100 KHz field modulator. Electronic absorption spectra of the reaction solutions were recorded on a Hitachi Model 330 UV/VIS/NIR spectrophotometer fitted with a thermostatted cell holder. The pH values of the reaction solutions were measured using a Systronics type 335 digital pH meter. Deionized water was used for all the experiments described below.

Reaction of SO_2(g) *with* $KMnO_4$ *in Aqueous Solution in the Presence of Fluoride* (F^-).—(*i*) *Isolation and characterization of reaction intermediates.* (*a*) *Reaction intermediate* $K_2[MnF_3(SO_4)]$. Potassium permanganate (1.0 g, 6.33 mmol) was thoroughly mixed with KHF_2 (0.98 g, 12.55 mmol), to give an Mn:F ratio of 1:4. The mixture was then dissolved in water (30 cm^3) and SO_2(g) was bubbled through the solution with constant stirring until a brown solid precipitated. The flow of SO_2(g) was continued whereupon the solid redissolved to give a clear solution from which a crystalline pink solid precipitated on further bubbling of SO_2(g). The pH of the reaction solution was found to be in the region 2–2.5 and the flow of SO_2(g) was stopped at this stage. The product obtained as above was filtered, washed with ethanol two or three times, and finally dried *in vacuo* over concentrated H_2SO_4. The product analysed as $K_2[MnF_3(SO_4)]$ (Found: F, 20.3; K, 27.55; Mn, 19.3; SO_4^{2-}, 33.65. Calc. for $F_3K_2MnO_4S$: F, 19.90; K, 27.30; Mn, 19.2; SO_4^{2-}, 33.55%). IR (cm^{-1}): 1230s, 1145s and 1030s (ν_3), 975s (ν_1), 680s, 635s and 605s (ν_4) (ν_1, ν_3 and ν_4 are all S–O modes) and 525s [ν(Mn–F)]. Reflectance spectrum (cm^{-1}): 13,700 ($^5B_{1g} \longrightarrow {}^5A_{1g}$), 18 200 ($^5B_{1g} \longrightarrow {}^5B_{2g}$) and 21 650 ($^5B_{1g} \longrightarrow {}^5E_g$). μ_{eff} (Gouy method): 4.1 μ_B at 290 K.

(*b*) *Reaction intermediate* $K_2[MnF_5]\cdot H_2O$. Potassium permanganate (1.0 g, 6.33 mmol) and KHF_2 (2.47 g, 31.64 mmol) were dissolved in water (30 cm^3) maintaining the ratio of Mn:F at 1:10. Gaseous sulfur dioxide was bubbled through the solution with stirring until a rose-pink solid precipitated. At this stage, the pH of the reaction solution was found to be in the region 2–2.5. The rose-pink product obtained was isolated by filtration followed by washing twice with ethanol and finally drying *in vacuo* over concentrated H_2SO_4. The product was identified as $K_2[MnF_5]\cdot H_2O$ (Found: F, 37.95; K, 31.55; Mn, 22.40. Calc. for $F_5K_2Mn\cdot H_2O$: F, 38.6; K, 31.75; Mn, 22.3%). IR (cm^{-1}): 615m [ν(Mn–F), ν_3], 565s [ν(Mn–F), ν_4], 3468s [ν(O–H)] and 1635m [δ(H–O–H)]. Reflectance spectrum (cm^{-1}): 12 000 ($^5B_{1g} \longrightarrow {}^5A_{1g}$), 18 500 ($^5B_{1g} \longrightarrow {}^5B_{2g}$) and 21 000 ($^5B_{1g} \longrightarrow {}^5E_g$). μ_{eff} (Gouy method): 3.2 μ_B at 300 K.

(*ii*) In situ *methods for detection of reaction intermediates.* (*a*) *EPR experiments.* The solution EPR experiments were conducted at room temperature. A solution of a mixture of $KMnO_4$ and KHF_2 in a molar ratio of 1:2 ($Mn:F^- = 1:4$) was prepared. The solution strength was maintained at 10^{-3} mol dm^{-3} with respect to $KMnO_4$.

A regulated flow of SO_2(g) was maintained by using a mechanical regulator and a microjet. The pH of the reaction solution was recorded with a direct-reading digital pH meter.

† *Non-SI unit employed:* $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

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The solution registered a pH of *ca.* 5.5 prior to the initiation of bubbling of SO_2 gas. The reactant gas was then slowly bubbled through the solution into which the electrodes of the pH meter were already dipped so that the pH could be recorded simultaneously with the progress of flow of the gas. The SO_2 gas flow was stopped at every 0.2 pH interval followed by withdrawing a small volume of the solution and recording its EPR spectrum

(*b*) *Electron absorption spectra* A procedure similar to that above was performed except that electron absorption spectra, instead of EPR spectra, were recorded at different pH values. The spectra were recorded at ambient temperature

Elemental analyses. A Perkin Elmer model 2380 atomic absorption spectrophotometer was used for the analysis of K and Mn. Sulfate and F^- were estimated following the methods described earlier.[4] The oxidation state of manganese was determined chemically by a method elaborated previously [3]

Results and Discussion

It was perceived that Mn^{III}, if formed in the $[MnO_4]^-$–SO_2 reaction, could be trapped in aqueous solution by F^-. Accordingly, the $[MnO_4]^-$/SO_2 reactions were conducted with Mn:F ratios being maintained at 1·4 or 1:10 A general observation was the lowering of the pH of the solution upon bubbling of SO_2(g) through it The reaction carried out with an $Mn{\cdot}F^-$ ratio of 1.4 indicated that the process involved three different stages. (*i*) formation of a brown solid 1 at pH 3–2 5 with the mother-liquor becoming practically colourless, (*ii*) complete dissolution of this brown species with concomitant precipitation of a pink solid 2 at pH 2 5–2 and finally (*iii*) dissolution of the pink product at pH < 2 accompanied by decolorization of the reaction solution When an analogous reaction was conducted with an Mn F^- ratio of 1.10, the reaction course was very similar except that at pH 3–2 5 a brown solution, rather than a brown solid, was observed, and at pH 2 5–2 a rose-pink product 3, instead of the pink species 2, was obtained.

In order to get an insight of the $[MnO_4]^-$–SO_2 redox process, it was considered important to isolate the products 1–3 and ascertain the oxidation level of the metal The brown product 1 and the pink species 2 both analysed for fluoride, SO_4^{2-} and Mn, while 3 contained no sulfate Since both F^- and SO_4^{2-} are redox innocuous species, there was no interference in the chemical determination of the oxidation state of manganese. The iodometrically estimated oxidation level was ascertained to be +III in each case Though the product 1 did not comply with any stoichiometric formula, the Mn^{III}. F ratio was consistently > 2:1. The IR spectra suggested the occurrence of co-ordinated sulfate. The products 2 and 3 were identified as $K_2[MnF_3(SO_4)]$ and $K_2[MnF_5]{\cdot}H_2O$, respectively As it was not the central theme of this work to provide new methodologies for the synthesis of these compounds, they are not discussed further, indeed there are already very good synthetic methods for the preparation of similar compounds [4,5]

In situ Methods for Detecting Reaction Intermediates in the $[MnO_4]^-$–SO_2 *Redox Reactions*—Although it is certainly plausible that manganese(III) is involved as an intermediate in the reaction under investigation, the results of the above experiments do not in themselves provide conclusive evidence Thus, further experimentation involving *in situ* methods for detection of reaction intermediates was required

In order to obtain *in situ* evidence, two different experimental techniques *i.e.* EPR and electronic absorption spectroscopy were performed on the reaction solutions (see Experimental section). The stock solution (pH 5 5) was 10^{-3} mol dm^{-3} with respect to $[MnO_4]^-$ and KHF_2 was added to give a Mn:F ratio of 1·4. The EPR spectra of the solution upon treatment with SO_2(g) were recorded at pH intervals of 0 2 The solution was EPR silent until pH 1 7 when it displayed a six-line spectrum typical of divalent manganese.[6] The pattern remained unaltered down to pH 1.3, below which no measurement was made The EPR results suggest that under the present experimental conditions manganese(II) is not formed until the reaction pH is brought down to less than 2 The formation of manganese(III) at pH > 2 is thus more likely.

To complement the EPR observations electronic absorption spectroscopic experiments were conducted on similar solutions Spectra were recorded at pH values similar as those for the EPR experiments The parent solution (pH 5 5) showed the spectrum of $KMnO_4$,[7] as expected, with the charge-transfer bands appearing at *ca.* 32 100, *ca* 19 000 and *ca* 18 300 cm^{-1} Upon bubbling of SO_2(g) through the solution with concomitant lowering of pH, these charge transfer bands gradually disappeared with the simultaneous appearance of new bands at *ca.* 20 700, *ca.* 18 000 and *ca.* 12 900 cm^{-1}. The spectrum obtained at pH 3 3 showed absorptions only at these values This spectral pattern is typical of manganese(III)[3,8] attributable to the $^5B_{1g} \longrightarrow {}^5E_g$, $^5B_{1g} \longrightarrow {}^5B_{2g}$ and $^5B_{1g} \longrightarrow {}^5A_{1g}$ transitions, respectively. The spectrum remained virtually unaffected until pH 2 1. Further lowering of the pH (to *ca* 2) of the solution by reaction with SO_2(g) however led to the disappearance of the spectrum and the solution displayed virtually no absorption bands in agreement [9] with the formation of Mn^{II}. A combination of EPR and electronic absorption spectroscopic results thus provides strong evidence for the occurrence of a manganese(III) intermediate in the $[MnO_4]^-$–SO_2 redox process

In conclusion, the results of this investigation serve to favour the suggestion that, in the presence of fluoride ion, Mn^{VII} is directly reduced to Mn^{III} and thence to Mn^{II}.

Acknowledgements

We should like to thank the Department of Atomic Energy, Government of India, for financial support, Council of Scientific and Industrial Research, New Delhi for fellowships to P C P and P S and University Grants Commission, New Delhi for a fellowship to G C. M

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Received 9th June 1993, *Paper* 3/03328G

Reprinted from
Proceedings of the Indian Academy of Sciences
CHEMICAL SCIENCES

Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 104, No. 4, August 1992, pp. 479–481.

A simple synthesis of *bis*(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$

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MS received 27 February 1992; revised 22 April 1992

Abstract. A new and direct route to *bis*(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$, based upon the reaction of $UO_3 \cdot 4H_2O$ with acetylacetone ($C_5H_8O_2$), is described.

Keywords. *Bis*(acetylacetonato)dioxouranium(VI) dihydrate; mass spectrometry.

1. Introduction

Bis(acetylacetonato)dioxouranium(VI) dihydrate has been one of the most important compounds of uranium especially because of its moderate volatility, solubility in a variety of organic solvents, and stability. The compound is a very good synthon for accessing organouranium products and is expected to be of great synthetic value in the preparation of inorganic materials. Synthesis of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ is a prerequisite and the widely used method of its preparation (Schlesinger *et al* 1953) requires a large amount of sodium hydroxide to maintain the appropriate pH of the reaction medium to enable coordination of the ligand with UO_2^{2+}. Similarly, the methods of syntheses of the monohydrate, $UO_2(C_5H_7O_2)_2 \cdot H_2O$ (Blume *et al* 1956; Comyns *et al* 1958), also use appreciably high amounts of alkali. Owing to the use of such amounts of alkali, the end product is often contaminated with the alkali itself as well as by the alkali diuranate that originates from the alkali-assisted decomposition of the metal acetylacetonate. In an attempt to modify the procedure, a new method was introduced in 1986 (Bhattacharjee *et al* 1986). The method has some advantages but involves extra preparation and purification steps for obtaining the starting material. In this method ammonium diuranate, $(NH_4)_2U_2O_7$, was first prepared by treating an aqueous solution of $UO_2(NO_3)_2 \cdot 6H_2O$ with concentrated aqueous ammonia. The diuranate then needed repeated washing with water to render it free from the alkali. Particularly tedious and time consuming was the purification (making alkali-free) step. In order to overcome all the difficulties, a straightforward synthesis was sought. Here we describe a simple synthesis of the title compound. A combination of chemical analyses of the constituents, verification of uranium content of the product by atomic absorption spectrometry, and mass spectrometry has been used to judge the purity of the product.

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2. Experimental

Elemental analyses were performed by the Microanalysis Laboratory of our University. Uranium was estimated with a Perkin-Elmer 2380 AA spectrometer. IR spectra (Bhattacharjee *et al* 1990), pH values (Bhattacharjee *et al* 1990) and mass spectra (Bhattacharjee *et al* 1986) were recorded as earlier.

2.1 *Synthesis*

In a typical synthesis, 1·0 g (2·79 mmol) of $UO_3 \cdot 4H_2O$ was reacted with 4 cm^3 (39·95 mmol) distilled acetylacetone with continuous stirring on a steam-bath ($\approx$ 10 min) until a clear orange-yellow solution resulted. The pH value at this stage was found to be 5–5·5. The solution on being cooled to room temperature ($\approx$ 22°C) afforded orange-yellow crystals of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$. The compound was separated by filtration and dried by pressing between folds of filter paper. The yield was 1·3 g (92%); (Found: U, 47·08; C, 23·63; H, 3·74. Calcd: U, 47·20; C, 23·82; H, 3·61%).

3. Results and discussion

We describe a direct 'one-pot' rapid synthesis of the title compound based on the acid–base concept. The oxide UO_3 being basic in nature readily reacted with weakly acidic acetylacetone ($C_5H_8O_2$) to provide $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ in nearly quantitative yield.

$$UO_3 + C_5H_8O_2 \rightarrow UO_2(C_5H_7O_2)_2 + H_2O$$

The colour, solubility properties, and the results of chemical analysis and IR measurements conform to the formula of the compound as $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ and agree very well with those reported in the literature (Schlesinger *et al* 1953; Bhattacharjee *et al* 1986). Further support of the identity was obtained from mass spectral studies. The salient characteristic features of the spectrum (recorded at an ion-source temperature of 100°C) were the molecular ion signal at *m/z* (55%) $[UO_2(C_5H_7O_2)_2]^+$, the most dominant (100%) signal at *m/z* 369 $[UO_2(C_5H_7O_2)]^+$, and a medium intensity (45%) signal at *m/z* 270 $[UO_2]^+$. These and the other features were similar to those reported (Bhattacharjee *et al* 1986). The clear advantages of the method are that it is simple and rapid and does not require any buffer or alkali, thus eliminating chances of contamination of the end product. In addition, the new method does not need any extra preparation and purification thereby rendering this procedure superior to the existing ones. The importance of having $UO_2(acac)_2$ in pure form lies in its probable application in isotope enrichment of uranium, since this requires a pure compound of the metal. Besides this, the purity of the product is expected to render it a better starting material for the synthesis of other compounds of uranium, in particular, organo-uranium derivatives. The procedure can be regarded as a general one applicable to many acetylacetonato-metals. For instance, hydrous oxides or hydroxides of iron(III), cobalt(II), nickel(II), copper(II), and zinc(II) reacted with acetylacetone to provide $Fe(C_5H_7O_2)_3$, $Co(C_5H_7O_2)_2 \cdot 2H_2O$, $Ni(C_5H_7O_2)_2 \cdot 2H_2O$, $Cu(C_5H_7O_2)_2 \cdot 2H_2O$, and $Zn(C_5H_7O_2)_2 \cdot 2H_2O$, respectively, in very high yields.

Acknowledgement

The Department of Atomic Energy is thanked for providing financial assistance.

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Journal of Fluorine Chemistry, 56 (1992) 305–307

First reported synthesis of ammonium hexafluorodioxouranate(VI), $(NH_4)_4[UO_2F_6]$

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(Received May 1, 1991; accepted October 23, 1991)

Abstract

Bis(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$, reacts with NH_4F in the presence of an excess of acetylacetone and a trace of water to produce $(NH_4)_4[UO_2F_6]$ in high yield. The results of chemical analyses, molar conductance, IR and laser Raman spectroscopic studies have been used for characterisation of the compound.

Introduction

The syntheses of many oxofluoro complexes of hexavalent uranium are well documented [1, 2], but that of $[UO_2F_6]^{4-}$ seems, to the best of our knowledge, missing from the literature, although some physicochemical studies involving the complex appear to have been conducted [3, 4]. Hence, a synthetic procedure for hexafluorodioxouranate(VI) seems warranted. Accordingly, the present investigation has been addressed to the reaction of $UO_2(acac)_2 \cdot 2H_2O$ with NH_4F in the presence of acetylacetone and a trace of water enabling the synthesis of $(NH_4)_4[UO_2F_6]$.

Experimental

Reagent grade chemicals were used for the synthesis. Acetylacetone was distilled before use. IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer and laser Raman (LR) on a SPEX Ramalog 1403 spectrophotometer using the 4880 Å laser line from a Spectra–Physics model 165 Argon laser. The pH was measured using a Systronics type 335 digital pH meter and also with BDH indicator paper. Molar conductances were measured with a Systronics type 304 digital direct-reading conductivity meter. Bis(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$, was prepared by a method developed in this laboratory [5].

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0022-1139/92/$5.00

Synthesis of ammonium hexafluorodioxouranate(VI), $(NH_4)_4[UO_2F_6]$

A mixture consisting of 1.0 g (1.98 mmol) of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ and 0.3 g (8.1 mmol) of NH_4F was allowed to react in the presence of 20.0 cm^3 (199.75 mmol) of distilled acetylacetone and a trace of water (1 cm^3). The atomic ratio of U:F was maintained as 1:4. The solution was stirred continuously in a 100 cm^3 polyethylene beaker and heated over a steam bath for *c.* 6 h until a yellow solid formed. The pH of the mother liquor was found to be *c.* 4. The yellow solid thus formed was separated by filtration, washed several times with ethanol, and finally dried *in vacuo* over conc. H_2SO_4. The yield of $(NH_4)_4[UO_2F_6]$ was 0.6 g (66.7%). Analysis: Calc. for $(NH_4)_4[UO_2F_6]$: U, 52.17; F, 24.99; N, 12.28; H, 3.54%. Found: U, 51.87; F, 24.81; N, 12.25; H, 3.66%. Molar conductance: 495 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): 356 [ν(U–F)]; 913 [ν_{as}(U=O), ν_3]; 1418 [ν(N–H), ν_4]; 3025 [ν(N–H), ν_1]; 3160 [ν(N–H), ν_3]. LR (cm^{-1}); 340 [ν(U–F)]; 853 [δ(O–U–O), ν_1]; 951 [ν_{as}(U=O), ν_3]; 1379 [ν(N–H), ν_4].

Elemental analyses

Uranium was estimated gravimetrically as uranyl oxinate [6a]. Fluoride was precipitated as PbClF and chloride estimated by Volhard's method from which the fluoride content was calculated [6b]. Nitrogen and hydrogen were determined by the Micro Analytical Laboratory, Department of Chemistry, NEHU, Shillong 793 003.

Results and discussion

Since the acetylacetonate ion ($C_5H_7O_2^-$) generally binds to a metal centre through its oxygen atoms, it was anticipated that in an acidic environment the ligand would be detached from $UO_2(C_5H_7O_2)_2$ to produce acetylacetone ($C_5H_8O_2$) and UO_2^{2+} *in situ*. The uranyl ion would then interact with the nucleophile F^- to afford fluoro compounds of the metal. Alternatively, the reaction might proceed via the formation of intermediate fluoro-(acetylacetonato)dioxouranate(VI) complex ions to finally produce oxo-(fluoro)uranates(VI). With this strategy, $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ and NH_4F (molar ratio 1:4) were allowed to react in an acetylacetone medium containing a very small amount of water (*vide* Experimental section) to afford a yellow microcrystalline compound. The product analysed for N, U and F^- in an atomic ratio of 4:1:6. The compound appeared to be stable both in the solid state as well as in solution, with its molar conductance being 495 Ω^{-1} cm^2 mol^{-1}. The conductance measured as a function of time over a period of several days did not reveal any significant change, supporting the evidence of the stability of the material in water. Based upon the results obtained, the compound has been formulated as $(NH_4)_4[UO_2F_6]$.

Yellow $(NH_4)_4UO_2F_6]$ is non-hygroscopic, but on long exposure to moist air, slow etching of a glass slide was observed. The structural assessment of the compound has been based upon the results of IR and laser Raman

(LR) spectroscopic investigations. Thus, the IR spectrum displayed a strong band at 913 cm^{-1} owing to ν(U=O) [*trans*-linked O=U=O] [7] and another strong band at 356 cm^{-1} attributed to the ν(U–F) mode of coordinated fluoride. In addition, IR features attributed to the NH_4^+ ion were observed at 3160(m), 3025(s) and 1418(s) cm^{-1}. These correlate very well with those observed for the ammonium ion [8] of fluorometallate systems and have been assigned to the ν_3, ν_1 and ν_4 modes of NH_4^+. Because of the large polarisability changes involved in U–O and U–F bonds, the complex was amenable to LR spectroscopic studies. Thus, LR signals were observed at 951, 853 and 340 cm^{-1} due to ν(U=O)(ν_3), δ(O–U–O)(ν_1) [*trans*-linked O=U=O] [7] and ν(U–F), respectively. The range covered in the present LR experiment was 200–1500 cm^{-1} which enabled detection of a further strong signal occurring at 1379 cm^{-1} whose origin is attributed to the ν_4 mode of the N–H vibration of the NH_4^+ ion. The results of the IR and LR spectroscopic studies are thus in full agreement with the formula $(NH_4)_4[UO_2F_6]$ for the compound.

Acknowledgement

The authors thank the Department of Atomic Energy for financial assistance.

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Polyhedron Vol 12, No 2, pp 227–234, 1993
Printed in Great Britain

0277–5387/93 $6 00 + 00

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF MIXED-FLUORO COMPLEXES OF UO_2^{2+} CONTAINING AMINO ACIDS, ACETYLACETONATE OR ACETATE AS THE CO-LIGANDS AND THE FIRST REPORT ON THE HEPTAFLUORODIOXOURANATE(VI) COMPLEX $[UO_2F_7]^{5-}$

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(*Received* 17 *July* 1992; *accepted* 10 *September* 1992)

Abstract—The synthesis of mixed-ligand fluoro complexes of UO_2^{2+} of the types $A_3[UO_2(GlyH)_2F_5]\cdot 3H_2O$ [A = K (**1**) or NH_4^+ (**2**)], $K_3[UO_2(AlanH)_2F_5]\cdot 2H_2O$ (**3**), $(NH_4)_5[UO_2(CysH)_2F_5]\cdot 2H_2O$ (**4**), $[UO_2(acac)F(H_2O)_2]\cdot 3H_2O$ (**6**), $K_2[UO_2(acac)F_3]$ (**8**) and $[UO_2(CH_3COO)F(H_2O)_2]$ (**9**) (GlyH = glycine, AlanH = alanine, $CysH^-$ = cysteinate and $acac^-$ = acetylacetonate) is described. The complexes have been characterized by a combination of chemical analyses, solution conductance measurements and spectroscopic studies. Vibrational spectroscopy has been used for their structural assessment. Laser Raman spectrum could be recorded only for $K_2[UO_2(acac)F_3]$ (**8**), while an extensive fluorescence foiled such attempts on the other complexes. Each of the three amino acid co-ligands acts in a unidentate manner, being coordinated to UO_2^{2+} through the caroxylate oxygen atom. While glycine and alanine occur in the zwitter-ionic form, cysteine seems to be present as a uninegative ligand. The reaction of $[UO_2(acac)F(H_2O)_2]\cdot 3H_2O$ (**6**) with aqueous HF produced $[UO_2F_2]\cdot 3H_2O$ (**7**). Treatment of $K_3[UO_2(GlyH)_2F_5]\cdot 3H_2O$ (**1**) with water afforded the hitherto unreported potassium heptafluorodioxouranate(VI) dihydrate, $K_5[UO_2F_7]\cdot 2H_2O$ (**5**), in a high yield with satisfactory analysis and electrical conductance measurement (590 Ω^{-1} cm^2 mol^{-1}). IR and laser Raman spectra provide clear evidence for the presence of *trans*-linked O=U=O and coordinated flouride. The solution Raman spectrum of **5** is similar to that of its solid indicating that the structure in aqueous solution is the same as the solid. Scanning electron microscopy has been used to ascertain its homogeneity and crystalline nature.

Uranium(VI) generally occurring as uranyl (UO_2^{2+}) has been known to form stable fluoro and mixed-ligand fluoro complexes.[1] Notable among the binary fluoro complexes[1,2] are $[UO_2F_3]^-$, $[UO_2F_4]^{2-}$, $[UO_2F_5]^{3-}$ and $[(UO_2)_3F_7]^-$. For the mixed-ligand fluoro complexes of UO_2^{2+} the co-ligands were drawn largely from sulphate,[3] carbonate,[3b] oxalate,[4] acetate,[1c] acetylacetonate,[5] propionate[6] and malonate.[6]

Interestingly, the fluoro complexes of the types $[UO_2F_6]^{4-}$ and $[UO_2F_7]^{5-}$ were not included in the earlier reports. We addressed ourselves to these complexes and the first synthesis of $(NH_4)_4[UO_2F_6]$ has been achieved very recently.[7] A fortuitous synthesis of heptafluorodioxouranate(VI), obtained as $K_5[UO_2F_7]\cdot 2H_2O$ (**5**), enables us now to make the first report on the complex. In addition, we have been interested in the complex chemistry of UO_2^{2+} [8–11] and some of our previous publications have dealt with mixed-ligand peroxo complexes, including fluoroperoxouranates(VI).[11]

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In this investigation we included the synthesis of a few selective mixed fluoro complexes with amino acids, such as glycine, L-alanine and L-cysteine, acetylacetonate and acetate as the co-ligands.

Incidentally, amino acids,[12–15] acetylacetonate[16] and acetate[1c,1d] have been known for a long time to form complexes with UO_2^{2+}, although their isolation in the solid state varied from case to case. In addition, the reaction solution pH conducive to the formation of such complexes, particularly with regard to amino acids and acetylacetonate ligands, seems to be an important parameter. One of our main concerns in this context was to ascertain appropriate experimental conditions leading to the synthesis of the desired complexes.

Herein are reported the synthesis of the mixed-fluoro complexes $A_3[UO_2(GlyH)_2F_5]\cdot 3H_2O$ [A = K (**1**) or NH_4^+ (**2**); GlyH = glycine], $K_3[UO_2(AlanH)_2F_5]\cdot 2H_2O$ (**3**) (AlanH = L-alanine), $(NH_4)_5[UO_2(CysH)_2F_5]\cdot 2H_2O$ (**4**) ($CysH^-$ = cysteinate), $[UO_2(acac)F(H_2O)_2]\cdot 3H_2O$ (**6**), $K_2[UO_2(acac)F_3]$ (**8**) ($acac^-$ = acetylacetonate) and $[UO_2(CH_3COO)F(H_2O)_2]$ (**9**), their spectroscopic characterization and the interaction of **1** with water, thus enabling us to make the first report on the heptafluorodioxouranate(VI) complex $K_5[UO_2F_7]\cdot 2H_2O$ (**5**).

EXPERIMENTAL

The chemicals used were of reagent grade quality and acetylacetone was distilled before use. IR spectra were recorded on a Perkin–Elmer Model 983 spectrophotometer and laser Raman (LR) on a SPEX Ramalog 1403 spectrophotometer using the 4880 Å laser line from a Spectra-Physics Model 165 argon laser. The pH values of the reaction solutions were measured using a Systronics type 335 digital pH meter and BDH indicator paper. Solution electrical conductances were measured using a Systronics type 304 digital direct reading conductivity meter. Bis(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2\cdot 2H_2O$, was prepared by a method developed in this laboratory.[16,17]

Preparation of $UO_3\cdot 4H_2O$

Uranyl nitrate hexahydrate, $UO_2(NO_3)_2\cdot 6H_2O$ (5.0 g, 9.96 mmol), was dissolved in water (100 cm^3), to which was added pyridine (10 cm^3) whereupon a yellow precipitate appeared. This was separated by decantation, washed three or four times with water, twice with acetone and finally dried on a steam bath to obtain yellow uranium trioxide, $UO_3\cdot 4H_2O$ (yield: 2.8 g; 78.4%).

Syntheses

$A_3[UO_2(GlyH)_2F_5]\cdot 3H_2O$ [A = K (**1**) *or* NH_4^+ (**2**)]. $UO_3\cdot 4H_2O$ (1.0 g, 2.79 mmol) was dissolved in an aqueous solution of a combination of aqueous HF (12 mmol) and AF (8.38 mmol) (A = K or NH_4^+). To the clear lemon yellow solution thus obtained was added an aqueous solution (5 cm^3) of glycine (0.42 g, 5.57 mmol) and the solution was stirred for *ca* 10 min. The solution after concentration by heating on a steam bath to nearly half of its volume afforded a lemon–yellow solid. The pH of the reaction solution was recorded to be *ca* 2.5. The compound was isolated by filtration and dried *in vacuo* over concentrated H_2SO_4. The yields of $K_3[UO_2(GlyH)_2F_5]\cdot 3H_2O$ (**1**) and $(NH_4)_3[UO_2(GlyH)_2F_5]\cdot 3H_2O$ (**2**) were 1.2 g (63%) and 1.1 g (65%), respectively.

$K_3[UO_2(AlanH)_2F_5]\cdot 2H_2O$ (**3**) *and* $(NH_4)_5[UO_2(CysH)_2F_5]\cdot 2H_2O$ (**4**). These complexes were prepared by a method similar to that employed for **1** and **2**, except that AHF_2 was used as the fluorinating agent instead of AF and HF. $UO_3\cdot 4H_2O$ (1.0 g, 2.79 mmol) was dissolved in an aqueous solution (5 cm^3) of AHF_2 (8.37 mmol). This was followed by the addition of L-alanine or L-cysteine (5.57 mmol). The pH of the resulting clear solution was *ca* 2.5. The solution upon concentration over a steam-bath produced **3** and **4**, respectively. The compounds were isolated in a manner similar to that of **1** and **2**. The yields of **3** and **4** were 1.3 g (66%) and 1.4 g (68%), respectively.

Treatment of **1** *with water and isolation of* $K_5[UO_2F_7]\cdot 2H_2O$ (**5**). A suspension of $K_3[UO_2(GlyH)_2F_5]\cdot 3H_2O$ (**1**) (1.0 g, 1.46 mmol) in water (10 cm^3) was stirred constantly for *ca* 5 min, whereupon the solid slowly dissolved. On further agitation, the solution deposited a bright lemon–yellow crystalline solid. The pH of the mother liquor was recorded to be *ca* 1.7. The solid thus obtained was collected by filtration and finally dried *in vacuo* over concentrated H_2SO_4 (yield: 0.7 g; 76%).

Synthesis of $[UO_2(acac)F(H_2O)_2]\cdot 3H_2O$ (**6**). (1) $UO_3\cdot 4H_2O$ (1.0 g, 2.79 mmol) in water (5 cm^3) was reacted with 48% HF (0.2 cm^3, 4.8 mmol) in the presence of acacH (1.0 cm^3, 10 mmol) and the resultant reaction mixture was stirred constantly on a steam bath for *ca* 15 min, whereupon a yellow solid precipitated out. The pH of the reaction solution was found to be *ca* 3.5. The yellow solid was collected by filtration and washed with ethanol (yield: 1.0 g; 77%).

(2) Alternatively, to an aqueous suspension (5 cm^3) of $UO_2(acac)_2\cdot 2H_2O$ (1.0 g, 1.98 mmol) was added 48% HF (0.2 cm^3, 4.8 mmol). The reaction solution upon stirring on a steam bath for *ca* 15

min afforded a yellow solid. The pH of the reaction solution measured at this stage was *ca* 3.5 (yield: 0.7 g; 74%).

Synthesis of $K_2[UO_2(acac)F_3]$ (**8**). Uranyl nitrate hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$ (1.0 g, 1.99 mmol), was dissolved in water (15 cm^3) and 20% KOH solution was added until the yellow precipitate formation was complete. The precipitate was filtered off and washed free from alkali and nitrate. To a suspension of the yellow precipitate in an excess of acetylacetone (10 cm^3, 100 mmol) was added KF (0.7 g, 12 mmol), maintaining the atom ratio of U:F at 1:6. The reaction solution was stirred constantly over a steam bath for *ca* 2 h until the formation of a bright yellow compound was complete. The pH of the reaction solution at this stage was measured to be *ca* 3.5. The compound was separated by filtration and dried *in vacuo* over concentrated H_2SO_4 (yield, 0.7 g; 70%).

Synthesis of $[UO_2(CH_3COO)F(H_2O)_2]$ (**9**). $UO_3 \cdot 4H_2O$ (1.0 g, 2.79 mmol) was dissolved in a minimum amount of glacial acetic acid (2 cm^3, 35 mmol). To the resulting clear solution was added 48% HF (0.2 cm^3, 4.8 mmol) and the reaction solution was concentrated over a steam bath to afford a lemon–yellow solid. The pH of the reaction solution was *ca* 2.5. The solid was isolated by filtration, washed with ethanol and finally dried *in vacuo* over concentrated H_2SO_4 (yield: 0.8 g; 74%).

Elemental analyses

Uranium was estimated gravimetrically as uranyl oxinate.[18a] Fluoride was precipitated as PbClF and chloride estimated by Volhard's method, from which the fluoride content was also calculated.[18b] Carbon, nitrogen and hydrogen were determined by the Micro Analytical Laboratory of our university. Potassium was estimated using a Perkin–Elmer Model 2380 atomic absorption spectrophotometer. The uranium content was also checked using the Perkin–Elmer Model 2380 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

The synthesis of mixed-ligand fluorodioxouranates(VI) with the co-ligands drawn from amino acids, such as glycine, L-alanine and L-cysteine, and acetylacetonate and acetate required first the development of the appropriate experimental conditions. It is known[19] that amino acids do not coordinate with UO_2^{2+} below pH *ca* 1.8, while above pH 4–4.5 there is a strong tendency for hydrolysis of the complexes. Evidence for the formation of binary amino acid-uranyl complexes at pH *ca* 2 has been provided by pH titration and solvent extraction experiments.[14] Thus, it was anticipated that a pH range 2–4.5 might be conducive to the coordination of an amino acid to UO_2^{2+} in the presence of F^-. Incidentally, the reaction of $UO_3 \cdot 4H_2O$ with AHF_2 in the case of L-alanine and L-cysteine or a combination of AF and HF in the case of glycine gave rise to a natural pH of *ca* 2.5. The complexes were thus isolated as $A_3[UO_2(GlyH)_2F_5] \cdot 3H_2O$ [A = K (**1**) or NH_4^+ (**2**)], $K_3[UO_2(AlanH)_2F_5] \cdot 2H_2O$ (**3**) and $(NH_4)_5[UO_2(CysH)_2F_5] \cdot H_2O$ (**4**), respectively, in high yields.

The mixed-ligand amino acid fluoro complexes of UO_2^{2+} were unstable in aqueous solutions, undergoing decomposition to form intractable products, except for $K_3[UO_2(GlyH)_2F_5] \cdot 3H_2O$ (**1**). Significantly, **1** underwent hydrolysis affording a well-defined but hitherto unknown binary fluoro complex, $K_5[UO_2F_7] \cdot 2H_2O$ (**5**), enabling us to make the first report on the heptafluorodioxouranate(VI) species. Although it is difficult to say how exactly the formation of **5** from **1** occurred, presumably at least the hydrolysis of the complex $[UO_2(GlyH)_2F_5]^{3-}$ and a reorganization of the coordination sphere of the UO_2^{2+} ion must have occurred to afford the complex $[UO_2F_7]^{5-}$. The solution pH on the formation of the compound $K_5[UO_2F_7] \cdot 2H_2O$ (**5**) was recorded to be 1.7, which might have facilitated dissociation of the co-ligand GlyH.

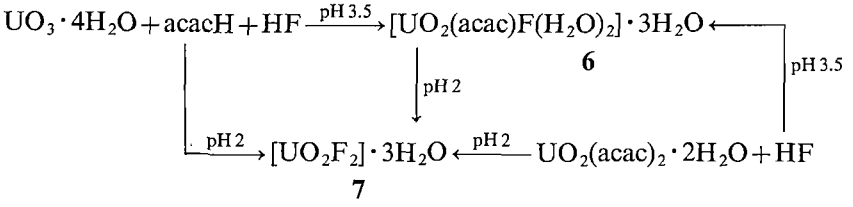
In some recent reports, direct syntheses of $UO_2(acac)_2 \cdot 2H_2O$ have been dealt with.[16,17] A pH of 5–5.5 was ascertained to be necessary for coordination of $acac^-$ to UO_2^{2+}. In order to design suitable experimental conditions for the synthesis of fluoro(acetylacetonato)dioxouranium(VI) complexes it was felt that the pH of the reaction medium might be important.

Our experience in dealing with uranyl systems[7–11] led us to believe that the reactions of $UO_2(acac)_2 \cdot 2H_2O$ with a controlled amount of F^- in acidic medium should be appropriate for accessing fluoro(acetylacetonato)dioxouranates(VI). It was important in this context to avoid a higher F^- ion concentration which would inhibit the formation of binary fluoro complexes. As shown here (see Experimental), the reaction of $UO_3 \cdot 4H_2O$ with aqueous HF and acacH at pH 3.5 (attained spontaneously) afforded the molecular complex $[UO_2(acac)F(H_2O)_2] \cdot 3H_2O$ (**6**). However, on lowering the pH to *ca* 2 by the addition of aqueous HF, a known fluoro compound, $[UO_2F_2] \cdot 3H_2O$[1a] (**7**), resulted. It should be mentioned that in two separate reactions $[UO_2(acac)_2] \cdot 2H_2O$ and $[UO_2(acac)F(H_2O)_2] \cdot 3H_2O$ (**6**) were reacted with excess aqueous HF to yield **6** and **7**, respectively.

An important implication of the observed sequential loss of coordinated acetylacetonate ligands from $[UO_2(acac)_2]\cdot 2H_2O$ at the pH values *ca* 3.5 and *ca* 2 is that an enhanced acidity appears to be detrimental to the formation of fluoro(acetylacetonato) complexes of the metal. In other words, $[UO_2(acac)F(H_2O)_2]\cdot 3H_2O$ (**6**) may be regarded as an isolable intermediate in the process $[UO_2(acac)_2]\cdot 2H_2O$ to $[UO_2F_2]\cdot 3H_2O$.

5–**9** are stable in water under the present experimental conditions. It may be important to mention that the reported solution electrical conductances for the salts of the complex ions $[UO_2F_3]^-$, $[UO_2F_4]^{2-}$ and $[UO_2F_6]^{4-}$ were *ca* 130,[22a] 216[22b] and 495[7] Ω^{-1} cm^2 mol^{-1}, respectively.

The common features of the IR spectra of complexes **1**–**9** are the bands at *ca* 900 and 375 cm^{-1},



The knowledge obtained from the preceeding results suggested that if a reaction of UO_2^{2+} with acacH and an excess of fluoride were conducted at pH *ca* 3.5, it would be possible to gain access to the anionic fluoro(acetylacetonato) complex of UO_2^{2+}. Indeed this is what has happened in one of the reactions where $K_2U_2O_7$ was reacted with KF and acetylacetone at pH 3.5 leading to $K_2[UO_2(acac)F_3]$ (**8**).

Our success in the synthesis of $[UO_2(acac)F(H_2O)_2]\cdot 3H_2O$ (**6**) caused us to anticipate that the adoption of a similar synthetic methodology might enable the preparation of analogous molecular mixed fluoro complexes with the co-ligand derived from a weak acid. To test this, the strategy was applied to a fluoro-acetato system and the compound $[UO_2(CH_3COO)F(H_2O)_2]$ (**9**) has been successfully synthesized.

The compounds are either yellow or lemon–yellow in colour and stable in the solid state. Their analytical data, molar conductance values and important IR and LR spectral bands along with their assignments are summarized in Tables 1 and 2, respectively. The results of the conductance experiments are of particular value in determining the mode of ionization of coordination compounds.[20,21] The conductances of dilute (10^{-3} M) solutions of 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 5 types of electrolytic complexes are expected[20] to be *ca* 120, 240, 360, 480 and 600 Ω^{-1} cm^2 mol^{-1}, respectively, with the average value of ion conductance being *ca* 60 Ω^{-1} cm^2 mol^{-1}. For complexes **1**–**4** conductance measurements were not attempted due to their instability in aqueous solution; however, the solution (10^{-3} M) electrical conductances for compounds **5**, **6**, **7**, **8** and **9** were 590, 5, 7, 175 and 6 Ω^{-1} cm^2 mol^{-1}, respectively, which conforms to the formulations. This also implies that complexes assigned to ν(U=O)[23] (*trans* linked O=U=O) and ν(U—F)[23c] modes, respectively. The amino acids glycine and L-alanine form complexes with metals in either their zwitter-ionic or ionic forms,[24–26] and coordinate either through the N,O atoms in a bidentate manner or through the carboxylate oxygen atoms in a monodentate fashion. In addition to glycine and L-alanine, L-cysteine[27] was the other amino acid co-ligand included in the study which contained a sulphhydryl group as an additional coordination site.

Incidentally, the chosen amino acids are interesting probes useful in the IR spectroscopic determination of their modes of coordination.[26] There was a general pattern in the spectra of complexes **1**–**3**; for instance, the bands at *ca* 1600s [$\nu_{as}(COO^-)$], 1400s [$\nu_s(COO^-)$], 1120 m [$\rho_r(NH_3^+)$], 680m [$\rho_w(COO^-)$] and 580m [$\delta(COO^-)$] cm^{-1}. The observed pattern and band positions are clear reflections of the occurrence of glycine and alanine in their zwitter-ionic forms,[26,28a] thus being coordinated through their carboxylate oxygen atoms in the respective complexes. However, unlike complexes **1**–**3**, cysteine in **4** occurs in its cysteinate form ($CysH^-$). Important in this context have been the absorptions at 2565 cm^{-1} due to the S—H stretch[27] and at 1650s and 1385s owing to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ modes, respectively. Notably, the observed shifts of $\nu_{as}(COO^-)$ to higher and $\nu_s(COO^-)$ to lower wave numbers than the corresponding values of free cysteine[27] provide evidence for the coordination of $CysH^-$ through its carboxylate oxygen atom. The complementary ν(U—O) mode was observed at 451m cm^{-1}. The fact that the nitrogen atom has not involved itself in coordination is clear from the unaltered NH_3^+ deformation band[27] observed at 1483 cm^{-1} for **4**. Thus, based upon the IR results described above, it

Table 1. Analytical data and solution electrical conductances of the compounds

Compound (colour)	Conductance (Ω^{-1} cm^2 mol^{-1})	Analysis: Found (Calc.) U	F	C	N	H	K
$K_3[UO_2(GlyH)_2F_5]\cdot 3H_2O$ (**1**)	d	34.1	13.6	7.1	4.0	2.4	17.3
(lemon–yellow)		(34.7)	(13.8)	(7.0)	(4.1)	(2.4)	(17.1)
$(NH_4)_3[UO_2(GlyH)_2F_5]\cdot 3H_2O$ (**2**)	d	37.7	15.4	7.6	11.1	4.7	—
(lemon–yellow)		(38.2)	(15.2)	(7.7)	(11.2)	(4.5)	
$K_3[UO_2(AlanH)_2F_5]\cdot 2H_2O$ (**3**)	d	34.2	13.5	10.2	4.0	2.8	16.8
(lemon–yellow)		(34.2)	(13.6)	(10.3)	(4.0)	(2.6)	(16.8)
$(NH_4)_5[UO_2(CysH)_2F_5]\cdot 2H_2O$ (**4**)	d	32.3	13.6	9.6	13.3	4.7	—
(green)		(32.5)	(13.0)	(9.9)	(13.4)	(5.0)	
$K_5[UO_2F_7]\cdot 2H_2O$ (**5**)	590	37.4	21.1	—	—	—	30.6
(lemon–yellow)		(37.5)	(21.0)				(30.8)
$[UO_2(acac)F(H_2O)_2]\cdot 3H_2O$ (**6**)	5	49.5	4.1	12.6	—	3.6	—
(yellow)		(49.8)	(4.0)	(12.6)		(3.6)	
$[UO_2F_2]\cdot 3H_2O$ (**7**)	7	65.9	10.3	—	—	1.8	—
(yellow)		(65.7)	(10.5)			(1.7)	
$K_2[UO_2(acac)F_3]$ (**8**)	175	46.8	11.5	11.4	—	1.7	15.6
(yellow)		(47.2)	(11.3)	(11.9)		(1.4)	(15.5)
$[UO_2(CH_3COO)F(H_2O)_2]$ (**9**)	6	60.8	4.4	5.8	—	1.7	—
(yellow)		(62.0)	(5.0)	(6.3)		(1.8)	

d = decomposed in water, GlyH = glycine ($C_2H_5NO_2$), AlanH = L-alanine ($C_3H_7NO_2$), $CysH^-$ = cysteinate ($C_3H_6NS^-$), $acac^-$ = acetylacetonate ($C_5H_7O_2^-$).

may be assumed that the amino acid in complexes **1–4** has acted as a monodentate ligand, coordinated with the metal centre through the carboxylate oxygen atom. In addition, the spectra exhibited the lattice water modes in their usual positions[28b] (Table 2). Unfortunately, no information could be extracted from laser Raman spectroscopic experiments on complexes **1–4** owing to extensive fluorescence.

The IR spectrum of potassium heptafluorodioxouranate(VI) dihydrate, $K_5[UO_2F_7]\cdot 2H_2O$ (**5**), is very straightforward. As expected, the spectrum exhibited only a few prominent bands; for instance, one at 866s [ν(U=O), *trans*-linked O=U=O] and another at 373 cm^{-1} [ν(U—F)], in addition to the ν(OH) and δ(HOH) modes of lattice water at 1640 and 3455 cm^{-1}, respectively. It may be mentioned that the ν(O—H) band at *ca* 3450 has been generally observed for complexes containing lattice water.[28a] Indeed, the ν(O—H) value of 3455 cm^{-1} has been argued to be rather typical of uncoordinated H_2O.[29] Incidentally, this is one of the few compounds, from among those reported herein, which exhibited a laser Raman spectrum with signals located at 920 cm^{-1} due to ν(U=O) (*trans*-linked O=U=O) and 314 cm^{-1} attributed to ν(U—F). These results not only complement the corresponding IR spectral observation but also augment our assumptions on the characteristic spectral features of the complex $[UO_2F_7]^{5-}$ species. The stability of the complex in water enabled recording its solution Raman spectrum. Significantly, the principal features of the spectrum include the appearance of the ν(U=O) and ν(U—F) signals at 915 and 325 cm^{-1}, respectively. The pattern resembles that of the corresponding solid, thus indicating that the structure of the complex $[UO_2F_7]^{5-}$ ion in aqueous solution is the same as the solid. It may be worth noting that the recently characterized[7] complex $[UO_2F_6]^{4-}$ displayed related bands at 951 and 340 cm^{-1}. The corresponding ν(U=O) and ν(U—F) modes for $[UO_2F_5]^{3-}$ were observed at *ca* 865s and 387m cm^{-1}, respectively, in the IR spectra[30,31] of the complex.

In order to gain an idea about the crystallinity and homogeneity of the product (**5**), it was subjected to Scanning Electron Microscopy (SEM). The SE micrograph (Fig. 1) attests to the homogeneity of the product as well as its crystalline character.

For compounds **6**, **8** and **9** the IR spectra provide, in addition to ν(U=O) and ν(U—F) bands, a pattern typical of chelated acetylacetonate[28c] for **6** and **8**, and bidentate acetate[28d] for **9**. Some of the charac-

Table 2. IR and LR spectral data of the complexes with their assignments

Compound	IR (cm^{-1})	LR (cm^{-1})	Assignment
$K_3[UO_2(GlyH)_2F_5]\cdot 3H_2O$ (1)	377m	—	ν(U—F)
	900s		ν(U=O)
	1585s		$\nu_{as}(COO^-)$
	1400s		$\nu_s(COO^-)$
	1120m		$\rho_r(NH_3^+)$
	680m		$\rho_w(COO^-)$
	580m		$\delta(COO^-)$
	1645		δ(H—O—H)
	3450		ν(O—H)
$(NH_4)_3[UO_2(GlyH)_2F_5]\cdot 3H_2O$ (2)	372m	—	ν(U—F)
	910s		ν(U=O)
	1590s		$\nu_{as}(COO^-)$
	1402s		$\nu_s(COO^-)$
	1115m		$\rho_r(NH_3^+)$
	680m		$\rho_w(COO^-)$
	585m		$\delta(COO^-)$
	1640		δ(H—O—H)
	3445		ν(O—H)
	1420s		ν(N—H)ν_4
$K_3[UO_2(AlanH)_2F_5]\cdot 2H_2O$ (3)	374m	—	ν(U—F)
	905s		ν(U=O)
	1600s		$\nu_{as}(COO^-)$
	1395s		$\nu_s(COO^-)$
	1110m		$\rho_r(NH_3^+)$
	685m		$\rho_w(COO^-)$
	575n		$\delta(COO^-)$
	1630		δ(H—O—H)
	3440		ν(O—H)
$(NH_4)_5[UO_2(CysH)_2F_5]\cdot 2H_2O$ (4)	372m	—	ν(U—F)
	902s		ν(U=O)
	1650s		$\nu_{as}(COO^-)$
	1385s		$\nu_s(COO^-)$
	451m		ν(U—O)
	2568m		ν(S—H)
	1418s		ν(N—H)ν_4
	1483m		NH_3^+ (symm. def.)
	1640		δ(H—O—H)
	3440		ν(O—H)
$K_5[UO_2F_7]\cdot 2H_2O$ (5)	373	314	ν(U—F)
	866	920	ν(U=O)
	1640		δ(H—O—H)
	3460		ν(O—H)
$[UO_2(acac)F(H_2O)_2]\cdot 3H_2O$ (6)	369	—	ν(U—F)
	890		ν(U=O)
	612		ring def. + ν(U—O)
	295		ν(U—O)
	725		$\rho_r(H_2O)$
	1635		δ(H—O—H)
	3450		ν(O—H)
$[UO_2F_2]\cdot 3H_2O$ (7)	374	425	ν(U—F)
	857	866	ν(U=O)
	1625		δ(H—O—H)
	3358		ν(O—H)

Table 2—*continued*

Compound	IR (cm^{-1})	LR (cm^{-1})	Assignment
$K_2[UO_2(acac)F_3]$ (**8**)	366	438	ν(U—F)
	900	890	ν(U═O)
	615		ring def. + ν(U—O)
	290		ν(U—O)
$[UO_2(CH_3COO)F(H_2O)_2]$ (**9**)	387	—	ν(U—F)
	905		ν(U═O)
	1468s		ν_s(OCO)
	1545s		ν_{as}(OCO)
	725m		$\rho_r(H_2O)$
	670m		δ(OCO)

Fig. 1.

teristic bands have been cited in Table 2. In agreement with their formulae the IR spectra of **6** and **9** showed a band at *ca* 725 cm^{-1}. We believe this originates from the rocking mode of coordinated water.[28b] The absence of a similar mode in the spectrum of **8** lends support to the aforementioned assignment. The only other compound which gave a good LR spectrum was **7**. In the region 1200–200 cm^{-1} there have been only two signals, one at 867 cm^{-1} assigned to ν(U═O) (*trans*-linked O═U═O) and another centred at 425 cm^{-1} due to ν(U—F), with the latter being broad.

Acknowledgement—Financial assistance from the Department of Atomic Energy is gratefully acknowledged.

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