SYNTHESIS AND STRUCTURAL ASSESSMENT OF FLUORO COMPLEXES OF BERYLLIUM AND PEROXO COMPLEXES OF URANIUM AND A NEW REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

(ABSTRACT)

PRANAB K. TARAFDER

DEPARTMENT OF CHEMISTRY
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NEHU

A THESIS SUBMITTED
IN

FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

TO

THE NORTH-EASTERN HILL UNIVERSITY
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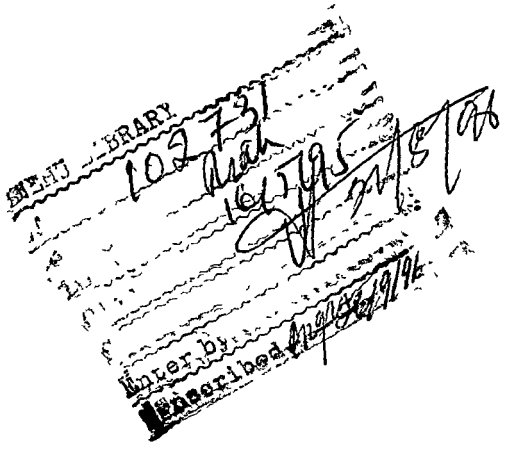

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(i) $A_2[BeF_3(HC_2O_4].nH_2O$ (A = NH_4 or Na, n = 1; A = K, n = 0),

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The compounds are all stable under ordinary conditions. The laser Raman (LR) spectrum of $K_2[BeF_3(HC_2O_4)]$ has been particularly

important as it provided a clean evidence for $HC_2O_4^-$ by showing an intense signal at 1630 cm^{-1} in support of the contention. In addition, the IR spectra of ammonium salt of the complexes demonstrated the presence of hydrogen bonding.

Chapter IV of the thesis includes the synthesis, characterisation and structural assessment of new heteroligand monoperoxouranates(VI) of the type,

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Vibrational Spectroscopy being the powerful tool in probing the structural motifs of the compounds was used in characterising the compounds. It was inferred from the IR spectra of these complexes that while phosphate occurring as $H_2PO_4^-$, was coordinated to metal centre in a chelated bidentate manner, at least one of the fluorides in peroxofluorouranates(VI) might be acting as a bridging ligand. The mode of peroxide coordination to the UO_2^{2+} centre in both the heteroligand peroxouranates, i.e., peroxo(phosphato) and peroxo(difluoro)uranates, is in a triangular bidentate manner(C_{2v} local symmetry) as ascertained by vibrational spectroscopic studies.

Chapter V of the thesis deals with the results of studies on complex diperoxouranates(VI). The salient features of the content of this Chapter are:

(i) the synthesis of newer diperoxouranates(VI), $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4, Na or K) and investigation of their reactions with $SO_2.xH_2O$, CO_2(g) and HF_2^- in aqueous medium and (ii) synthesis of newer heteroligand diperoxouranates(VI) of the type, $Na_4[UO_2(O_2)_2(CO_3)].2H_2O$ and $(NH_4)_3[UO_2(O_2)_2Q].4H_2O$ (Q = 8-quinolinolate).

While the binary diperoxo uranates(VI), $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4, Na or K) were synthesised by the direct reaction of $UO_2(NO_3)_2.6H_2O$ with H_2O_2 at pH 10, adjusted by the addition of the corresponding alkali hydroxide solutions or aqueous ammonia, the corresponding heteroligand complexes, $Na_4[UO_2(O_2)_2(CO_3)].2H_2O$

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In order to explore their reactivity profiles, reactions of the newly synthesised diperoxouranates with inorganic substrates, viz., $SO_2.xH_2O$, $CO_2(g)$ and HF_2^- were conducted in aqueous medium. Consequently, newer sulphato, $A_2[UO_2(SO_4)_2].nH_2O$ (A = NH_4 or K, n = 1 and A = Na, n = 4), peroxocarbonato, $A_2[UO_2(O_2)(CO_3)].2H_2O$ (A = Na or K), and fluoro complexes, $A_6[UO_2F_8].nH_2O$ (A = NH_4, n = 0 and A = Na, n = 2), were obtained.

The newly synthesised compounds and their reaction products were all characterised by chemical analyses, molar conductance measurements, IR and LR spectroscopic studies. Vibrational spectroscopy clearly demonstrated that both the peroxides in $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4,Na or K) were coordinated to UO_2^{2+} centre in a triangular bidentate (C_{2v}) manner. Evidences for coordinated H_2O were also obtained in support of the formulations, $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4, Na or K). As regards the structural motifs of heteroligand diperoxo complexes of UO_2^{2+}, here again, the peroxides were coordinated to the UO_2^{2+} centre in a triangular bidentate manner (C_{2v} local symmetry), while the heteroligands, CO_3^{2-} and 8-quinolinolate, in the respective complexes were bonded to UO_2^{2+} in a chelated bidentate manner.

Chapter VI, indeed the concluding Chapter of the thesis, addresses to the studies on the development of a newer

spectrophotometric method for the determination of uranium(VI) using a new reagent, o-hydroxyanisole, commonly known as guaiacol. This reagent reacts rapidly with UO_2^{2+} at pH 6-8, forming a stable yellowish-orange chelate, suitable for spectrophotometric determination of uranium. The presence of methoxy and OH^- groups in 1 and 2 positions, respectively, of the benzene ring facilitates chelate formation. Effects of variables for optimum colour development were studied. Adherence to Beer's law was tested and precision and accuracy were ascertained. The molar absorptivity and Sandell's sensitivity of the new method are 3.72×10^3 $l.mol^{-1}cm^{-1}$ and 0.063 $\mu g cm^{-2}$, respectively. The selectivity of the method has been improved by the solvent extraction of uranium(VI) in TBP (tributylphosphate) and then developing the colour in solution. The method has been successfully applied to real samples (rock samples of diverse compositions) and the results obtained are found to be favourably comparable with those obtained separately from fluorimetry and radiometry.

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Chapter-IV

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Chapter VI

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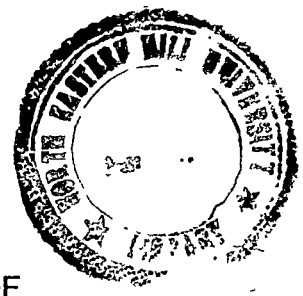

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DECEMBER, 1993

Dedicated
to
my Mother

Phone : 226593
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North - Eastern Hill University

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Department of Chemistry

Dr.Mihir K.Chaudhuri, Ph.D., Dr.rer.nat(W.Germany), FASc.,FNA,
Professor of Chemistry

I certify that the thesis entitled "SYNTHESIS AND STRUCTURAL ASSESSMENT OF FLUORO COMPLEXES OF BERYLLIUM AND PEROXO COMPLEXES OF URANIUM AND A NEW REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM" , submitted by Mr.Pranab K.Tarafder for the degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered, and the thesis presented is worthy of being considered for the Ph.D. Degree. This work has not been submitted for any degree of any other University.

Date: 01 December, 1993

Place: Shillong

Signature of the Supervisor

CONTENTS

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P K Tarafder

(P. K. TARAFDER)

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CHAPTER I

GENERAL INTRODUCTION

The need for newer synthetic methodologies and synthesis of newer materials renders the field of synthetic inorganic chemistry a thrust area of contemporary research. Depending upon the specific need and interest, many groups of workers have engaged their attention to the synthetic inorganic chemistry and have been trying to attack the problems from different angles while searching for the solutions. Incidentally,the backbone of the present Ph.D. research has been basically the synthesis of newer compounds, in addition to a small piece of analytical work. The central metals of choice for the present studies are beryllium (Be) and uranium (U). In an attempt to render the chosen aspects of the present research relevant, it was thought proper to introduce the text with a brief but relevant backdrop information of the two chosen metal's chemistry.

Beryllium is normally divalent in its compounds, the first ionization potential (Be-Be+) being 9.32 eV, the second ($Be-Be^{2+}$),18.21 eV and its standard electrode potential

(E_{Be}^{2+}/Be),1.70 Volts. Although the atomic radius of beryllium is 0.93A, its ionic radius is only 0.31Å. Because of its high ionic potential of 6.45 (cf.1.05 for sodium ion), beryllium has a tendency to form co-valent rather than ionic compounds. The ability of the group II elements to form complex ions is greatest with beryllium and thus it resembles aluminum in its chemistry rather than magnesium. Using the Pauling relationship, the percentage ionic character of the Be-X bond (X=F,Cl,Br or I) is 80, 42, 35 and 25%, respectively[1]. Thus the fluoride has considerable ionic character and forms no stable complexes with neutral ligand (L) of the type $LxBeF_2$ but forms many stable anionic fluoride complexes. In contrast, the other three halides behave as though they are essentially covalent and forms numerous stable complexes with neutral ligands. The Be-F bond is thermodynamically stable in aqueous solution because the bond energy is greater than that of Be-O, whereas the Be-X (X = Cl, Br or I) bond energies are less than that for Be-O, hence thermodynamic instability. Owing to wide application of beryllium and its compounds,the current interest in the chemistry of beryllium and its compounds is probably because of unique chemical and physical properties[2] possessed by the element besides its present day use in Science and Technology, especially in nuclear industries[2]. Beryllium fluorides are important industrially as intermediates in the preparation of metallic beryllium. Uses of beryllium and its alloys have been discussed in a review[3].

The metal is used as a moderator in nuclear reactors[4] and as barrier metal in silicon MIS (Metal-Insulator-Semiconductor) Solar cells[5]. Sodium beryllium fluoride has been used in the manufacture of glass having high ultraviolet permeability, as a flux in certain porcelain enamels and in coating special welding rods[2]. Literature survey shows that simple tetrafluoroberyllates of the type $A_2[BeF_4]$ (A = NH_4, Na or K) are often quoted probably because of their academic as well as multifaceted industrial uses[2]. Interestingly, when a solution contains a metal ion and at least two different ligands, there exists always a finite possibility of formation of a mixed ligand complex. In view of potential donating ability of many anions and solvents, there are very few cases indeed when this is out of consideration[6]. Various types of mixed ligand complexes of different metals were studied, methods regarding the determination of their stability constants worked out in detail and their importance in chemical and biosystems[7] were emphasised by others. Statistically,mixed ligand complex formation is always favoured which has been later supported by elementary electrostatic consideration, steric effect and back coordination[8]. Many mixed ligand complexes have been shown to have manifested other interesting properties[9] and a few have got presumably biochemical significance[10]. It has been observed that beryllium forms innumerable cationic complexes[2] but on the other hand, anionic complexes are very limited in number and reports on corresponding mixed fluoro complexes are rather scanty although there have been some reports on organoberyllium complexes[11-14]. However, high toxicity of beryllium compounds together with the air sensitive nature of organometallic

derivatives, have limited study in this promising area of chemistry. Much of the experimental development of an understanding of this area is due to work by Coates and coworkers between 1964 and 1974. Since then publication on experimental work have diminished considerably and there has been a much greater emphasis on molecular orbital studies, so that there are now many theoretical studies of both real and fanciful organoberyllium systems[15-18].

Kolditz and Bauer[19] had earlier reported mixed fluoro oxalato complexes of beryllium having a composition of $A_2[BeF_2C_2O_4].nH_2O$ (A = NH_4,Na or K). The said authors had later refuted the existence of such complexes and had redesignated those as double salts of beryllium fluoride and oxalate[2]. It is known that a few fluoroberyllates are responsible for manifesting ferroelectric property. Not all the complexes are ferroelectric but those fluoroberyllate molecules which have got inherent molecular asymmetry, manifest this property. A necessary prerequisite for a solid to be ferroelectric is the absence of a centre of symmetry and the presence of hydrogen bonds are essential in the polarization of some ferroelectrics. Triglycinefluoroberyllate, $(NH_2CH_2COOH)_3.H_2BeF_4$, is one of the examples[2] of such compounds of beryllium which show ferroelectricity.

Besides these, fluoro complexes of metals are as such important because many inorganic fluoro compounds are used in optical instrument making, laser technology, microelectronics, in the production of pure metals by the thermal reduction, in the manufacture of electrochemical cells with solid electrolyte and

in some other fields of technology[20]. Further, consequent upon high electronegativity of fluoride ion, many metal fluoro complexes have been shown to be insulators or large band-gap semiconductors[21].

Recently, multinuclear NMR study has revealed that fluoride, beryllium and ADP combine as a ternary complex in aqueous solution[22]. These complexes consisted of monofluoroberyllate (Be-F) or difluoroberyllate (BeF_2) bound to two phosphates of 1 mole of ADP as a bidentate chelate. The relevance of this study to the biological effects of fluoride and beryllium on various enzymatic reactions has been shown. In view of the above, it became necessary to explore the possibility of synthesising at least a few heteroligand fluoro complexes of beryllium. Heteroligands chosen were oxalate, glycinate and acidphosphate etc. Synthetic methodologies were worked out and reaction conditions were optimised as a part of the present Ph.D. research programme. It is anticipated that the chosen heteroligands might bring about a centre of asymmetry to the target molecules. In addition, the probability of formation of hydrogen bonds in such molecules is expected so that they might manifest ferroelectric properties. Accordingly, for an access to this area of interest, synthesis of the suitable complexes is a prerequisite.

Like beryllium, uranium has got acknowledged use in atomic energy programmes. Uranium is used as a fuel in nuclear reactor for sustaining nuclear fission chain reaction. The uranium chemistry has been attended to because of the potential complex forming ability of the metal with a large number of inorganic and organic

ligands. Moreover, many uranium compounds have found definite utility in Science and Technology. The intrinsic importance of uranium compounds as well as our own interest on the chemistry[23-25] of the metal have prompted us to extend our endeavour to some selected aspects of uranium chemistry.

Uranium is a naturally occurring actinide element having ground state electronic configuration (Rn) $5f^3 6d^1 7s^2$. It is the heaviest element to occur in nature. It may be mentioned in passing that the metal has three naturally occurring isotopes. The abundances are $^{238}U_{92}$ (99.28%), $^{235}U_{92}$ (0.71%) and $^{234}U_{92}$ (0.005%). All are α-emitters[26]. Oxidation states range from +3 to +6 and the corresponding f^n configuration ranges from f^3 to f^0. The hexavalent state is the most stable oxidation level. The ligands which stabilize this oxidation state of the metal include nitrate, fluoride, carbonate, oxalate, acetate, sulphate, phosphate, β-diketonates and peroxide etc. UO_2^{2+} is the most common form which exists both in solution and solids. It forms stable complexes with neutral or anionic ligands. The +5 oxidation state is not usually stable except when it is present in dil. H_2SO_4 medium and with organic complexing agents. The oxo-cation, UO_2^{2+} undergoes rapid disproportionation in aqueous solution, hence not stable. While the U^{4+} ion is stable only in absence of air or other oxidizing agents, the U^{3+} ion, which is produced in solution by the action of powerful reducing agents, is amenable to oxidation[26]. Some complexes of UO_2^{2+} are important owing to their possible application in solar energy conversion systems, their inherent spectral properties and many are

expected to have potential use in photogeneration of oxygen, a process of great importance for the photocleavage[27,28] of water. Historically, the possible interaction of peroxide and UO_2^{2+} has been recognized for a very long period though the interaction is believed to be very complicated. The peroxide (O_2^{2-}) acts as a stabilizing ligand for uranium and the metal is known to form peroxo complexes in its highest oxidation state. It may be mentioned that the peroxo derivatives of metals, besides having an intrinsic interest of their own, are of considerable and growing importance in relation to the catalysis of oxidation[29] involving hydrogen peroxide[30] or oxygen gas, the catalytic decomposition of H_2O_2 itself and the storage and transport of oxygen in biological [31,32] systems. Some transition and actinide metal peroxides have found application as reagents for expoxidation of olefins, and hydroxylation of alkenes and aromatic hydrocarbons[30,33,34]. Molecular oxygen refers to free uncoordinated O_2 with ground state configuration $3\Sigma_g$. The term dioxygen is a generic designation for O_2 moiety in any of its several forms and can be referred to O_2 in either a free or combined state[35]. Therefore, metal dioxygen complex is a common term for any compound where O_2 is coordinated to metal centre either as a neutral ligand or as any one of its reduced forms. According to the rationalisation made by Vaska[35], transition and actinide metal peroxides involve covalently bound dioxygen resembling O_2^{2-} in the peroxo configuration. A common characteristic of these complexes is the O-O distance which occurs between 1.4 and 1.52Å (1.49 for O_2^{2-}), and the corresponding infrared frequency ν(O-O) that lies between 800

and 950 cm^{-1} (802 cm^{-1} for O_2^{2-}). Simple peroxo compounds of metals consist of peroxides, hydroperoxides and water molecules. Whereas heteroligand peroxo complexes contain one to three coordinated peroxo groups and one or more monodentate to polydentate ligands. Heteroligands may range from monodentate ions to bulky porphyrins[32]. Commonly coordinated heteroligands with UO_2^{2+} metal centre include F^-, Cl^-,NH_3,$C_2O_4^{2-}$,SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, $P_2O_7^{2-}$, NTA, EDTA, bpy, phen, oxine, glycine, and pyridine 2,6 dicarboxylic acid etc.

Incorporation of specific heteroligand in coordination sphere of a metal enhances stability of the peroxo complexes. Many simple metal peroxides are sensitive to shock, decompose above 0°C and are often prone to spontaneous explosion due to their instability. Also, many of them are never found as stoichiometric compounds[36]. On the other hand a host of mixed ligand peroxo complexes are highly stable as evidenced by the fact that they can withstand heating *in vacuo*, recrystallization from boiling aqueous solutions and remain unchanged for prolonged periods if stored in closed containers[37]. The biochemical relevance of peroxo metal complexes has been well documented in literature[31,32,38-43]. The reactivity[44-46] of peroxides and the lability of metal oxygen bonds in special heteroligand environments in solutions are of particular interest to biochemistry although not easy to measure directly. The chemistry of unreduced dioxygen heteroligand complexes is quite different from that of the corresponding peroxo complexes because of two extra electrons in the antibonding O-p^* orbitals of the peroxide ion[32]. Consequently, the electron rich O_2^{2-} ion preferably forms

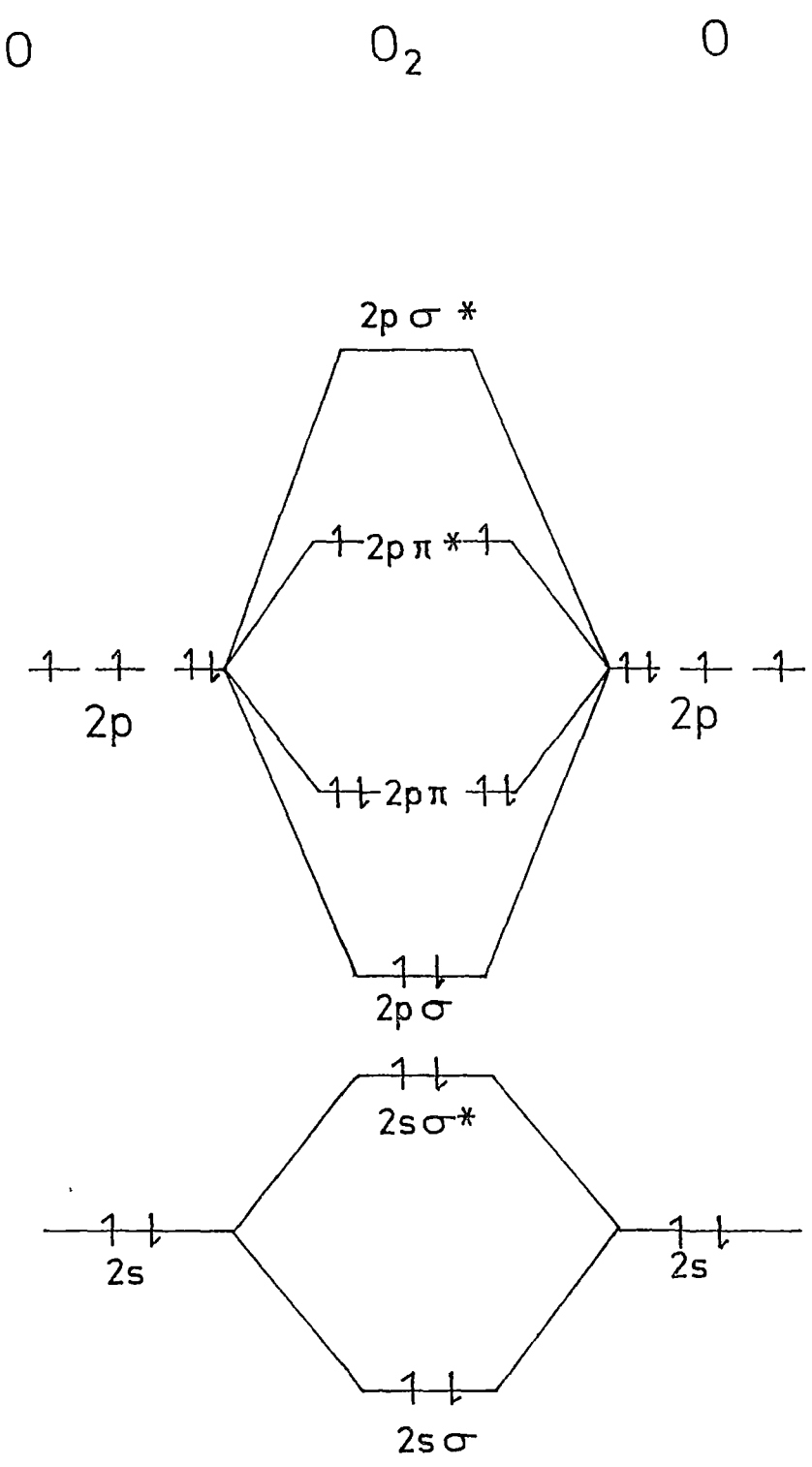


Fig. 1.1: Molecular orbital diagram for O_2

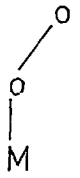
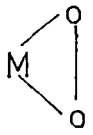
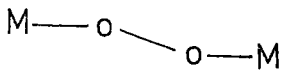
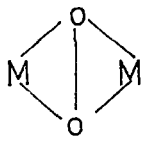
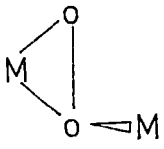
Structural type	Structural designation	Vaska Classification
	η^2 dioxygen	Type Ia (Superoxo)
	η^2 dioxygen	Type IIa (peroxo)
	η^1: η^1 dioxygen	Type Ib (Superoxo)
	η^1: η^1 dioxygen	Type IIb (peroxo)
	η^2: η^2 dioxygen	-
	η^1: η^2 dioxygen	-

Fig. 1.2: Structural Classification of dioxygen complexes

complexes with metal ion of low d^n including d° and also of f° electronic configurations. On the other hand the neutral dioxygen molecule favourably forms complexes with metals of high d^n configuration. However,both the species (peroxo and neutral dioxygen) are stabilized by specific heteroligand sphere and both are biochemically important. There is definite importance of neutral dioxygen complexes in biochemistry.[31]

Molecular oxygen is a paramagnatic molecule having a triplet $3\Sigma_g^-$ ground state, a molecular orbital description of $3\Sigma_g^-$ level is $O_2KK\ (2\ S\sigma g)^2\ (2S\sigma^*u)^2\ (2P\sigma g)^2\ (2p\pi^*u)^4,\ (2p\pi^*g)^1\ (2p\pi^*g)^1$, where KK term indicates that the K shells of the two oxygen atoms are filled. Two unpaired electrons in the $3\Sigma_g^1$ ground state are found in the two degenerate antibonding $2P\pi^*$ orbitals leaving O_2 with a formal bond order of two. The addition of one or two electrons to a neutral O_2 results in the formation of the superoxide(O_2^-) and peroxide(O_2^{2-}) species, respectively, leaving O_2^- with a bond order 1.5 and the peroxide O-O link with a bond order of one (Table 1.1). The peroxo group coordinates to the metal centre either as symmetrical bidentate or as a terminal-monodentate mode, including all possible angles in between them. Molecular orbital diagram of O_2 and rationalised structural classification of dioxygen complexes by Vaska[35] can be depicted in Fig.1.1 and 1.2, respectively.

Table 1.1: Some properties of O_2^+, O_2, O_2^- and O_2^{2-}

Species	Bond order	Compound	O-O distance (A)	Bond energy (K cal/mol)	ν(O-O) Cm^{-1}
O_2^+	2.5	O_2PtF_6	1.12	-	1905[47]
O_2	2	O_2	1.207	117.2	1554[48]
O_2^-	1.5	KO_2	1.28	-	1145[49]
O_2^{2-}	1	Na_2O	1.49	35	842[50]

The configurations of bridging μ-peroxo could vary from cis-planer and trans-planer to trans-nonplaner. An unusual symmetrical double bridging was also found[51-53], however, such examples are seldom met with. It has been found that deviation from ideal symmetry is not uncommon. In most of the heteroligand peroxo complexes, the symmetry is decided by the inherent symmetry of different donors. Additional pπ electron delocalisation to the metal ion is anticipated, which would therefore favour d^o/f^o or low d^n metal ion configuration. The stereochemical polyhedra in heteroligand peroxo complexes are often fairly predictable. The pentagonal bipyramidal arrangement is most common in oxoperoxo heteroligand surroundings for transition metal complexes. Usually in such geometries the two coordinated peroxo groups are in cis position and oxo group is in

the axial position. Although less structural information is available, the situation would be different for heteroligand peroxo complexes of UO_2^{2+}. Infrared spectroscopy is one of the important tools for the characterisation of complex containing peroxo groups. Bidentate peroxide (C_{2v} local symmetry) is expected to display three IR active modes[54]. These are the peroxo stretching (A_1) and symmetric and asymmetric M-O_2 stretching A_1 and B_2. The ν(O-O) band is the most sensitive and intense one characteristically occurs between 800-950 cm^{-1}. The frequency of this band is fairly independent of the heteroligand environment but is affected by the mass of the metal ion, indicating some degree of coupling of the (O-O) with M-O_2 vibration. The most familiar way for bonding of O_2^{2-} group to the metal centre is in a triangular bidentate manner. Similar type of bonding of dioxygen in oxyhemoglobin was proposed by Griffith[55], although subsequently it was disproved and crystallographic studies on oxyhemoglobin[56] have confirmed the bent, end - on bonding mode. Besides IR, Raman spectroscopy is equally important in characterising peroxo complexes owing to the fact that all the three IR active modes as mentioned above are also Raman active. Thus the results obtained from Raman spectroscopic studies complement the IR results. Moreover, Raman spectroscopy can also be applied to solutions and the results of which provide further information concerning identity and structure of a complex species in solution.

As already mentioned, the complexity involved in peroxouranate chemistry is an acknowledged problem[36] and the system is exceedingly complicated[57] owing to the formation of a host of

different peroxouranate(VI) species with a slight variation of pH of reaction medium. Peroxouranates containing O_2^{2-} : U as 1:1, 1:2, 2:1, 3:1, 3:2 and 5:2 were described in literature[58,59] in addition to a few more which were rationalized only on the basis of peroxide to uranium ratio[60,61]. Of these, however, $UO_2(O_2).nH_2O$ (n = 2 or 4) is the best characterised one. This species has been known for quite sometime[62] and extensive studies have been done on it[63,64]. Nevertheless, its constitution was a matter of controversy. Different groups ascribed its composition in different manners i.e., true peroxide hydrate or a peroxide having the composition, U_2O_7, a peroxyacid or an addition compound of uranium oxide, $UO_3.H_2O_2.H_2O$[64,65]. Gordon and Taube[66] finally showed it to be a true peroxide hydrate on the basis of their isotopic tracer studies on thermal decomposition of uranium peroxide system. As stated in the preceding section, many peroxo complexes reported[36] in older literature with different $U:O_2^{2-}$ stoichiometries were poorly characterised. Ambiguity as to the exact composition and structure of such complexes still exists in many cases. Amongst the few[36] solid diperoxo and triperoxouranates(VI) of reported existence, one of the better characterised[67] is $Na_4[UO_2(O_2)_3].9H_2O$ (Structure has been ascertained by X-ray crystallography). Similar is the case with heteroligand peroxo complexes of UO_2^{2+}. The importance of heteroligand complexes of metals has been already emphasised in this Chapter and therefore, further discussion on their importance is redundant. Until recently, reports on heteroligand peroxo compounds of UO_2^{2+} were rather scanty, except for some carbonato and oxalato peroxouranates[36] and the only fluoro

peroxouranate[36], $Na[UO_2(O_2)F(OH_2)].4H_2O$. Relatively recent reports on heteroligand peroxouranates deal with a few nonelectrolytic peroxouranates[68] of the type $[UO_2(O_2)L_2]$ (L = Ph_3PO, Ph_3ASO, Py-N-oxide and Quinoline N-oxide) and a unique μ_2- peroxobridged complex benzyl-trimethylammonium μ_2-peroxobis [trichlorodioxouranate (VI)][53]. The above mentioned chloroperoxo complex is one of the rare examples of a complex containing a dioxygen molecule being bonded as μ_2-peroxo group. In addition, subsequently in 1981, a few more novel mono and diperoxo complexes of uranium containing organic ligands were reported[69]. Recently, from our laboratory, syntheses and characterisation of a series of heteroligand peroxo complexes of UO_2^{2+} have been reported[23-25,70]. Heteroligands have been drawn from F^-, CO_3^{2-}, SO_4^{2-},ethylenediamine (en), glycine (glyH), 2,2' bipyridine (bipy), 1,10-phenanthroline (O-phen). Although reports on mono-peroxo heteroligand complexes of UO_2^{2+} are now ample, the corresponding binary diperoxo and heteroligand diperoxo complexes of UO_2^{2+} are still scanty[36,69]. Very recently a predecessor from this laboratory has, however, reported a 1:1.5 ($U:O_2^{2-}$) type of peroxouranate[71].

Notwithstanding the synthesis and characterisation of simple and heteroligand peroxo metallates, a major thrust of contemporary research on peroxo chemistry of metal and nonmetal has been their reactivity with different organic and inorganic substrates. The reactivity of coordinated dioxygen in low valent transition metal compounds has received a considerable attention in recent years, particularly in respect of its ability to oxidize organic and

inorganic substrates, viz., olefins[72-74], carbon dioxide[75,76], sulfur dioxide[77-79] and nitric oxide[78,79]. In most cases, the coordinated dioxygen behaves as a nucleophile. It is evident from these reports that the coordinated peroxide shows a characteristic reactivity pattern towards inorganic polar substrates like SO_2, CO_2, NO_2 and NO etc. by way of producing coordinated sulphate[43,80,81], carbonate and nitrate, respectively. Formation of coordinated sulphate from coordinated O_2^{2-} can be summarised as :

Coordinated(O_2^{2-}) + SO_2 ——> coordinated (SO_4^{2-}).

Corresponding theoretical studies on the mechanistic details of the steps involved in the formation of SO_4^{2-} were also carried out. In contrast, there have been a very few number of reports specifically devoted to the interaction of $SO_2(g)$ with peroxo metal complexes[43,82]. Albeit, extensive reactivity studies have been carried out by different workers on transition metal dioxygen complexes[42,72-83] but a full justice has not been done with actinide peroxo complexes except for a few such as $UO_2(O_2).nH_2O$[34] and the compound, $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$. Thus it is imperative to investigate the reaction profiles of peroxouranate(VI) systems with inorganic substrates, viz., $SO_2(g)$, $CO_2(g)$ and $NO_2(g)$.

In the light of the above discussion it certainly appears rewarding to undertake studies in the field of peroxouranium chemistry emphasizing on the synthesis of novel peroxo and heteroligand peroxo complexes of UO_2^{2+} followed by looking into their reaction profiles.

Interestingly, hydrogen peroxide has been also very useful in context of the estimation of uranium. Indeed there exists a method[84] of quantitative determination of uranium content by use of H_2O_2. In the course of syntheses and characterisation of peroxo and mixed ligand peroxo complexes of uranium(VI), we found that the metal ion (UO_2^{2+}) instantaneously reacted with O-hydroxyanisole (commonly known as guaiacol) at pH 5-8, producing *in situ* a yellowish-orange chelate suitable for spectrophotometric determination of uranium(VI) in ppm level. The most stable complexes of uranium involve oxygen bonding. Bonding to sulfur and nitrogen is next in the order of stability.

There are a number of methods for spectrophotometric determination of uranium[85-113]. Although a few among these are sensitive, most of them are not selective and require extra manipulations. Due to the lack of specificity, colorimetric methods are usually preceded by a separation of uranium. Liquid-liquid extraction, the simplest and most effective means of separating uranium from interfering species, is particularly applicable for rapid analysis by the *in situ* technique. In this technique the chromogenic agent in a miscible solvent is added to the organic phase containing the extracted uranium. The colour of the complexes of uranium(VI) with common inorganic anions, viz., perchlorate, nitrate, chloride and sulphate is yellow. Each complex also has a characteristic ultraviolet spectrum. The maximum molar absorptivity is about 30 in the visible and almost 3000 in the ultraviolet regions. Because these complexes are

weak, careful control of anion concentration is required for a direct colorimetric method and the methods are very sensitive to diverse ion interference. Despite this, the methods are widely used because of their simplicity. A few simple methods involve with KCNS[113], ferrocyanide[114], H_2O_2[84], azide[115], 8-hydroxyquinoline[116] and benzoyltrifluoroacetone[117] etc. as the reagents.

To this end, we thought of making a humble contribution by providing yet another method for determination of the metal. Guaiacol(O-hydroxyanisole) is known to form complex[118] with Fe^{3+}. Till date, no report is available on UO_2^{2+} — Guaiacol system, to the best of our knowledge. The presence of one hydroxo group in ortho position to methoxy group, is expected to facilitate coordination of UO_2^{2+} through oxygen atoms of OCH_3 and OH^- at pH 6-8. At this pH, OH should be deprotonated whereby favouring the chelate formation. The reaction scheme is shown as follows

$$(C_7H_8O_2)_2 + UO_2^{2+} \xrightarrow[5-8]{pH} (C_7H_7O_2)_2UO_2$$

This prompted us to undertake studies pertaining to optimization of reaction conditions and variables.

Scope of Work

In cognizance of the preceding nonexhaustive overview, it appears rewarding to undertake the following investigations.

(i) To develop methodologies for the synthesis of newer mixed ligand fluoroberyllates(II) containing oxalate, glycinate, phosphate, etc. as the co-ligands and to make an evaluation of their structures and properties.

(ii) To ascertain experimental conditions conducive to the synthesis of heretofore unreported heteroligand monoperoxo complexes of UO_2^{2+} followed by their physico-chemical characterisation. The heteroligand, may be drawn from fluoride, phosphate, arsenate etc. It might also be interesting to make an internal comparison of their properties.

(iii) To improvise synthetic strategies for obtaining both binary and a few heteroligand diperoxo complexes of UO_2^{2+} and evaluate their structural motifs and compare the vibrational spectroscopic features in the light of the effect on an increased number of coordinated O_2^{2-} ligands on the $\nu(O-O)(A_1)$ mode with reference to mono vis-a-vis diperoxodioxouranates(VI).

(iv) To investigate the reactivity profiles of a few chosen mono and diperoxo uranates(VI), with inorganic substrates like SO_2, CO_2, F^- etc. from among the proposed type of complexes.

(v) Finally, to make an attempt to develop a new method for spectrophotometric determination of UO_2^{2+} and comment on the method on a comparative basis.

It is hoped that the results of the proposed investigation will throw light on the chosen aspects in addition to providing newer materials for further studies.

The present Chapter gives a nonexhaustive background information pertaining to the kind of work chosen for the present Ph.D. research and highlights the scope of work in the field. Chapter II provides details of the methods of elemental analyses and particulars of instruments/equipment used for characterisation and structural assessment. Chapter III to VI describe interpretive accounts of the results of studies on fluoro and peroxo compounds of beryllium and uranium(VI) as well as a spectrophotometric method developed for uranium(VI) determination. Each of the Chapters has been presented as a self contained one with a brief introduction, sections on experimental and results and discussion followed by relevant bibliography. A part of the new results has been published, while the rest are under communication.

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CHAPTER - II

PARTICULARS OF INSTRUMENTS/EQUIPMENT USED AND METHODS OF ELEMENTAL ANALYSES FOR CHARACTERISATION AND STRUCTURAL ASSESSMENTS OF COMPOUNDS

Detailed procedures for quantitative determinations of various constituents, and the relevant particulars of the instruments/equipment used for the characterisation and structural assessment of the newly synthesised compounds are described in this Chapter.

ELEMENTAL ANALYSES

Beryllium[1]

(i)Gravimetry[1]

An accurately weighed sample (0.1g) was taken in a 250 cm^3 beaker and 100 cm^3 of water was added. To it was added 5 cm^3 of

8 M HNO_3 and heated on a hot plate till dissolution. The solution was cooled and beryllium was precipitated as hydroxide by adding ammonia solution (1:1 v/v) at pH 8-9. The precipitate was filtered and then transferred back to the original beaker. The precipitate was dissolved in dilute mineral acid. The solution was diluted to 100 cm^3 and the pH was adjusted to 2. A 5 cm^3 of 15% diammonium hydrogen phosphate solution was added (the reagent solution was previously adjusted to a pH of 5.5). To it was added 5 cm^3 of ammonium acetate until the pH was 5.5. The solution was digested just below the boiling point for 5-10 min, cooled and filtered the grannular precipitate. The precipitate was redissolved in the minimum volume of hot 6M hydrochloric acid and reprecipitated by using only 1 cm^3 of the reagent. The precipitate was filtered again, washed with 0.5 M acetate buffer (3.5 g of ammonium acetate and 3.0 cm^3 of glacial acetic acid per 100 cm^3 of water) and finally ignited at 1000°C and weighed as $Be_2P_2O_7$ in the usual manner.

(ii)Atomic Absorption Spectrophotometry,(AAS)[2,3].

In order to verify the results, beryllium contents were also determined by AAS techniques by following standard procedures.

Oxalate[4]

An accurately weighed amount of the compound was treated with 25 cm^3 of 0.1 M Sodium hydroxide solution and then 100 cm^3 of water was added to it. The mixture was boiled for *ca.* 15 min followed by filtration. The precipitate was washed several times with water. The filtrate and washings were collected and from which

the oxalate content of the compound was determined by the following method. The combined filtrate and washings was neutralized with dilute sulphuric acid (0.5 M). An amount of 15 cm^3 of concentrated sulphuric acid was added to the solution. The resulting solution was then titrated against standard 0.02M potassium permanganate solution maintaining the temperature of the solution at *ca* 60°C.

$$1\ cm^3 \text{ of } 0.1M\ KMnO_4 = 0.22\ g \text{ of } C_2O_4^{2-}$$

Fluoride[5]

An accurately weighed amount of the compound was dissolved in water (for an insoluble compound, 1-2 cm^3 of conc. HNO_3 was added to assist dissolution). The compound was decomposed with 20-25 cm^3 of 30% aqueous NaOH Solution. The mixture was heated over a steam-bath for *ca.* 10 min to ensure complete decomposition.
The precipitate of metal hydroxide (in case of uranium compounds, hydroxide or hydrated oxide) formed due to the addition of aqueous ammonia (1:1 v/v) was separated out by filtration and washed several times with water. The filtrate and washings were collected for fluoride estimation. To the combined washing and filtrate, 2 or 3 drops of bromophenol blue indicator and 3 cm^3 of 10% sodium chloride solution were added, and the whole was diluted to *ca.* 250 cm^3. Dilute nitric acid was added to it until colour changed to just yellow, followed by the addition of 10% sodium hydroxide solution until the colour ultimately just changed to blue. The mixture was then treated with 1 cm^3 of concentrated hydrochloric acid and 5.0 g of lead nitrate, and then heated on a steam-bath. After all the lead nitrate had

dissolved, 5.0 g crystalline sodium acetate was added to the solution. The solution was digested on a steam-bath for about half an hour with occasional stirring, and then allowed to stand overnight. For the gravimetric estimation, the precipitated lead chloride fluoride, PbClF, was filtered through a weighed sintered glass crucible (grade 4) and weighed as PbClF after drying at 140 -150 °C to constant weight. In the volumetric estimation, the precipitated PbClF was quantitatively collected by filtration through a Whatman 542 filter paper and washed once with cold water, then 3 or 4 times with saturated solution of lead chloride fluoride, and finally once more with cold water. The precipitate was then dissolved in 100 cm^3 of 5% (V/V) nitric acid by heating on a steam-bath for 4 or 5 min. A known excess of 0.1M silver nitrate solution was then added to it, followed by digestion on a steam-bath for 30 min and then cooled to room temperature in the absence of light. The precipitated silver chloride was filtered through a sintered glass crucible (Grade 4) and washed with cold water. The unreacted silver nitrate in the filtrate and washings was titrated with a 0.1M potassium thiocyanate 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 silver nitrate consumed.

$$1\ cm^3 \text{ of } 1M\ AgNO_3 = 0.0190\ g \text{ of } F^-$$

Phosphate[6]

As beryllium of the dihydrogenphosphato(difluoro)beryllate compound interferes in gravimetric determination of phosphate in the form of ammonium magnesium phosphate hexahydrate, a spectrophotometric method employing ammonium molybdovanadate reagent was used. The reagent, ammonium molybdovanadate solution was prepared by dissolving 1.5 g NH_4VO_3 in 400 cm^3 of dilute HNO_3 (1:1 v/v) (solution A) and 90 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in 400 cm^3 of H_2O (Solution B) and mixing them together and then diluting the volume to 1 litre.

A known quantity of the compound (0.1g) was taken in a 250 cm^3 glass beaker and to it was added 5 cm^3 of conc. HNO_3 and heated on a hot plate till dryness. The beaker was cooled and 2 cm^3 of conc. HNO_3 and 50 cm^3 of water were added and again heated till complete dissolution. The solution was cooled and then transferred to a 250 cm^3 volumetric flask and the volume was made up to the mark. In a 50 cm^3 calibrated volumetric flask, 5 cm^3 aliquot of the sample solution was transferred and 15 cm^3 of ammonium molybdovanadate reagent was added while swirling the flask. The volume was made up to the mark and the solution was set aside for 15 min. Absorbance of this solution was measured at 430 nm against a reagent blank. The concentration of phosphate was found out from a standard calibration graph made similarly on a series of standard phosphate solution (25 to 250 µg phosphorus per 50 cm^3).

Uranium

(i) *Gravimetry*[7]

Uranium was estimated gravimetrically as U_3O_8. An accurately weighed amount of an uranium compound was dissolved in a minimum volume of dilute (2.0 M) H_2SO_4 in the presence of a few drops of methyl red indicator and the solution was heated to boiling. The hot solution was treated with dilute ammonia solution (1:1 v/v) until the indicator just turned yellow. A yellow precipitate was obtained at this stage. A Whatman accelerator was added and the solution was warmed for 1 or 2 min, precipitate was filtered off on a Whatman 541 filter paper, and washed well (3 or 4 times) with a hot 2% solution of ammonium nitrate. The wet filter paper along with the precipitate was dried in a platinum crucible over a Meker burner at a low temperature until the carbon was destroyed. The crucible was then heated strongly being placed in a slanting position so as to maintain a good oxidising condition. The crucible with its content was cooled in a desiccator and weighed. The ignition process was repeated until constant weight was attained. Uranium was finally weighed as U_3O_8.

(ii) *Spectrophotometry by* H_2O_2[8]

A 0.3g of the compound was taken in a 100 cm^3 glass beaker and 5 cm^3 of conc.HNO_3 and 30 cm^3 of water were added to it. The beaker was heated on a hot plate and the solution was boiled for 5-10 min. The solution was cooled and transferred to a 50 cm^3 volumetric flask and the volume was made up to the mark. In

another 50 cm^3 volumetric flask 5 cm^3 of the aliquot was transferred and to it were added 1 cm^3 of 30% H_2O_2 and 5 cm^3 of 50% sodium hydroxide. The volume was made up to the mark and the flask was shaken properly. This was set aside for 5 min and absorbance of the yellow solution was measured at 420 nm against a similarly prepared reagent blank. The concentration of uranium was found out from a calibration curve composed of a plot of absorbances vs. a series of known concentration of uranium solutions (1 to 5 mg of U per 50 cm^3).

(iii) ***Fluorimetry***[9]

As the fluorimetric method is highly sensitive, uranium determination in compounds was resorted to using very dil. sample solutions.

An amount of 0.1 g of the compound was dissolved in a 5 cm^3 of conc. HNO_3 in a 100 cm^3 beaker and heated on a hot plate till dryness to decompose peroxide. To it, 15 cm^3 of water was added and the residue was dissolved by using 1 or 2 cm^3 of conc.HNO_3 and then by heating. The solution was cooled and transferred to a 100 cm^3 volumetric flask and the volume was made up to the mark with distilled water. A 3 cm^3 of this solution was taken into a 100 cm^3 volumetric flask containing 10 cm^3 of conc. HNO_3 and the volume was made upto 100 cm^3. A 3 cm^3 aliquot of this solution was transferred to a shaking vial and 15 cm^3 of saturated solution of $Al(NO_3)_3.9H_2O$ was added. To this was added 10 cm^3 of ethylacetate and the vial was stoppered. It was shaken for 2 min. After 10 min, ~5 cm^3 of ethylacetate was separated out and filtered through a Whatman no. 1 filter paper into a dry

test tube. Aliquots of 0.1 cm^3 each of ethylacetate were pipetted to a series (usually 4 nos.) of platinum blanks (previously washed and cleaned) and the solutions were evaporated under IR lamp. Around 0.4g of dry NaF and Na_2CO_3 (1:4) flux in the form of pellets were added to each of the platinum blanks and fused at 850°C for 2 min in a muffle furnace. The beads formed in platinum blanks were cooled and fluorescence of these beads was measured after 15 min in a Jarrel-Ash Fluorimeter.The concentration of uranium in the unknown solution was found out from a calibration curve plotted between the fluorescence readings and the known concentrations of uranium.

Active Oxygen (Peroxo Oxygen)

(i) Permanganometry[10]

An accurately weighed amount of a peroxo compound was dissolved in 4.0 M sulphuric acid in the presence of about 4 g of boric acid. Boric acid was used to prevent any loss of active oxygen by forming perboric acid. The resulting solution was then titrated with a standard solution of potassium permanganate.

$$1\ cm^3 \text{ of } 1M\ KMnO_4 = 0.08505 \text{ g of } H_2O_2$$

(ii) *Iodometry*[11]

To a freshly prepared 1.0 M sulphuric acid solution, containing an appropriate amount of potassium iodide (1 g in 100 cm^3) was added an accurately weighed amount of the peroxo compound with continuous stirring. The mixture was allowed to stand for *ca.* 15 min in the dark under a CO_2 atmosphere. The liberated iodine was

then titrated with a standard sodium thiosulphate solution adding 2 cm^3 of freshly prepared starch solution when the iodine colour was nearly discharged.

$$1\ cm^3 \text{ of } 1M\ Na_2S_2O_3 = 0.01701\ g \text{ of } H_2O_2$$

Sulphate[12]

A known amount of the compound was treated with 25 cm^3 of water and was completely dissolved by the addition of a few drops of dilute HNO_3 (6M). A concentrated solution of aqueous ammonia (sp.gr. 0.9) was added to the solution slowly with stirring and the mixture was heated on a steam bath for *ca.* 30 min. The precipitate was separated by filtration, and it was carefully washed 2 or 3 times with cold water. The combined filtrate and washings was retained for the estimation of sulphate. The solution was concentrated by boiling and then neutralized with dilute (6 M) nitric acid (volume of the solution was 230 cm^3). The solution so obtained was acidified by the addition of 0.3 - 0.6 cm^3 of concentrated HCl solution and heated to boiling. A warm solution (10-12 cm^3) of 5% barium chloride (5 g of $BaCl_2.2H_2O$ in 100 cm^3 of water) was added from a burette or a pipette drop by drop with continuous stirring and the resultant precipitate was allowed to settle for *ca.* 2 min. The supernatant liquid was tested for complete precipitation by adding a few drops of barium chloride solution. The process was repeated until slight excess of barium chloride was present in the mixture to ensure complete precipitation. The mixture was kept covered on a steam-bath for 1 h in order to allow time for complete

precipitation of $BaSO_4$. The precipitated barium sulphate was filtered through a previously weighed sintered glass crucible(grade 4) using gentle suction. The precipitate was washed with warm water until the filtrate gave no precipitate with a few drops of silver nitrate solution. The crucible with its content was dried at *ca.* 110 °C and heated for 10-15 min at a higher temperature (*ca.* 600 °C) followed by cooling in a desiccator. The ignition process was continued until constant weight was attained. The sulphate content of the sample was finally weighed as $BaSO_4$.

Carbon, Hydrogen and Nitrogen

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

Preparation of deoxygenated water for reactivity studies

The water used for reactivity studies was deoxygenated by first boiling the water sample for *ca.* 30 min under N_2 atmosphere and cooling to room temperature followed by bubbling N_2 gas through it for a period of *ca.* 15 min. The deoxygenated water was stored in an airtight container. The water thus obtained has been used in the reactivity studies throughout.

PARTICULARS OF INSTRUMENTS/EQUIPMENT USED

pH Measurement

The pH values of the reaction solutions were measured by using a Systronics type 335 digital pH meter.

Conductance

The conductance values were measured in conductivity grade water using a Wayne Kerr Automatic Precision Bridge B 905 Conductometer and a Systronics type 304 digital Direct Reading conductivity meter.

Infrared Spectra

The infra-red (IR) spectra were recorded in KBr as well as in nujol mull on the following spectrophotometers.

(i) Perkin–Elmer Model–297

(ii)Perkin–Elmer Model–983

Laser Raman Spectra

Laser Raman (LR) spectra were recorded on a SPEX Ramalog model 1403 Raman Spectrometer. The 4880 Å Laser line from spectra-Physics model 165-09 Argon Laser and 5145 Å Laser line from spectra physics model 165 Argon Laser were used as the excitation sources. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube, followed by photon-count processing system. The sample was held either in quartz capillary or in the form of a pressed pellet. The recording was done at ambient temperatures.

Atomic Absorption Spectrophotometry

A Varian AA-1475 Atomic Absorption Spectrophotometer was used for the determination of beryllium, potassium, uranium, etc.

Colorimetry or Spectrophotometry

Absorbance measurements for the coloured complexes of uranium and phosphorus were made on a Varian 634-S double beam digital and on a Hitachi-2000 microprocessor based spectrophotometers. Electronic spectra were recorded using the later instrument.

Flame Photometry

Sodium and potassium were determined using a Fotoflame (Sr.No. 90957) model Flame photometer.

Fluorimetry

Fluorescence measurements for UO_2^{2+} determination was made on a Zarell Ash (Division of Fischer Scientific Company) fluorimeter.

Scanning Electron Microscopy (SEM)

All the SEM studies were made on a JEOL SEM JSM - 35CF model Scanning Electron Microscope equipped with an EDAX Model LINKS AN 10000 Data station. When a sample is subjected to electron beam excitation, several signals are generated which include secondary electrons, back scattered electrons, Auger electrons and characteristic x-rays. To analyse a compound visually i.e. to observe the picture of the compound,secondary electrons, back scattered electrons, and transmitted electrons are collected and

displayed. To determine the composition of the sample it is required to record characteristic X-rays or auger electron spectra. The equipment available in our University uses secondary electrons and X-rays for studying the morphology and composition of the specimen respectively. Following are the two types of detectors used for the present investigations:

(i) Secondary electron detector (for morphology)
(ii) X-ray detector (for energy dispersive spectrometry)

Preparation of a sample for such studies was made by spreading the microcrystalline powder of the compound on a graphite plate and then metallising it with either gold or graphite. In SEM experiments, samples were coated with gold by ion sputter coater.

Radiometry

Uranium was determined radiometrically by β minus γ technique[13]. The ECIL (Sr.No.2162) instrument was used for the determination. While a pancake type β tube was used for β detection, a thallium activated NaI crystal coupled with photomultiplier tube was used for γ detection. Brief description of the instrument is given below:

Specification of the Detectors

For β counting - β tube model No. 731
Window-1.5-2.0 mg/cm^3
Gass filled — Net halogen

Operative voltage - 1000 V

For γ Counting - NaI (Tl) Crystal Size - 2"x13/4"

P.M. Tube - 9514 B

Specification for Radiation Counting System

For β counting - model RCS 4027

For γ counting - (i) Preamplifier

(ii) Linear amplifier — PA-531

(iii) Single Channel Analyser — SC-604B

(iv) High voltage unit — HV — 216 D

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CHAPTER - III

COMPLEX FLUOROBERYLLATES. SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERISATION OF MIXED-FLUORO COMPLEXES OF BERYLLIUM CONTAINING ACIDOXALATE ($HC_2O_4^-$), GLYCINATE AND DIHYDROGEN PHOSPHATE ($H_2PO_4^-$) AS THE COLIGANDS*

Owing to the extensive application of beryllium and its compounds in industries, especially in nuclear industries, and in modern day science and technology, its chemistry is important[1]. Beryllium is used as a moderator in nuclear reactors[2] and in silicon MIS solar cells[3]. Its compounds have got multifaceted uses, especially in the diagnosis of tuberculosis and in the manufacture of glasses that have high ultraviolet permeability, low dissipation capacity of light on irradiation and high optical

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clarity. Uses of beryllium and its alloys have been discussed in a review[4]. Beryllium fluorides and fluoroberyllates are also important industrially. Many binary fluoroberyllates, apart from being used in industries for different purposes, for instance as a flux in porcelain enamels[1] and in coating special welding rods, manifest many other unique properties. Notable among them is their ferroelectric properties[1]. A prerequisite for a solid to be ferroelectric is the absence of centre of symmetry[5] and the presence of hydrogen bonds are necessary for the polarization of some ferro-electrics. As has been discussed in the general introduction of this thesis, fluoride being highly electronegative can not form stable complexes of the type L_xBeF_2 with neutral ligands (L). On the contrary, Cl^-,Br^- and I^- behave as though they are essentially covalent and accordingly form innumerable stable cationic complexes[1,6-8] with neutral ligands. Although fluoride is known to form anionic complexes of beryllium, number of such complexes are very much restricted to simple fluoroberyllate[1], $A_2[BeF_4]$ (A = NH_4, Na, K or Rb). While extensive studies have been carried out on physico-chemical properties[1] of tetrafluoroberyllates, to the best of our knowledge, efforts for the synthesis and characterisation of the corresponding heteroligand fluoroberyllates have not been made so far except a few. The importance[9] of heteroligand complexes of metals have already been discussed in the prelusive Chapter of the thesis, and therefore further discussion in this regard is redundant.

As described in the preceding section, lack of centre of symmetry of a molecule helps manifest ferroelectric property and in this context it is expected that incorporation of coligand in the fluoroberyllate moiety might bring about centre of asymmetry in the compound, resulting into the probable display of ferroelectric property. Moreover, biological implications of beryllium fluoro compounds are also documented in literature[10,11]. Although some fluoroberyllates are known to be ferroelectric [12,13] there is however, only a very limited accessibility to such compounds especially mixed fluoroberyllates.

For a number of years, we have been trying our hands in the field of fluoro and mixed fluoro metal compounds for a variety of reasons[14-17]. The interesting properties and applications of fluoroberyllium species[1-5,18] prompted us to undertake studies on fluoro chemistry of the metal.

The main concerns were to identify appropriate coligands, improvise practical routes to newer mixed fluoroberyllates, and isolate and characterise the compounds. We considered this to be important to provide new materials amenable to physical studies. Another important aim was to demonstrate the new synthesis directly from $Be(OH)_2$. This would reduce the extra steps involved in the preparation of BeF_2, a commonly used starting material for fluoroberyllates[1]. The coligands have been drawn from the anions of a dicarboxylic acid, $HC_2O_4^-$, an aminocarboxylic acid,eg., $NH_2CH_2COO^-$, and a tribasic acid, $H_2PO_4^-$ such that target species are obtained.

The present Chapter deals with the synthesis of new compounds of the types, $A_2[BeF_3(HC_2O_4)].H_2O$ (A = NH_4 or Na), $K_2[BeF_3(HC_2O_4)]$, $A_2[BeF_3(NH_2CH_2COO)].H_2O$ (A = NH_4 or Na), and $A_2[BeF_2(H_2PO_4)_2]$ (A = NH_4 or K) and the results of some physico-chemical studies on them.

EXPERIMENTAL

Reagent grade chemicals were used throughout the present work.

Synthesis of ammonium and sodium trifluoro-acidoxalatoberyllate monohydrate, $A_2[BeF_3(HC_2O_4)].H_2O$ (A = NH_4 or Na) and potassium trifluoro-acidoxalatoberyllate, $K_2[BeF_3(HC_2O_4)]$

To a solution of $BeSO_4.4H_2O$ (1.0 g, 5.65 mmol) in water (150 cm^3), dilute NaOH solution (5%) was added slowly with continuous stirring. The precipitate of $Be(OH)_2$ was filtered and washed 5 or 6 times with water. $Be(OH)_2$ was transferred into a polyethylene beaker. To it were added water (10 cm^3) and 16.95 mmol each of solid AF(NH_4, Na or K) and $H_2C_2O_4.2H_2O$ with stirring. The mixture was heated on a steam-bath for *ca.* 20 min to obtain a clear solution. The pH of the solution was recorded to be 2. The reaction solution was allowed to cool and to this ethanol was added to precipitate the product. The product was filtered and washed 3 or 4 times with ethanol and dried *in vacuo* over conc. H_2SO_4. The yields were 1g (85%) for $(NH_4)_2[BeF_3(HC_2O_4)].H_2O$, 1.1 g (88.7%) for $Na_2[BeF_3(HC_2O_4)].H_2O$, and 1.25g (95%) for $K_2[BeF_3(HC_2O_4)]$.

Ammonium and sodium trifluoro-glycinatoberyllate monohydrate, $A_2[BeF_3(NH_2CH_2COO)].H_2O$ (A = NH_4 or Na)

To an aqueous suspension of $Be(OH)_2$, obtained from $BeSO_4.4H_2O$ (1.0 g, 5.66 mmol) in a way similar to that described in the preceding synthesis, were added water (10 cm^3) and 16.95 mmol each of AF (NH_4 or Na) and glycine with continuous stirring. The mixture was heated over a steam bath for *ca.* 30 min. The pH of the reaction solution was 2.5. The solution was cooled to room temperature. Addition of ethanol to this afforded a white microcrystalline product. The compound was separated by filtration, washed 4 or 5 times with ethanol and dried *in vacuo* over conc.H_2SO_4.The yields were 1g (91%) for $(NH_4)_2[BeF_3NH_2CH_2COO)].H_2O$ and 1g(87%)for $Na_2[BeF_3(NH_2CH_2COO)].H_2O$.

Ammonium and potassium difluoro-dihydrogenphosphatoberyllates, $A_2[BeF_2(H_2PO_4)_2]$ (A = NH_4 or K)

To an aqueous suspension of $Be(OH)_2$, obtained from $BeSO_4.4H_2O$ (1.0g,5.66 mmol) as mentioned above, were added 16.95 mmol of AF (A = NH_4 or K) and 22.64 mmol of orthophosphoric acid (sp.gr. 1.75 gcm^{-3}) under stirring. The mixture was heated on a steam-bath for *ca.* 20 min and a clear solution was obtained.The pH of the solution was recorded to be 2. Addition of ethanol to this solution afforded a white microcrystalline product. The compound thus obtained was filtered and washed 3 or 4 times with ethanol and dried *in vacuo* over conc. H_2SO_4. The yields were 1.3 g (83%) for $(NH_4)_2[BeF_2(H_2PO_4)_2]$ and 1.5 g (83%) for $K_2[BeF_2(H_2PO_4)_2]$.

Elemental Analyses

Methods of chemical analyses and the details of equipment used for characterisation have been elaborated in Chapter II.

RESULTS AND DISCUSSION

Synthesis of fluoroberyllate complexes generally involves the use of BeF_2[1]. Its preparation requires high temperature[1]. Besides, this compound is hygroscopic and therefore its careful handling is recommended. In order to avoid the use of BeF_2, we have used $Be(OH)_2$ as a source of the metal throughout our work on beryllium as discussed in the present Chapter. Alkali free freshly prepared $Be(OH)_2$ was our starting material for the syntheses of fluoroberyllate complexes. In this context two important points are worth mentioning here, viz., (i) asymmetry of the metal centre and (ii) the occurrence of hydrogen bonding. While any mixed fluoroberyllate would fulfill the first condition, selection of an appropriate coligand is important to achieve the second point of contention. In order to achieve the goal, the chosen coligands were identified and reaction conditions for the syntheses were optimised. A favourable reaction condition was made to prevail by maintaining a pH value of 2-2.5 for all the syntheses because F^- as well as the chosen coligands were expected to react with the metal centre at this pH range. Thus, under the present reaction conditions $Be(OH)_2$ reacted with AF and oxalic acid to afford $A_2[BeF_3(HC_2O_4)].H_2O$ (A = NH_4 or Na) and $K_2[BeF_3(HC_2O_4)]$ in contrast to $A_2[BeF_2(C_2O_4)].nH_2O$ (A = Na or K) and $K_2[Be_2F_6(C_2O_4)].H_2O$ reported in literature[18].

Table 3.1 : Analytical data of $A_2[BeF_3(HC_2O_4)].H_2O$ (A = NH_4 or Na), $K_2[BeF_3(HC_2O_4)]$, $A_2[BeF_3(NH_2CH_2COO)].H_2O$ (A = NH_4 or Na) and $A_2[BeF_2(H_2PO_4)_2]$ (A = NH_4 or K)

Compounds	Analysis[a] (%)							
	A or N	Be	F	C_2O_4	PO_4	C	H	N
$(NH_4)_2[BeF_3(HC_2O_4)].H_2O$	-	4.23 (4.31)	27.38 (27.25)	41.63 (42.08)	-	11.18 (11.48)	5.19 (5.31)	12.95 (13.40)
$Na_2[BeF_3(HC_2O_4)].H_2O$	21.12 (21.00)	4.14 (4.11)	25.64 (26.02)	39.85 (40.18)	-	10.85 (10.97)	1.32 (1.38)	-
$K_2[BeF_3(HC_2O_4)]$	34.11 (33.52)	3.86 (3.86)	24.95 (24.44)	38.19 (37.74)	-	10.19 (10.30)	-	-
$(NH_4)_2[BeF_3(NH_2CH_2COO)].H_2O$	-	4.70 (4.64)	29.18 (29.35)	-	-	12.89 (12.37)	7.21 (7.28)	20.80 (21.64)
$Na_2[BeF_3(NH_2CH_2COO)].H_2O$	23.11 (22.54)	4.24 (4.41)	28.14 (27.93)	-	-	11.94 (11.77)	2.75 (2.97)	6.81 (6.87)
$(NH_4)_2[BeF_2(H_2PO_4)_2]$	-	3.28 (3.26)	13.55 (13.73)	-	70.15 (68.50)	-	-	-
$K_2[BeF_2(H_2PO_4)_2]$	23.89 (24.53)	2.78 (2.83)	11.21 (11.92)	-	59.24 (59.46)	-	-	-

[a] Calculated value in Parenthesis

Table 3.2: Structurally significant IR and LR bands of $A_2[BeF_3(HC_2O_4)].H_2O$ (A = NH_4 or Na), $K_2[BeF_3(HC_2O_4)]$, $A_2[BeF_3(NH_2CH_2COO)].H_2O$ (A = NH_4 or Na), and $A_2[BeF_2(H_2PO_4)_2]$(A = NH_4 or K)

Compounds	IR(cm^{-1})	LR(cm^{-1})	Assignments
$(NH_4)_2[BeF_3(HC_2O_4)].H_2O$	818 s,br	820	ν (Be-F)
	347 m,br		δ (F-Be-F)
	911 s		ν (Be-O)
	3450 s		ν (OH)
	1657 s		δ(H-O-H)
	1630 s		coord.$HC_2O_4^-$
	1668 s		$\nu_{asym}(COO^-)$
	1310 m		$\nu_{sym}(COO^-)$
	725 w		$\nu(CO_2^-)$
$Na_2[BeF_3(HC_2O_4)].H_2O$	810 s,br	815	ν(Be-F)
	345 m,br		δ(F-Be-F)
	920 s		ν (Be-O)
	3445 s		ν (O-H)
	1650 s		δ(H-O-H)
	1632 s		coord. $HC_2O_4^-$
	1670 s		$\nu_{asym}(COO^-)$
	1310 m		$\nu_{sym}(COO^-)$
	720 w		$\nu(CO_2^-)$

Table 3.2 (Contd.)

$K_2[BeF_3(HC_2O_4)]$	818 s,br	820	ν (Be-F)
	396 m,br		δ(F-Be-F)
	911 s		ν(Be-O)
	1630 s		coord.$HC_2O_4^-$
	1672 s		$\nu_{asym}(COO^-)$
	1338 m		$\nu_{sym}(COO^-)$
	719 w		$\nu(CO_2^-)$
$(NH_4)_2[BeF_3(NH_2CH_2COO)].H_2O$	802 s,br	805	ν (Be-F)
	363 m,br		δ (F-Be-F)
	930 s		ν (Be-O)
	1610 s		$\nu(COO^-)$
	3440 s,br		ν(O-H)
	1657 s		δ(H-O-H)
$Na_2[BeF_3(NH_2CH_2COO)].H_2O$	822 s,br	820	ν (Be-F)
	363 m,br		δ (F-Be-F)
	930 s		ν (Be-O)
	1615 s		ν (COO^-)
	3438 s		ν (O-H)
	1629 s		δ (H-O-H)

Table 3.2 (contd.)

$(NH_4)_2[BeF_2(H_2PO_4)_2]$	810 s,br	810	ν (Be-F)
	372 m,br		δ(F-Be-F)
	922 s		ν(Be-O)
	1000 — 1104 s,br		ν(P=O)
	2800 — 2854 w,br		ν(P-O-H)
$K_2[BeF_2(H_2PO_4)_2]$	815 s,br	815	ν(Be-F)
	373 m,br		δ(F-Be-F)
	926 s		ν(Be-O)
	1000 — 1108 s,br		ν(P=O)
	2800 — 2922 w,br		ν(P-O-H)

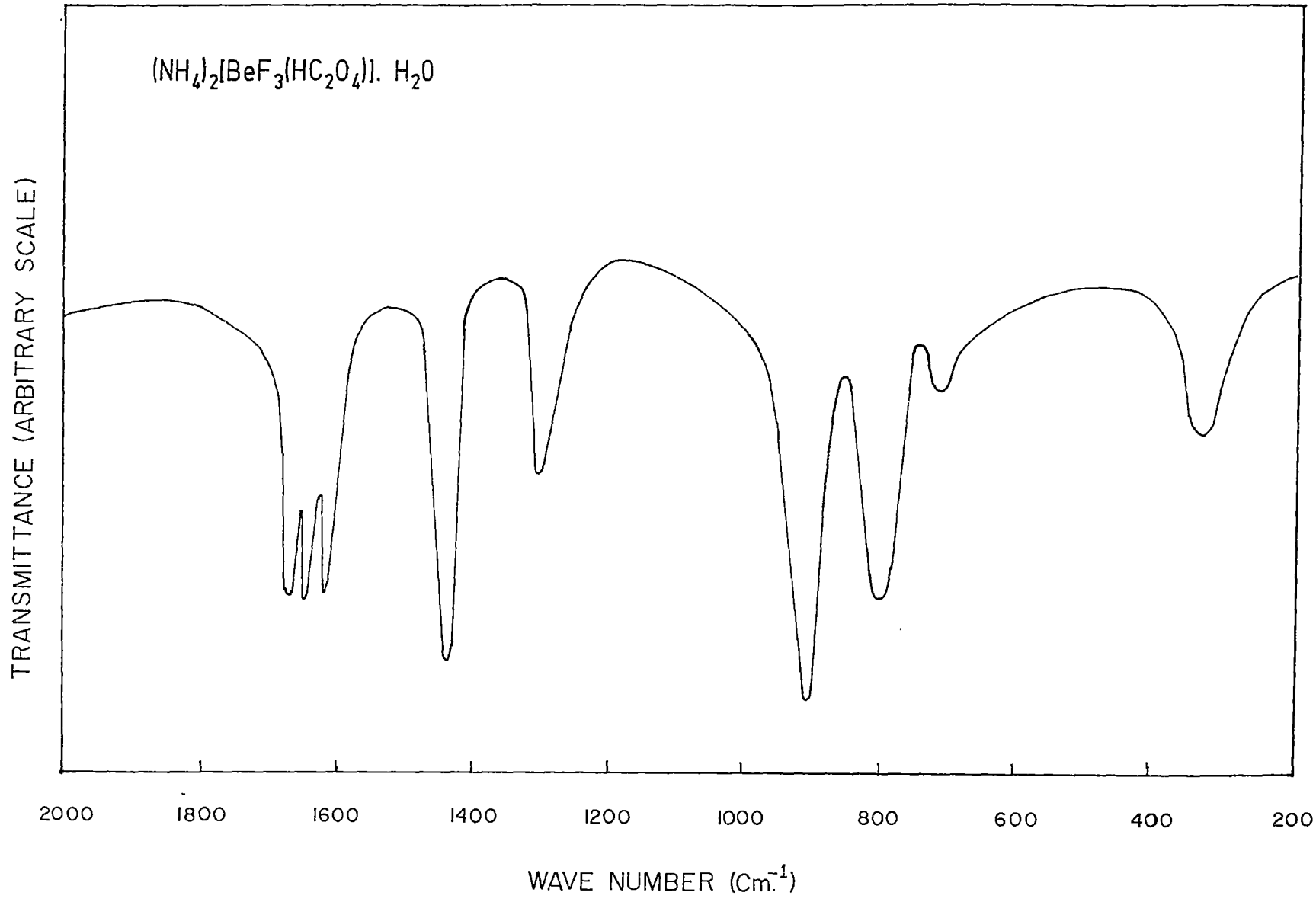

Fig. 3·1: IR SPECTRUM

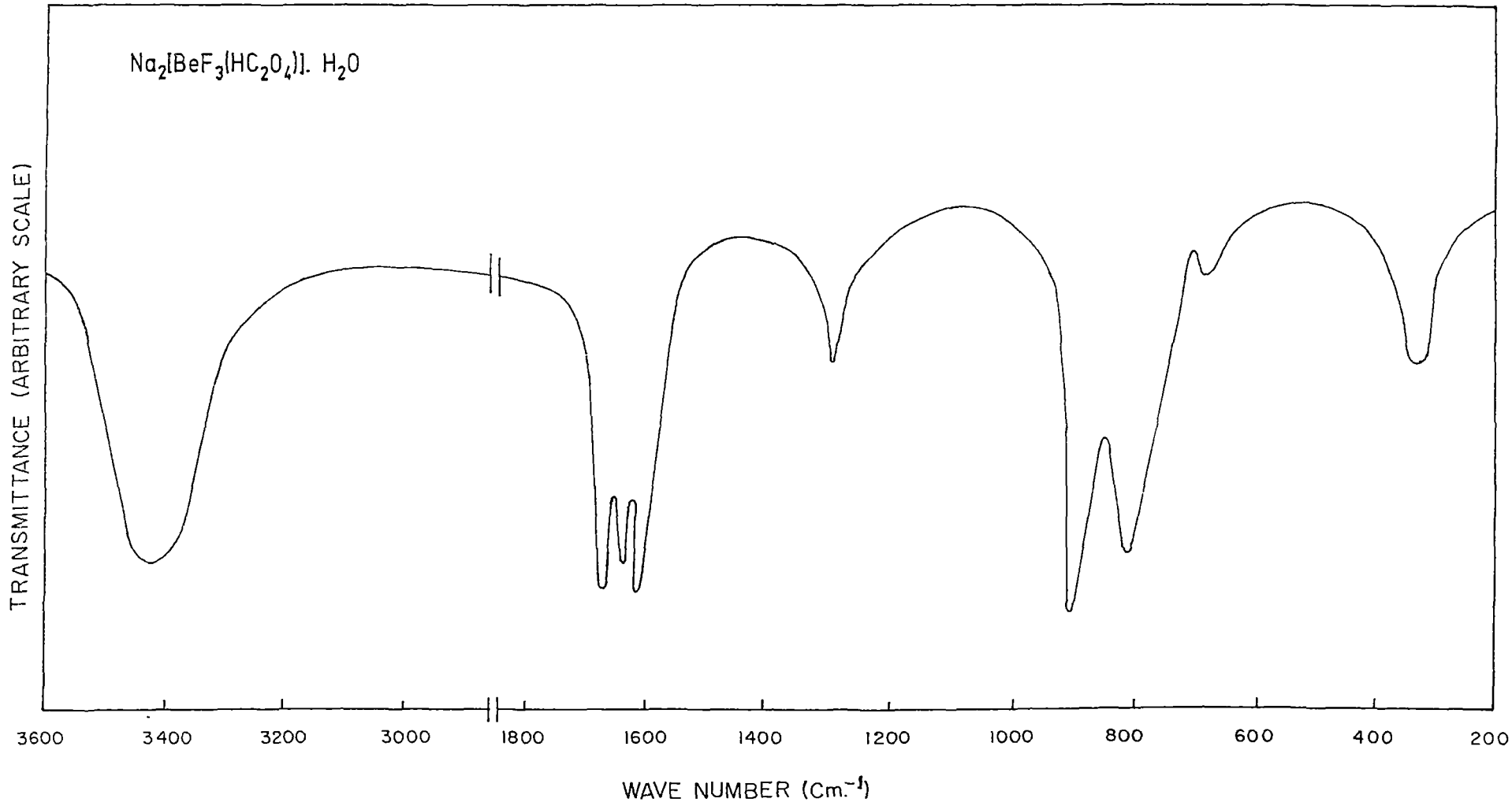

Fig. 3·2: IR SPECTRUM

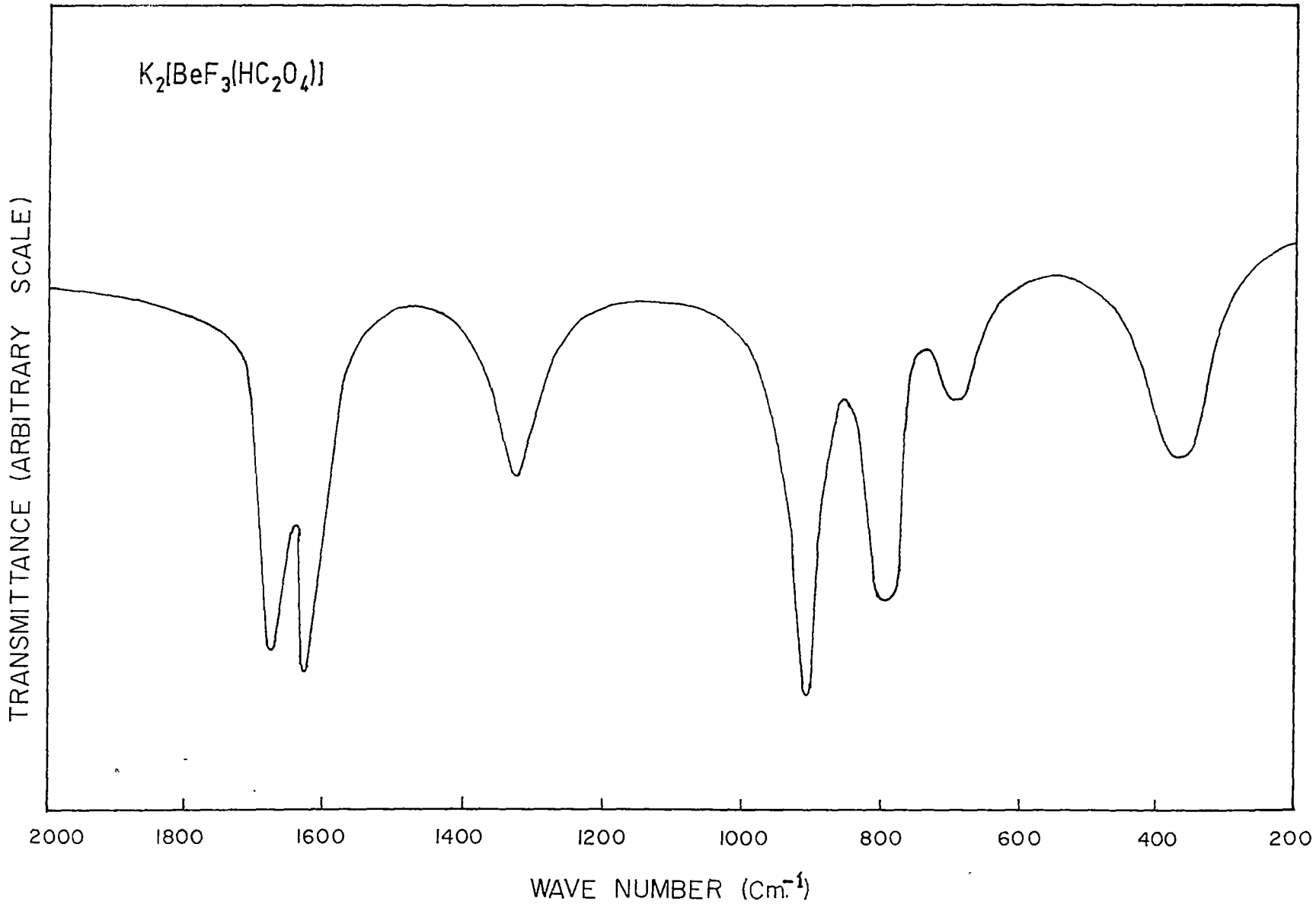

Fig. 3·3 : IR SPECTRUM

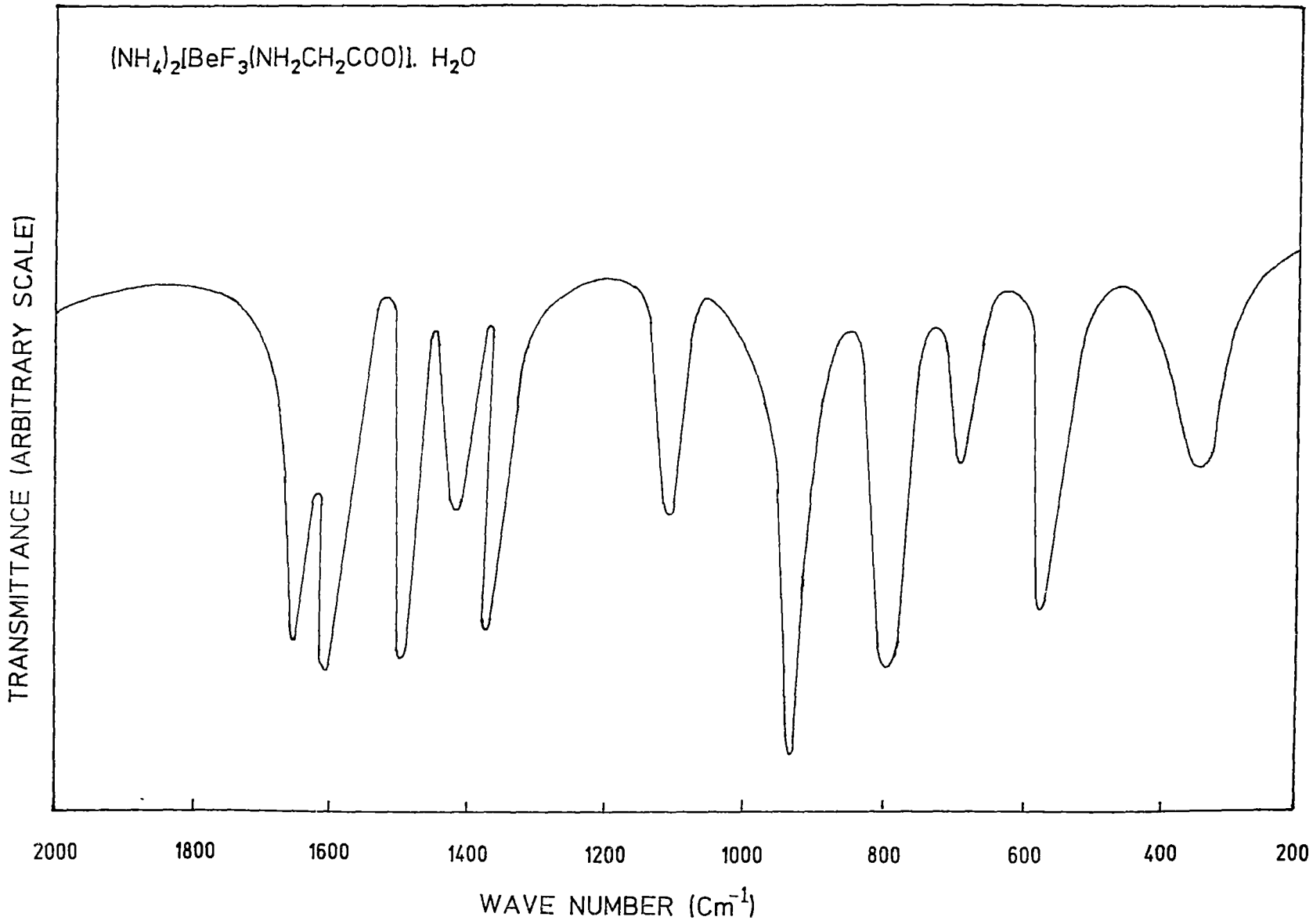

Fig. 3.4 : IR SPECTRUM

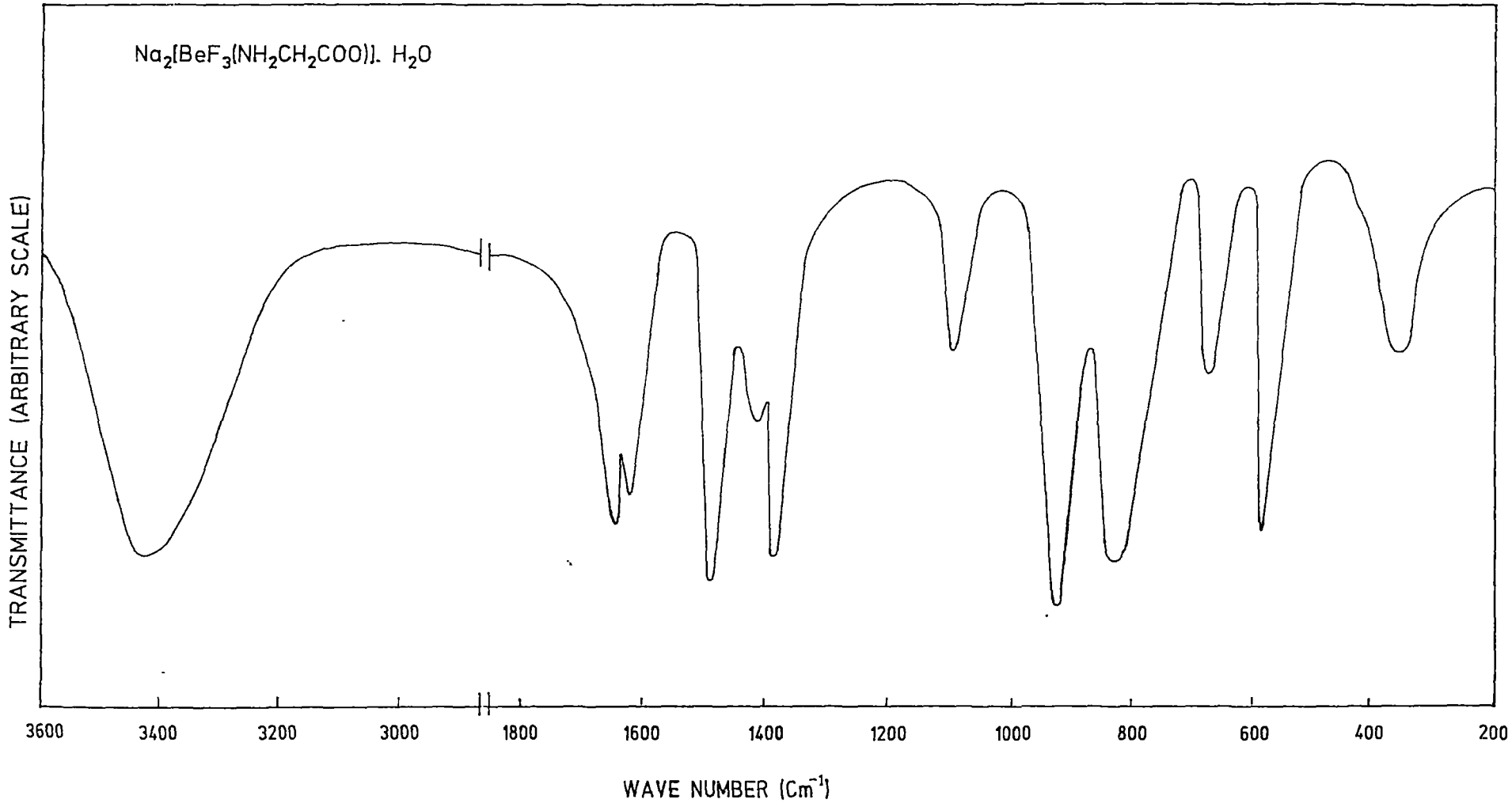

Fig. 3.5 : IR SPECTRUM

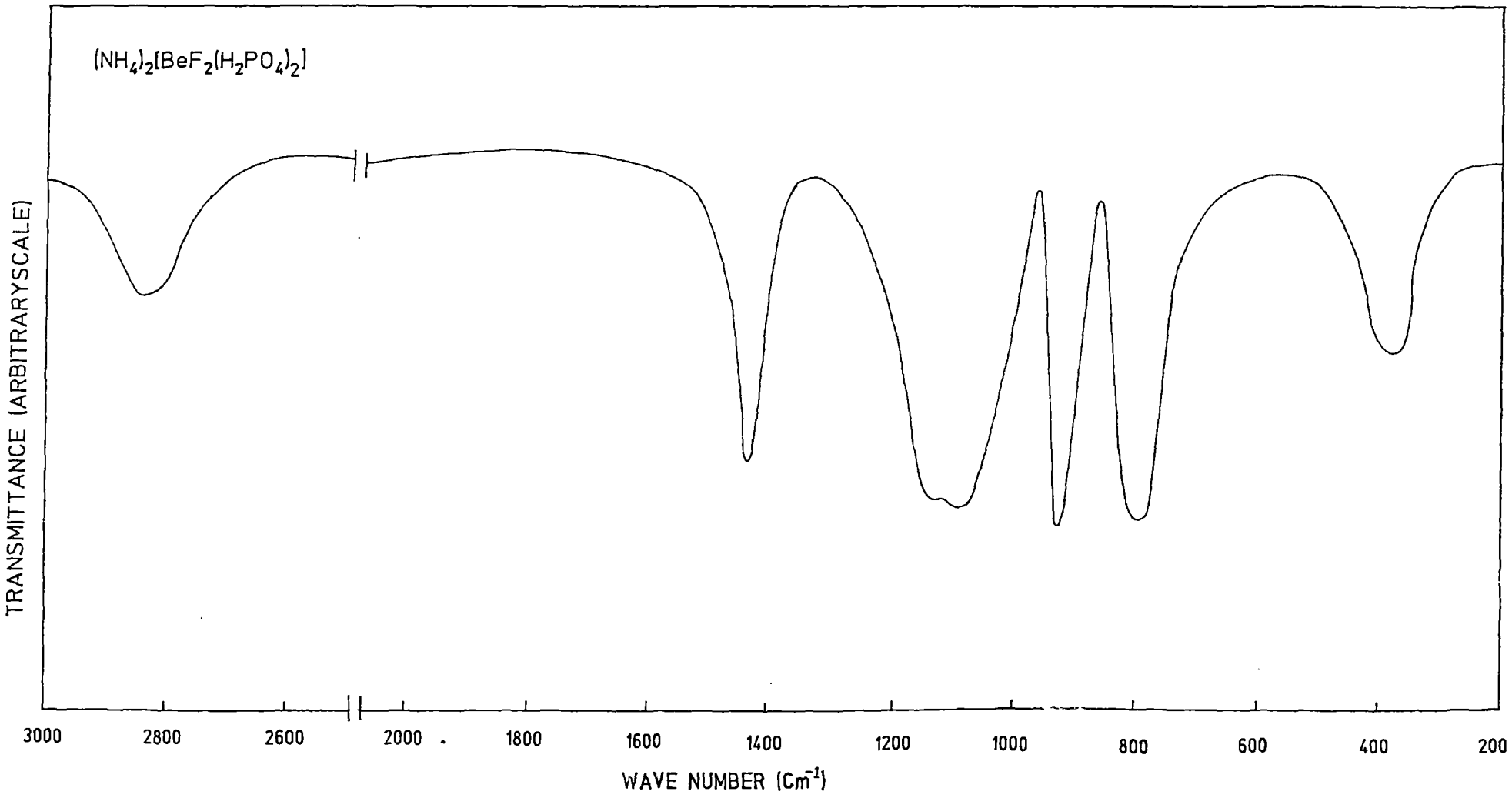

Fig. 3.6 : IR SPECTRUM

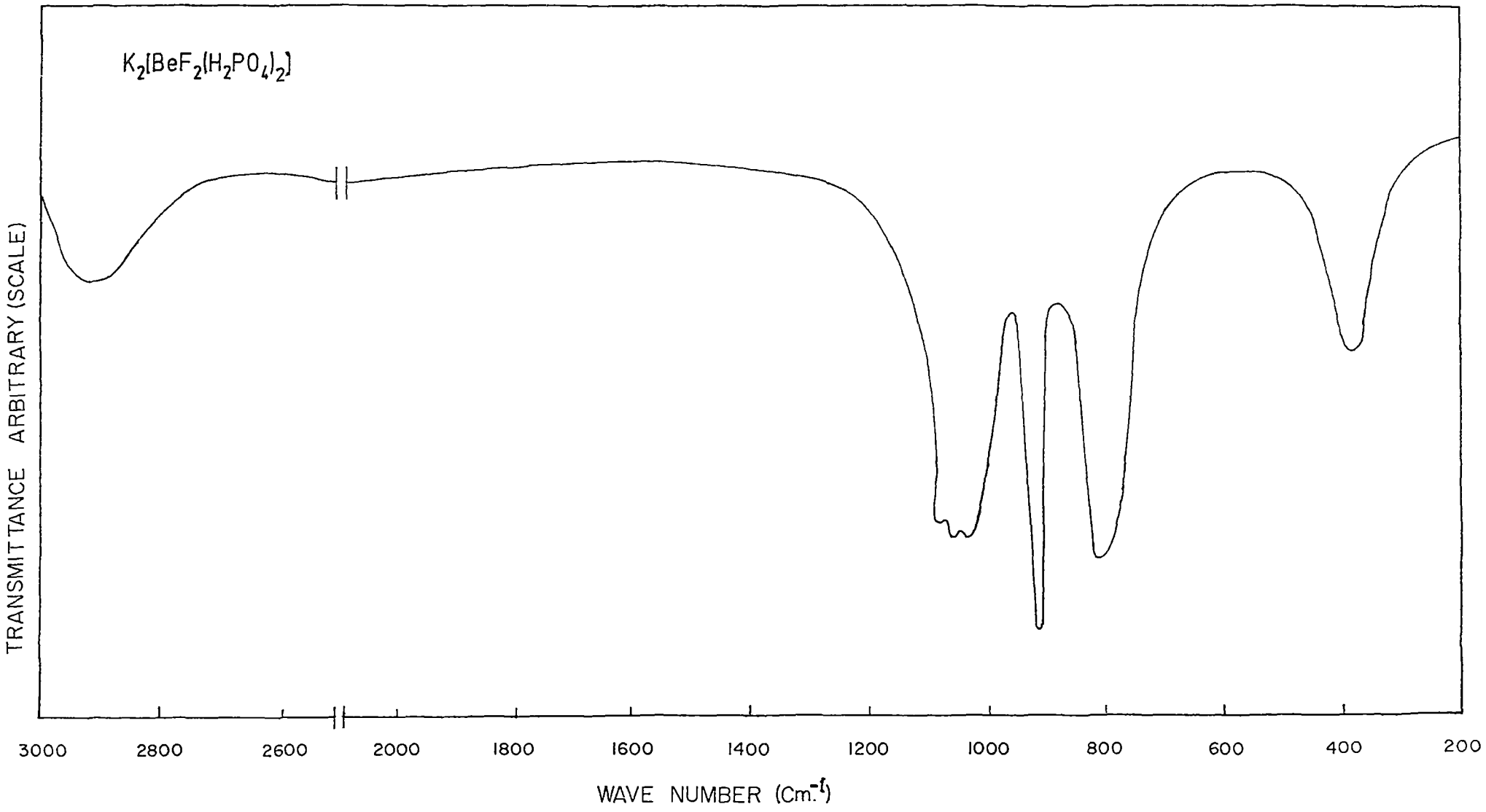

Fig. 3·7: IR SPECTRUM

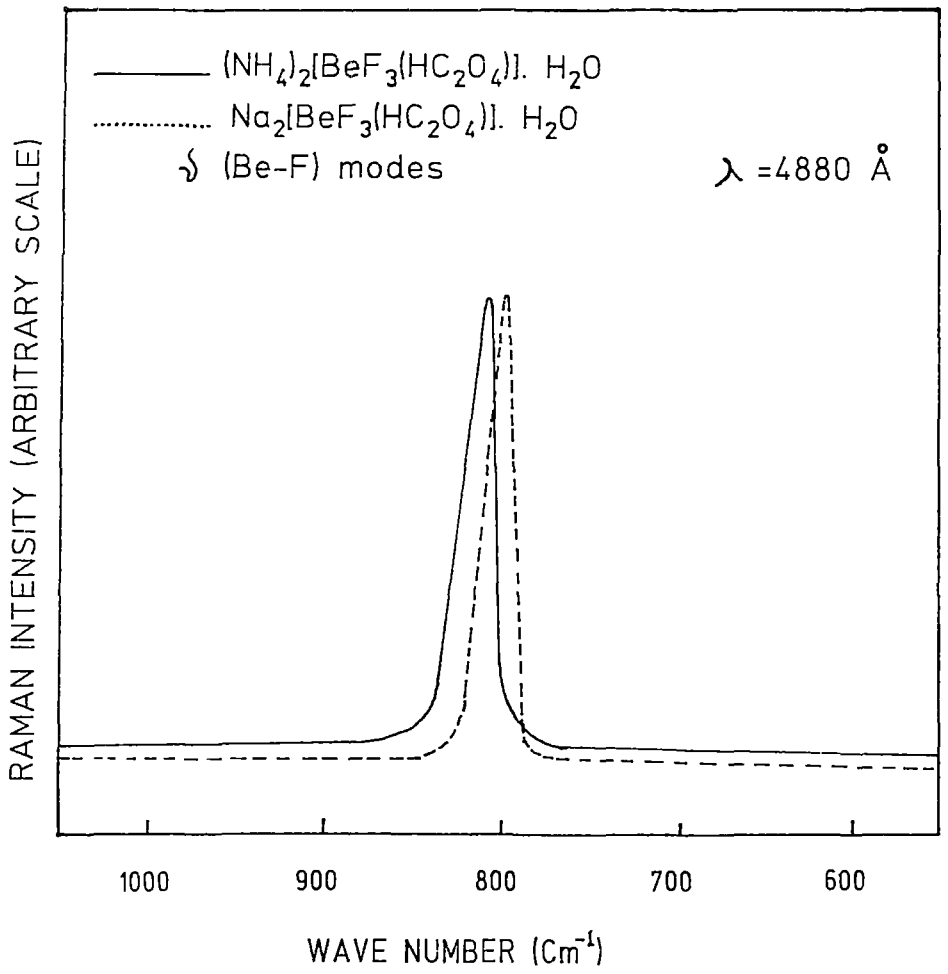

Fig. 3.8 : LASER RAMAN SPECTRA

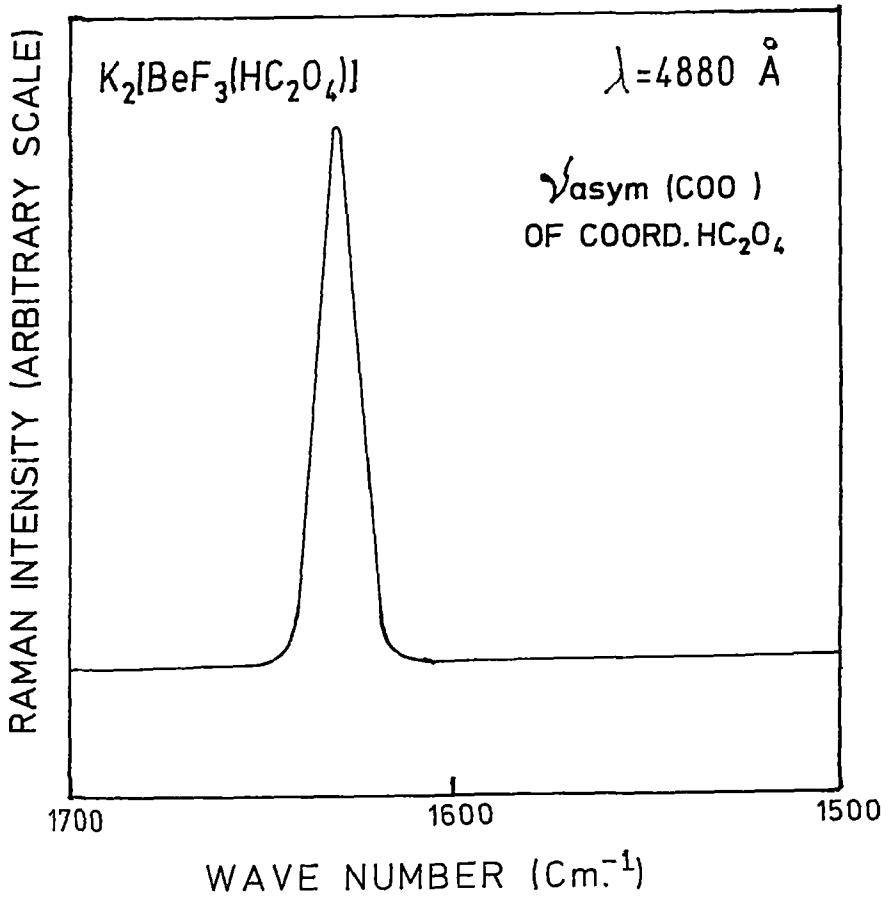

Fig. 3.9: LASER RAMAN SPECTRUM

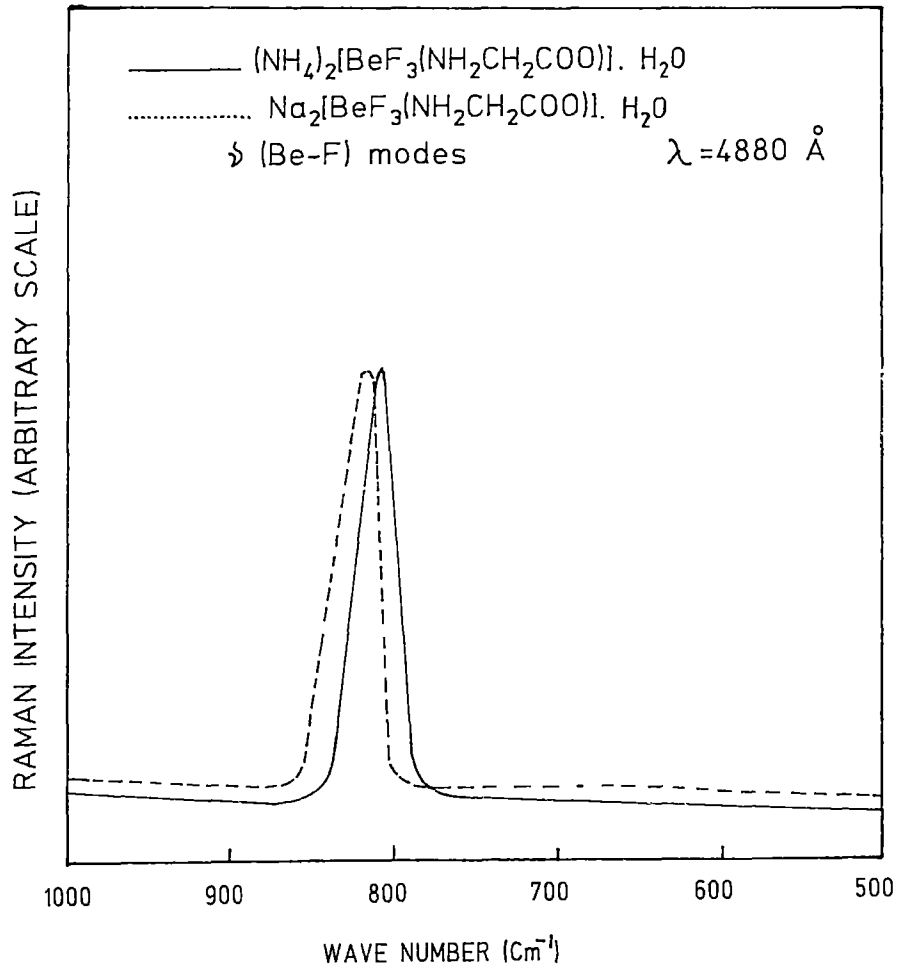

Fig. 3.10 : LASER RAMAN SPECTRUM

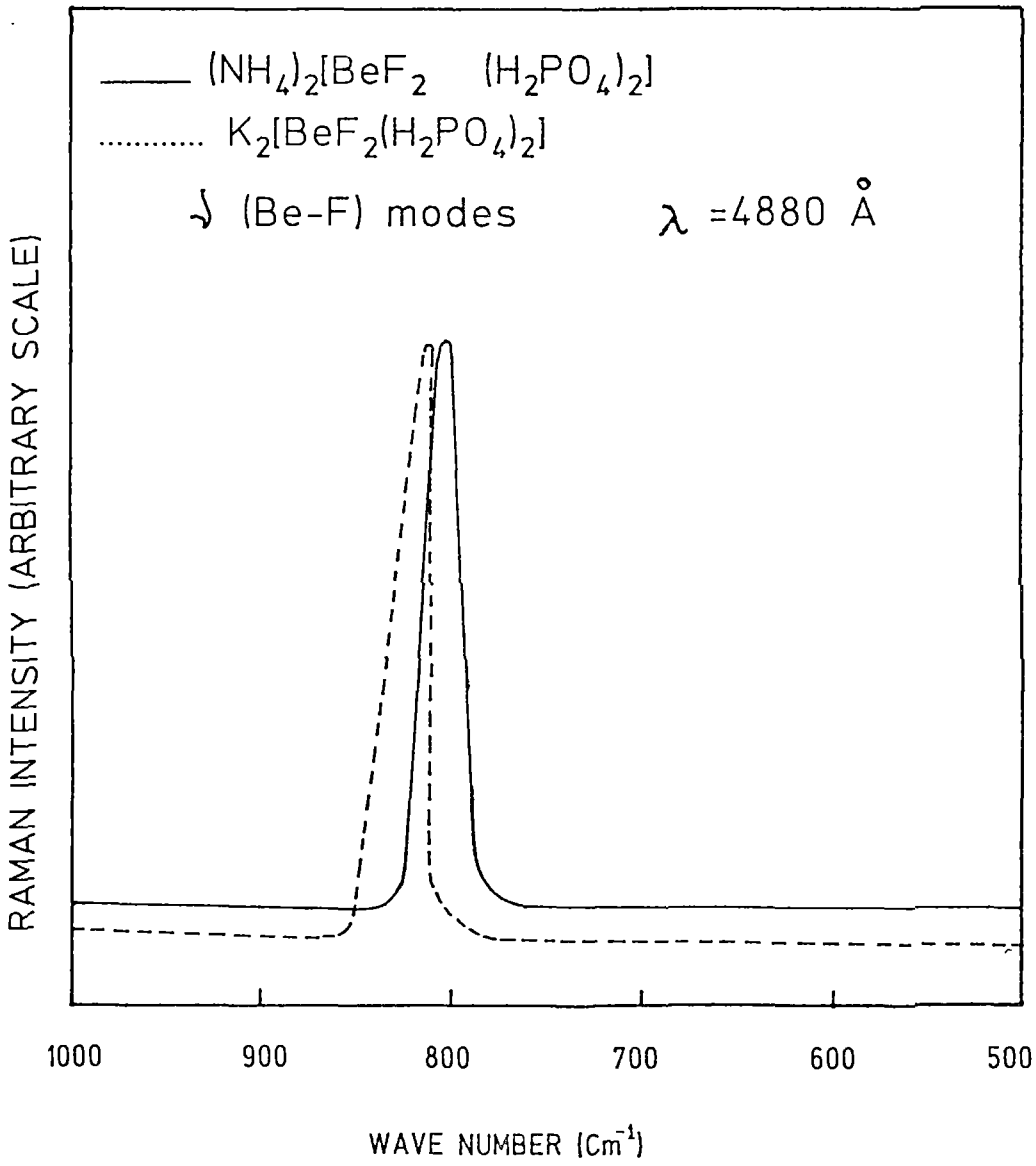

Fig. 3.11 : LASER RAMAN SPECTRA

An acidic condition (pH 2), seems to us, favoured $HC_2O_4^-$ formation which then coordinated with the metal centre to produce trifluoro(acidoxalato)beryllate, as obtained. Significant is the rarity, though not unprecedented[19,20], of acidoxalato as a ligand.

A glycinefluoroberyllate, $(NH_2CH_2COOH)_3.H_2BeF_4$ was reported quite sometime ago[21]. The compound is a glycine adduct of H_2BeF_4 and is very interesting because of its ferro-electric properties. We were interested in developing glycine coordinated fluoroberyllates. This has now been achieved through a direct interaction of $Be(OH)_2$ with alkalifluoride and glyH. It is believed that at pH 2-2.5, a coordinatively unsaturated fluoroberyllate was formed which then accommodated glycinate in its coordination sphere to provide $A_2[BeF_3(NH_2CH_2COO)].H_2O$ (A = NH_4 or Na). Incidentally, the experimental condition was favourable to the formation of glycinate ion enabling it to coordinate as an anionic ligand. The sequence of addition of the ligand, i.e., AF followed by glycine, is important since a reverse order did not yield the desired compound.

Phosphoric acid dissociates to generate $H_2PO_4^-$ at pH below 4[22]. Based upon this knowledge, a strategy was worked out and the reaction conducted at pH 2 (vide Experimental) to obtain $A_2[BeF_2(H_2PO_4)_2]$, (A = NH_4, or K). In this way, an access to a number of novel mixed fluoroberyllate complexes could be made to provide materials for further research on their physical properties. The methods are direct and do not require an extra preparation of BeF_2, thus offering many advantages.

Characterisation and assessment of structure

The white microcrystalline compounds are stable for a prolonged period. While the compounds $A_2[BeF_3(HC_2O_4)].H_2O$ and $A_2[BeF_2(H_2PO_4)_2]$ are insoluble in water,the corresponding fluoro-glycinato beryllate, $A_2[BeF_3(NH_2CH_2COO)].H_2O$ are highly soluble and stable in aqueous medium. The stability is attested by molar conductance lying between 232 and 238 $\Omega^{-1}cm^2mol^{-1}$. The values are also in agreement with 2:1 electrolytic nature of each of them. The IR spectroscopic signatures (Table 3.2) of the compounds provide clear evidence for the occurrence of coordinated fluoride[1]. Two absorption bands at *ca.* 800 and at *ca.* 380 cm^{-1} have been assigned to the ν(Be-F) and δ(F-Be-F) modes of coordinated fluoride. Laser Raman signals at *ca.*800 and *ca.* 385 cm^{-1} complement the assignments. In addition, consequent upon the presence of O-donor ligands in all the three types of complexes, the ν(Be-O) mode has been observed consistently at *ca.* 920 cm^{-1}. Pertinent is to mention that similar observations were made in the spectra of $BeCl_2$ complexes containing O-donor ligands[1,23]. A comparison of the results with that of chloro compounds of the metal clearly indicates that the change of halides does not have a significant effect on the Be-O band positions. Besides the common features discussed above, each type of the complexes displays a pattern typical of itself. The destinctive feature of the IR spectra of $A_2[BeF_3(HC_2O_4)].H_2O$ (Table 3.2) is the presence of a strong absorption band at *ca.* 1630 cm^{-1} attributable to $HC_2O_4^-$ ligand though such examples are far less encountered[20]. The $K_2[BeF_3(HC_2O_4)]$ complex was chosen as a representative

example, for it did not contain H_2O. Both IR and LR spectra of this compound clearly manifested intense signals at 1630 cm^{-1}, supporting this argument. This band was also observed in the IR spectra of the other two salts of the complex causing it to be a representative feature of the complexes under discussion. In addition, the IR frequencies at *ca.* 1670 [ν_{asym} (COO^-)], and *ca.* 1340 [ν_{sym}(COO^-)] were observed due to the coordination of $HC_2O_4^-$ through its carboxylate group as expected[24].

Glycine coordinates to the metal centre in different ways and these coordination modes can be easily ascertained from IR spectroscopic studies[25]. In the present case the distinctive feature in respect of coordinated glycine is the consistent appearance of a band at *ca.* 1610 cm^{-1} much separated from the δ(H-O-H) mode (1645 cm^{-1}) of lattice water. This observation as well as the absence of any absorption around 1700 cm^{-1} cause us to state that the coligand occurs in its ionic form and attaches itself to the beryllium centre through its carboxylic oxygen. The band at 1615 cm^{-1} has been assigned to ν(COO^-) stretching mode[25] of coordinated glycinate.

The IR spectral pattern of metal phosphato complexes are rather complicated owing to the peak broadening and poor resolution. The spectra of $A_2[BeF_2(H_2PO_4)_2]$ complexes exhibited a medium intensity band at *ca.* 1108 and a broad weak absorption at *ca.* 2850 cm^{-1} attributable to the presence of phosphates. These bands are rather typical of coordinated acid phosphato ligand[26] and are in conformity with the formulation. A striking feature of IR spectra of all the compounds described herein is the broadening

of both ν (Be-F) and δ(F-Be-F) modes. This is indicative of definite possibility of intramolecular hydrogen bonding in each of the compounds.

Conclusions.

Hitherto unknown mixed ligand fluoro complexes of beryllium have been successfully synthesised at pH 2 of the reaction medium. Acidic nature of the reaction medium favoured coordination of both F^- and the coligands chosen. Unusual coordination of oxalate with beryllium centre can be attributed to the prevailing high acidity of the reaction medium, where $H_2C_2O_4$ may exist as $HC_2O_4^-$.

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CHAPTER - IV

COMPLEX PEROXOURANATES. SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERISATION OF HETEROLIGAND MONOPEROXO COMPLEXES OF UO_2^{2+} CONTAINING PHOSPHATE AND FLUORIDE AS COLIGANDS AND STUDY OF REACTION OF $(NH_4)_2[UO_2(O_2)F_2\ (H_2O)_2]$ WITH SO_2. x H_2O

Owing to an intrinsic interest[1] in and practical use of peroxometallates, there has been a spurt of research in their chemistry. The peroxochemistry of uranium(VI) is particularly very complex[2,3] and until a few years back, the only known best characterised monoperoxo complex of uranium was $UO_2(O_2).nH_2O$ (n = 2 or 4). Relatively recent reports have described a few well characterised heteroligand(monoperoxo)uranates(VI)[4-6]. Incidentally, many of them have been synthesised in our laboratory. Nevertheless, a few reports on heteroligand monoperoxouranates(VI) of poorly defined compositions are known for quite sometime[3]. It should be emphasised that the

monoperoxouranates(VI), $UO_2(O_2).nH_2O$, was shown to be a very good reagent for the oxidation of olefins to epoxides as well as for the production of oxidative cleavage products[7]. Our group[8-10] and others[11] have shown recently the potential oxidising capacity of certain peroxo complexes of uranium and transition metals for organic and inorganic substrates. But much seem yet to be accomplished. Therefore, it was incumbent on us to undertake studies in the fascinating field of uranium peroxo chemistry. In doing so, the main thrust of our present work was directed towards the synthesis and physicochemical characterisation of newer heteroligand monoperoxo uranates. While selecting the coligands, our considerations were to choose such ligands that could also coordinate with UO_2^{2+} under conditions required for the O_2^{2-} coordination.

In cognizance of the progress made by the predecessors in the group and considering the necessity for attempting to a comprehensive account of the chosen aspect of uranium chemistry, phosphate and F^- have been incorporated in the present investigation as coligands. Both peroxide (O_2^{2-}) and phosphate are known to react with hexavalent uranium entailing a great deal of intricacies[2,12]. It appears from our experience in the area of complex peroxouranates(VI) that an appropriate methodology for accessing complex peroxouranates of a well defined composition requires monitoring of a number of parameters. Important among these are, for instance, molar stoichiometry of different reagents and sequential order of their additions, and the pH value of the reaction medium. Based upon these considerations, a few peroxouranium(VI) complexes were synthesised with F^-, $C_2O_4^{2-}$

SO_4^{2-}, CO_3^{2-}, amines and aminocarboxylic acids being the heteroligands[4-6,8] earlier in this laboratory. While working on this aspect of peroxo-uranium chemistry, our attention was drawn to an early report on the interference of phosphate in the spectrophotometric determination of the metal using peroxide and carbonate[13]. An important implication of this is the formation of a peroxophosphato complex of UO_2^{2+} in solution. This prompted us to devise an appropriate methodology for an access to heretofore unreported peroxo(phosphato)dioxouranates(VI) and characterise them by a combination of chemical and physico-chemical studies. Incidentally, the only known example of a peroxo(phosphato) complex of the metal is $Na_4[U_2O_4(O_2)_2(P_2O_7)].18H_2O$[13], albeit some binary phosphato-uranyl complexes were reported[14]. In addition, as a sequel to our interest in the peroxo chemistry, our attention was also drawn towards fluoroperoxo complexes of uranium(VI).

So far as F^- as the heteroligand is concerned, it might be worth mentioning that there is an intrinsic interest in the chemistry of uranium compounds that contained fluoride as a ligand. The importance of uranium(VI) fluorochemistry is well acknowledged[15-17]. Interestingly,mixed fluoro-peroxo uranates(VI) appear to be known since long with $Na[UO_2(O_2)F(H_2O)].4H_2O$ being the sole example until recently[13]. In 1985 the first full series[6] of a fluoro-peroxo complexes of UO_2^{2+} viz., $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb) were reported from this laboratory. A closer look at the existing reports in conjunction with the experience of our research group,

it appeared that complex anion of the type, $[UO_2(O_2)F_2(H_2O)_2]^{2-}$ should have a very fair possibility of being existed. This notion was reinforced by the pervasiveness of hexa-coordination of uranyl(UO_2^{2+}) in its complex chemistry. Therefore, it was percieved that it should be possible to synthesise $[UO_2(O_2)F_2(H_2O)_2]^{2-}$ under an appropriate reaction condition.

In addition, the reported routes[6] to the synthesis are cumbersome and tedious. The peroxofluoro complexes[6] reported earlier from our laboratory were synthesised from the reaction of a yellow product obtained by the addition of an alkali to a salt of uranyl with AF (A = NH_4, Rb, Cs or K) and H_2O_2 in the mole ratio of $UO_2(NO_3)_2.6H_2O$:AF:H_2O_2 of 1:4:110 at pH 6.5-7 in the presence of a small amount of HF. The complex, $Na[UO_2(O_2)F(H_2O)].4H_2O$ was synthesised by the action of H_2O_2 on sodium uranylfluoride, $Na[UO_2F_3].nH_2O$. The strategy of the present methodology involve reaction of $UO_2(NO_3)_2.6H_2O$, HF_2^- and H_2O_2 in the ratio, 1:5:110 at pH 7.

Based upon the above considerations, complexes of the type $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$ and $A_2[UO_2(O_2)F_2(H_2O)_2].2H_2O$ (A = Na or K) have been now synthesised. A detailed results of this investigation are presented in this Chapter. Also included herein are the results of the reactivity of $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$ with $SO_2.xH_2O$.

EXPERIMENTAL

Chemicals used were of reagent grade quality. A 5 or 6% solution of commercial grade SO_2 was used for the reactivity studies.

1.Synthesis of ammonium and potassium dioxoperoxo(phosphato)-diaquouranate(VI)tetrahydrate, $A_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$ (A = NH_4 or K) and sodium dioxoperoxo(phosphato)diaquouranate(VI) dihydrate, $Na_3[UO_2(O_2)(PO_4)(H_2O)_2].2H_2O$

In a typical procedure, 1.0 g of $UO_2(NO_3)_2.6H_2O$ (1.99 mmol) was dissolved in *ca.* 50 cm^3 of distilled water in a beaker. To it was added 3 mmol of A_2HPO_4 (A = NH_4, Na or K) with continuous stirring for 5-10 min. To this solution *ca.* 25 cm^3 of 30% H_2O_2 (220.5 mmol) was added. The content was stirred for an additional period of *ca.* 10 min. The pH of the reaction solution was then slowly raised to 7 by adding aqueous ammonia (sp.gr.0.9) or 5% NaOH or KOH solution. The reaction solution was stirred for another 2 or 3 min whereupon a yellow microcrystalline product was obtained. The product was filtered and then washed 3 or 4 times with water and finally with acetone. The compounds were finally dried *in vacuo.* over conc. H_2SO_4. The yields of $(NH_4)_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$, $Na_3[UO_2(O_2)(PO_4)(H_2O)_2].2H_2O$ and $K_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$ were 0.9g (81%), 0.8g (74.7%) and 0.9g (72%), respectively.

2.Synthesis of alkali metal dioxoperoxo(difluoro)-diaquouranates(VI)dihydrate, $A_2[UO_2(O_2)F_2(H_2O)_2].2H_2O$ (A = Na or K) and ammonium dioxoperoxo(difluoro)diaquouranate(VI), $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$

A 1.0 g (1.99 mmol) of $UO_2(NO_3)_2.6H_2O$ was taken in a 250 cm^3 polyethylene beaker and *ca.* 30 cm^3 of distilled water was added to dissolve it. To it was added 10 mmol of AHF_2 (A = NH_4, Na or K) and stirred well. To this was added *ca.* 5 cm^3 (44 mmol) of H_2O_2 and the mixture was stirred well for *ca.* 2 min. A clear solution was obtained. The pH of the solution was slowly raised to 7 with dropwise addition of dilute ammonia (sp.gr. 0.9) or 10% alkali solution (NaOH or KOH) followed by stirring. A yellow precipitate started appearing at this stage. Stirring was continued for another 10 min in order to achieve complete precipitation. The product was filtered and washed thrice with water and then twice with acetone. Finally, the compound was dried *in vacuo* over conc. H_2SO_4. The yields of $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$, $Na_2[UO_2(O_2)F_2(H_2O)_2].2H_2O$ and $K_2[UO_2(O_2)F_2(H_2O)_2].2H_2O$ were 0.7 g (85.3%), 0.70 g (76.7%) and 0.65g (66,6%), respectively.

Reactivity of $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$ with $SO_2.xH_2O$

An amount of 1.0 g of the compound was dissolved in 15-20 cm^3 of the SO_2 solution (5-6% solution) in a 100 cm^3 beaker and the solution was heated on a steam-bath until the volume of the solution was reduced to 5 cm^3. The solution was cooled and 20 to 30 cm^3 of acetone was added and it was then stirred continuously.

An oily mass separated out at the bottom of the beaker. The acetone layer was decanted out and fresh acetone (20-30 cm^3) was again added and stirring continued until the oily mass solidified. The solid was separated and dried *in vacuo* over conc. H_2SO_4. The yield of the compound, $(NH_4)_2[UO_2(SO_4)F_2].H_2O$, was 0.7 g (63%).

Table 4.1: Analytical results for $A_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$ (A = NH_4 or K), $Na_3[UO_2(O_2)(PO_4)(H_2O)_2].2H_2O$ and $(UO_2)_2P_2O_7$

Compounds	Found% (Cacld.%)			
	A or N	U	O_2^{2-}	PO_4^{3-}
$(NH_4)_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$	7.52 (7.43)	42.56 (41.79)	5.72 (5.81)	16.98 (17.12)
$Na_3[UO_2(O_2)(PO_4)(H_2O)_2].2H_2O$	12.82 (11.95)	44.24 (46.12)	5.94 (6.2)	17.65 (17.41)
$K_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$	18.84 (17.65)	38.24 (36.83)	5.14 (5.31)	15.26 (15.56)
$(UO_2)_2P_2O_7$	-	66.1 (66.76)	-	27.1 (26.63)

Table 4.2: Analytical results for $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$ and $A_2[UO_2(O_2)F_2(H_2O)_2].2H_2O$ (A = Na or K) and $(NH_4)_2[UO_2(SO_4)F_2].H_2O$

Compounds	Found% (Calcd.%)				
	A or N	U	O_2^{2-}	F^-	SO_4^{2-}
$(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$	6.85 (6.79)	57.53 (57.76)	8.1 (7.76)	9.75 (9.2)	-
$Na_2[UO_2(O_2)F_2(H_2O)_2].2H_2O$	10.75 (11.16)	51.95 (51.96)	7.32 (6.98)	7.85 (8.29)	-
$K_2[UO_2(O_2)F_2(H_2O)_2].2H_2O$	15.65 (15.91)	50.15 (48.57)	7.1 (6.53)	7.12 (7.75)	-
$(NH_4)_2[UO_2(SO_4)F_2].H_2O$	6.32 (6.11)	52.25 (51.96)	-	8.47 (8.29)	21.62 (20.96)

Table 4.3: Structurally significant infrared bands of $A_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$ (A = NH_4 or K), $Na_3[UO_2(O_2)(PO_4)(H_2O)_2].2H_2O$ and $(UO_2)_2P_2O_7$

Compounds	IR cm^{-1}	Assignments
$(NH_4)_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$	910 s	ν(O=U=O)
	880 s	ν(O-O) ν_1
	610 m	ν(U-O_2) ν_2
	630 w	ν(U-O_2) ν_3
	980 s,br 1010 s,br 1130 s,br	ν(PO_4) ν_3
	740 w	ρ_r(H_2O)
	3440 s	ν(O-H)
	1640 s	δ(H-O-H)
$Na_3[UO_2(O_2)(PO_4)(H_2O)_2].2H_2O$	905 s	ν(O=U=O)
	890 s	ν(O-O) ν_1
	615 m	ν(U-O_2) ν_2
	635 w	ν(U-O_2) ν_3
	970 s,br 1020 s,br 1145 s,br	ν(PO_4) ν_3
	738 w	ρ_r(H_2O)
	3438 s	ν(O-H)
	1642 s	δ(H-O-H)

Table 4.3 (contd.)

$K_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$	900 s	ν(O=U=O)
	889 s	ν(O-O) ν_1
	597 m	ν(U-O_2) ν_2
	634 w	ν(U-O_2) ν_3
	960 s,br	ν(PO_4) ν_3
	1007 s,br	
	1122 s,br	
	735 w	$\rho_r(H_2O)$
	3440 s	ν(O-H)
	1645 s	δ(H-O-H)
$(UO_2)_2P_2O_7$	910 s	ν(O=U=O)
	965 s,br	ν(P-O) modes
	1015 s,br	
	1135 s,br	

Table 4.4: Structurally significant infrared bands of $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$, $A_2[UO_2(O_2)F_2(H_2O)_2].2H_2O$ (A = Na or K) and $(NH_4)_2[UO_2(SO_4)F_2].H_2O$

Compounds	IR cm^{-1}	Assignments
$(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$	900 s	ν(O=U=O)
	860 s	ν(O-O) ν_1
	728 w	$\rho_r(H_2O)$
	355 s,br	ν(U-F-U)
	1400 s	ν(N-H) ν_4
$Na_2[UO_2(O_2)F_2(H_2O)_2].2H_2O$	905 s	ν(O=U=O)
	855 s	ν(O-O) ν_1
	740 w	$\rho_r(H_2O)$
	360 s,br	ν(U-F-U)
	3440 s	ν(O-H)
	1640 s	δ(H-O-H)
$K_2[UO_2(O_2)F_2(H_2O)_2].2H_2O$	910 s	ν(O=U=O)
	858 s	ν(O-O) ν_1
	738 w	$\rho_r(H_2O)$
	352 s,br	ν(U-F-U)
	3445 s	ν(O-H)
	1642 s	δ(H-O-H)

Table 4.4 (contd.)

$(NH_4)_2[UO_2(SO_4)F_2].H_2O$	920 s	ν(O=U=O)
	1195 s	ν_3
	1150 s	ν_3
	1050 s	ν_3
	672 s	ν_4
	620 s	ν_4
	559 s	ν_4
	440 m	ν_2
		ν(S-O)
	372 s,br	ν(F-U-F)
	3440 s	ν(O-H)
	1645 s	δ(H-O-H)

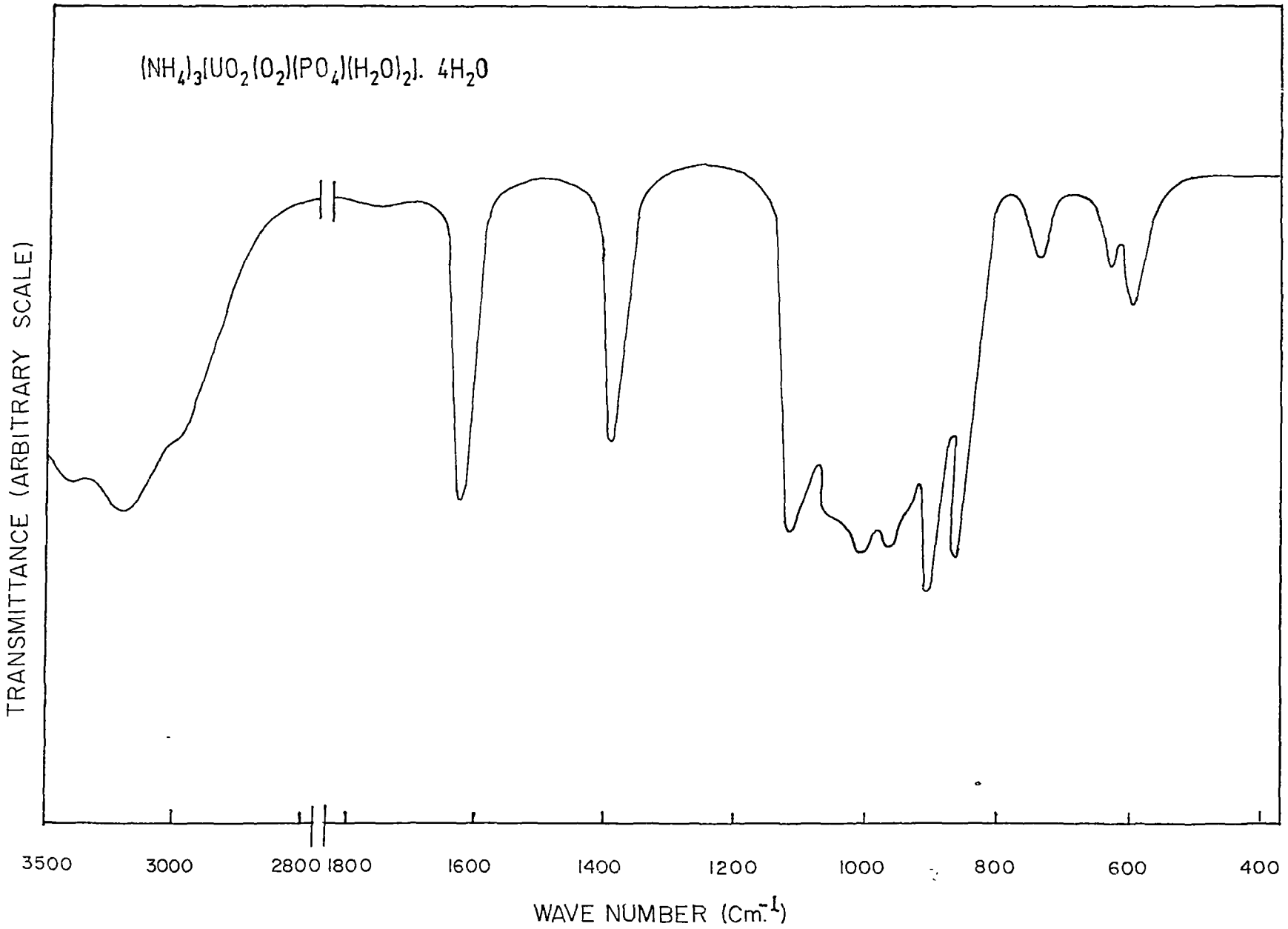


Fig. 4.1: IR SPECTRUM

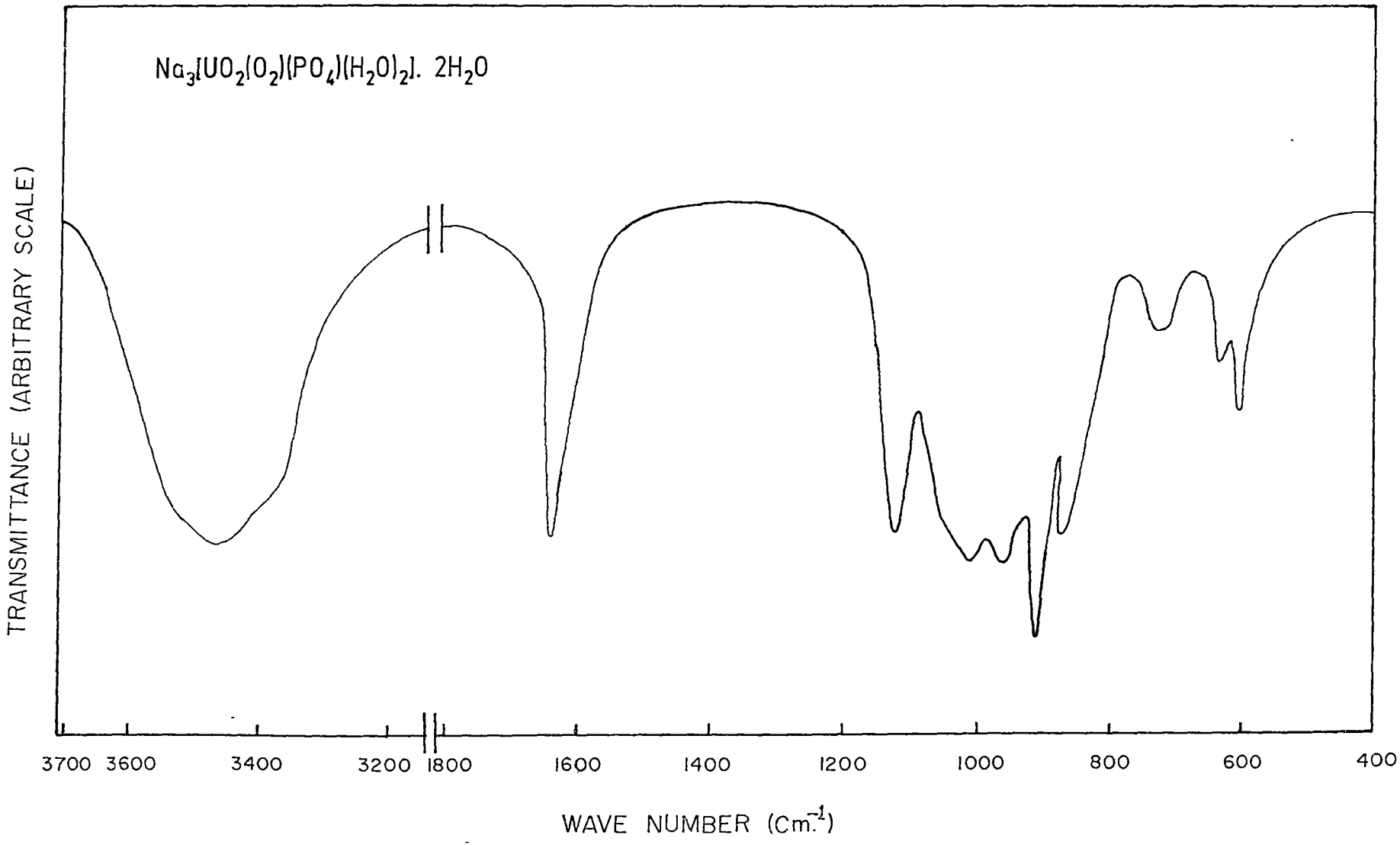


Fig. 4·2: IR SPECTRUM

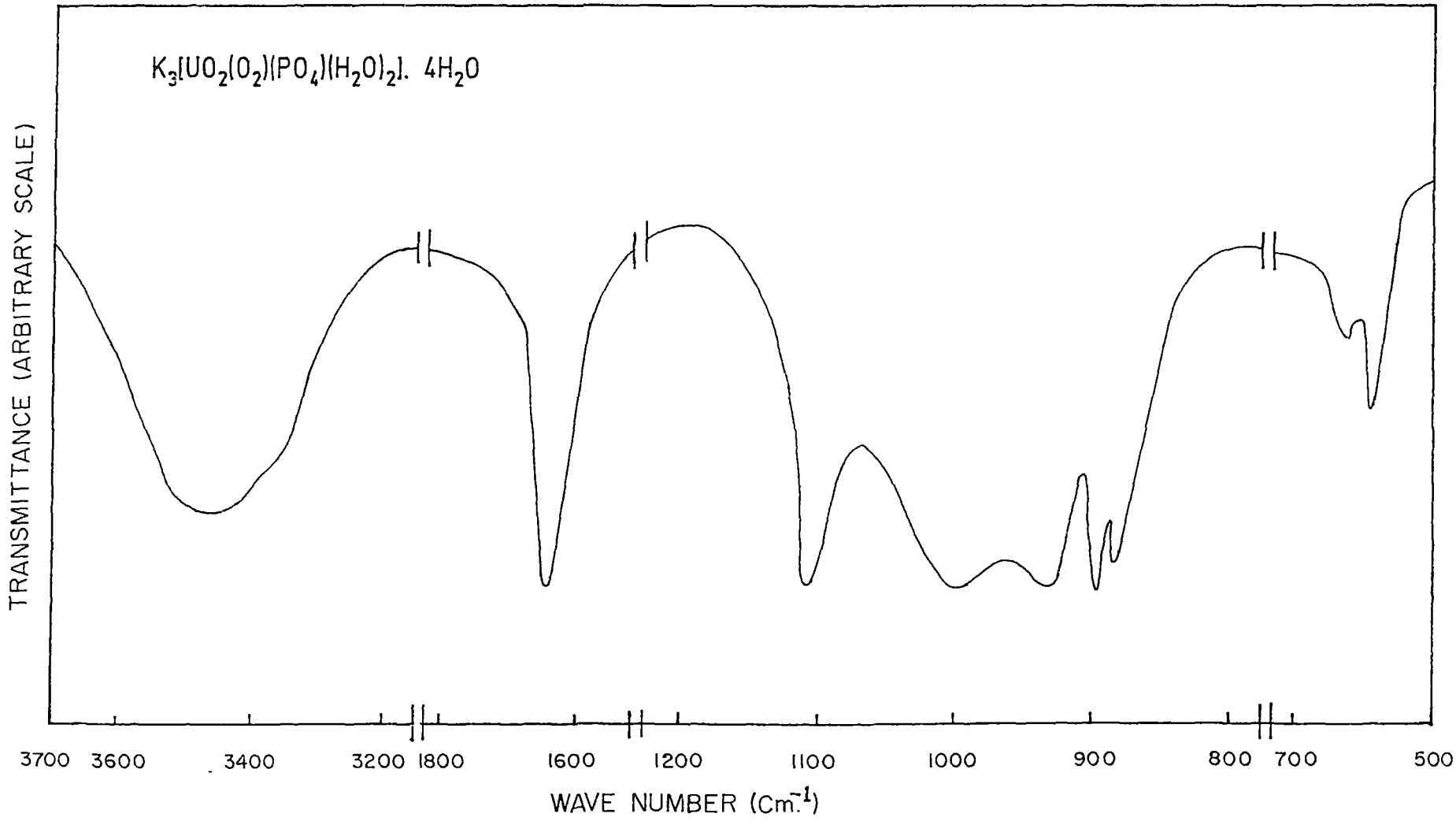


Fig. 4·3 : IR SPECTRUM

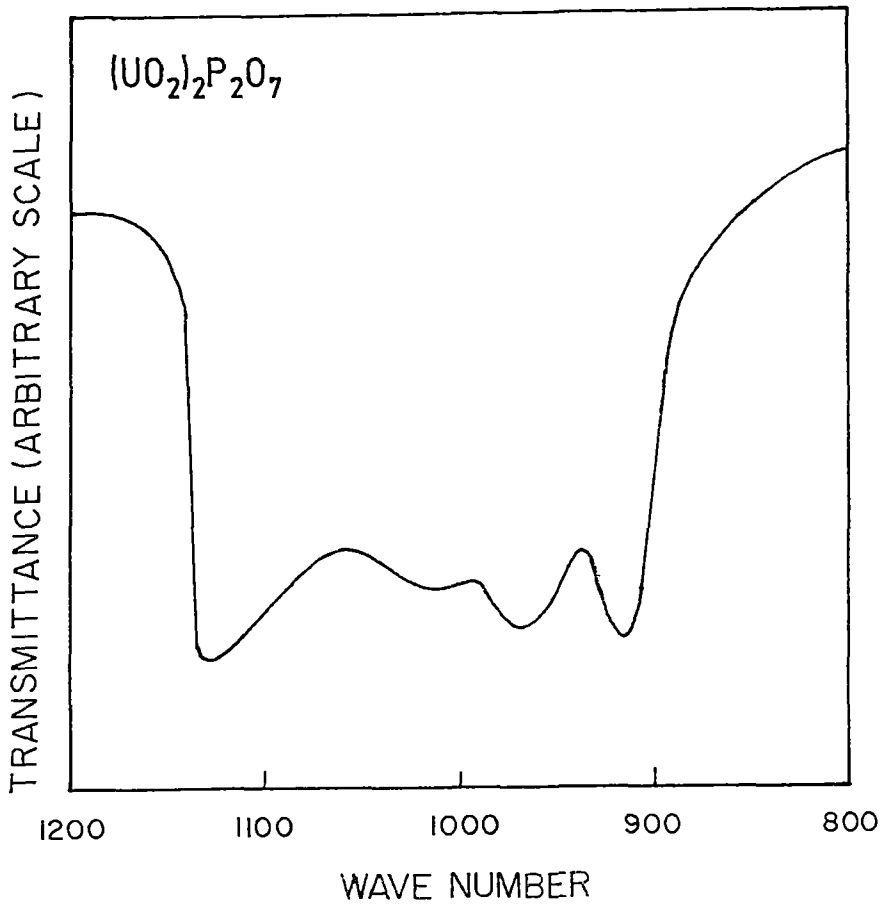


Fig. 4.4: IR SPECTRUM

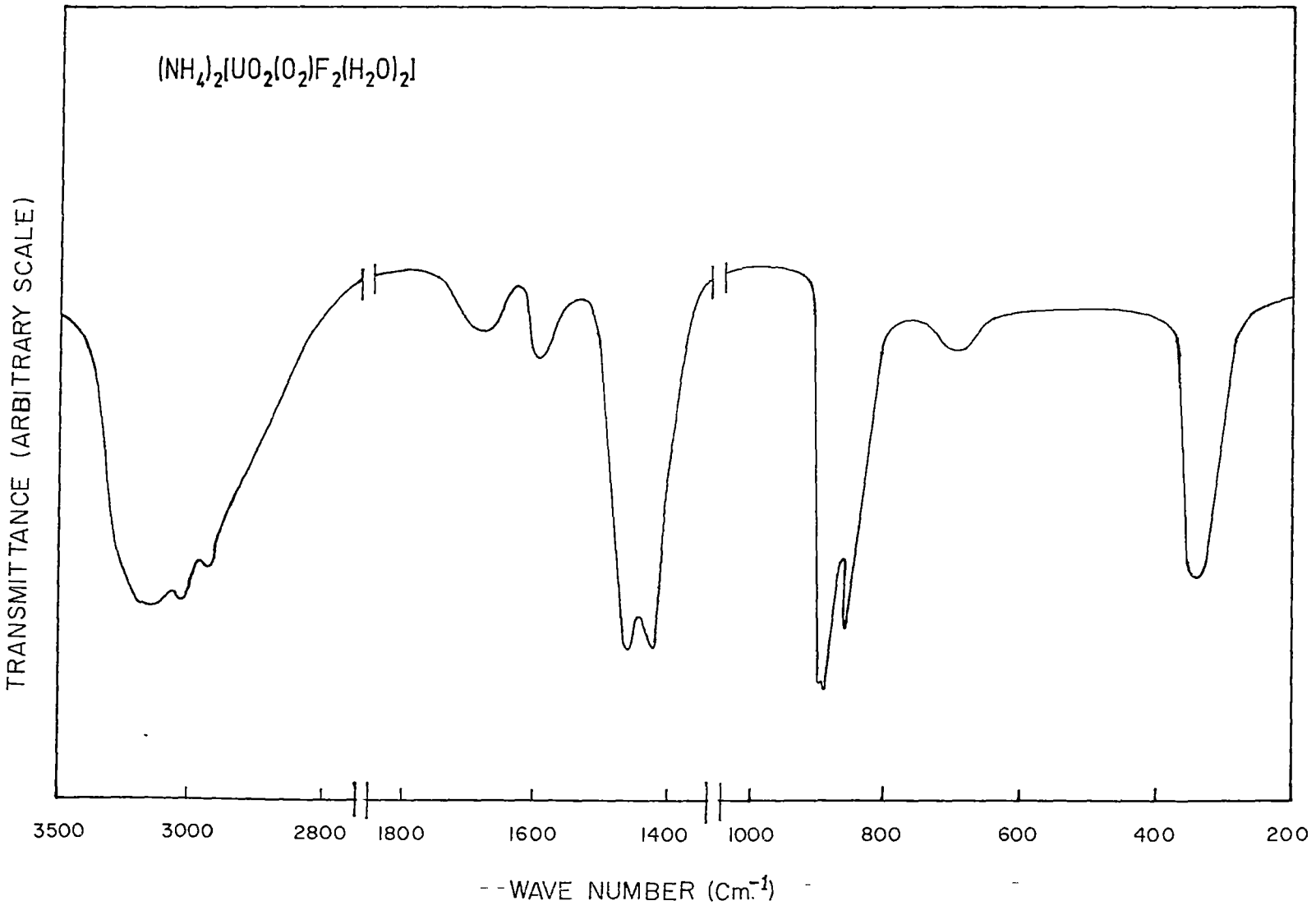


Fig. 4·5 : IR SPECTRUM

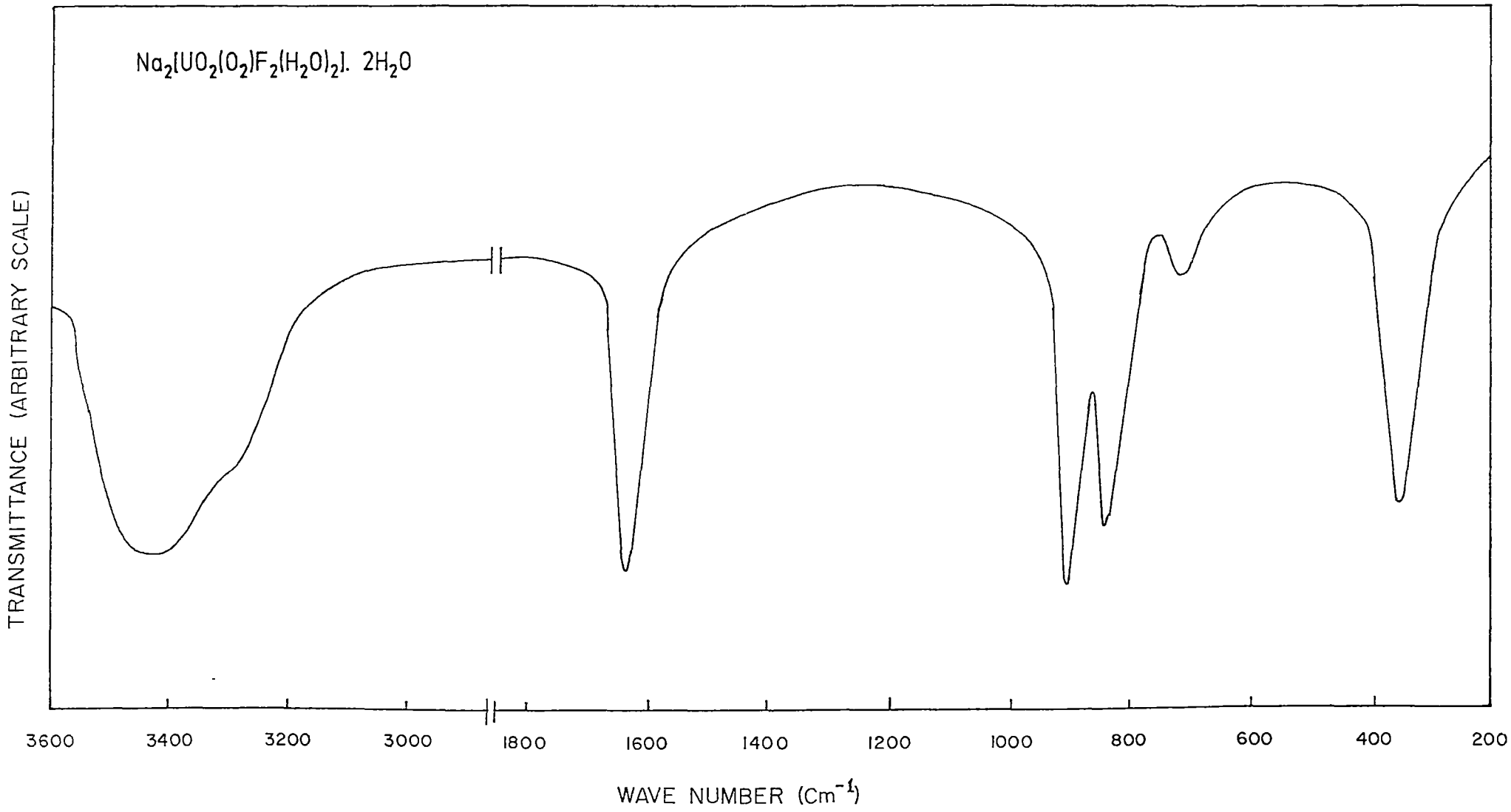
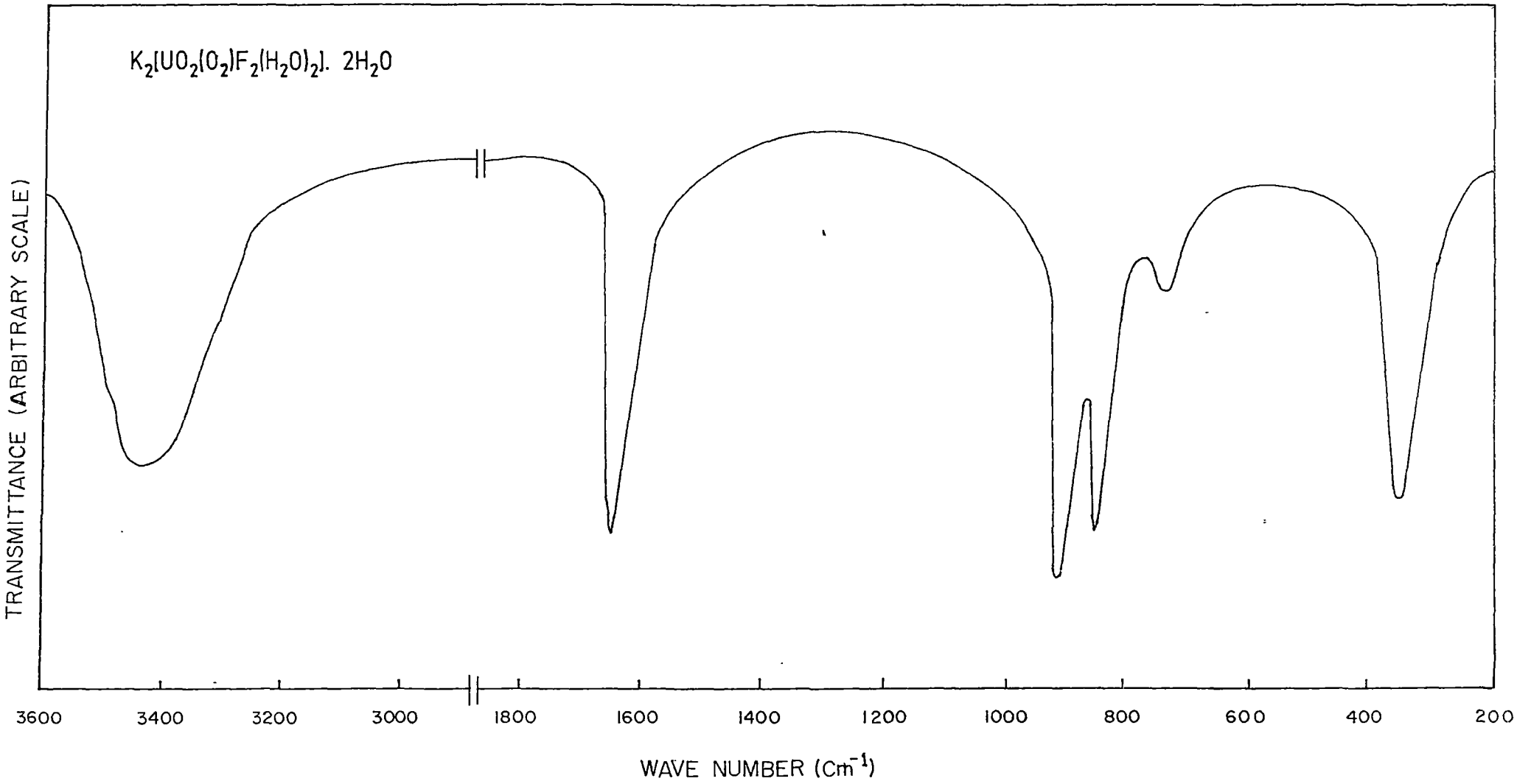


Fig. 4·6 : IR SPECTRUM



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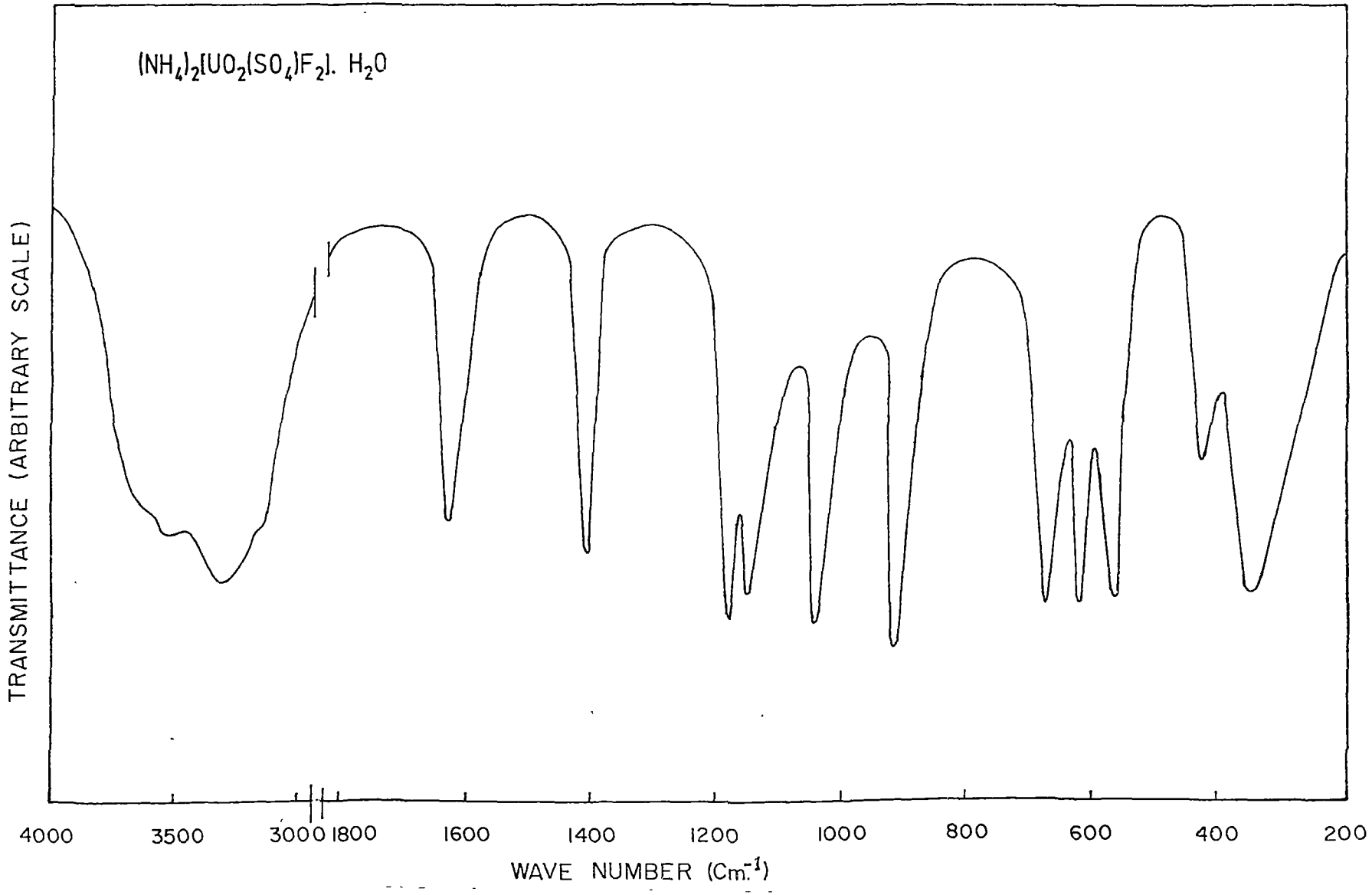

Fig. 4·8: IR SPECTRUM

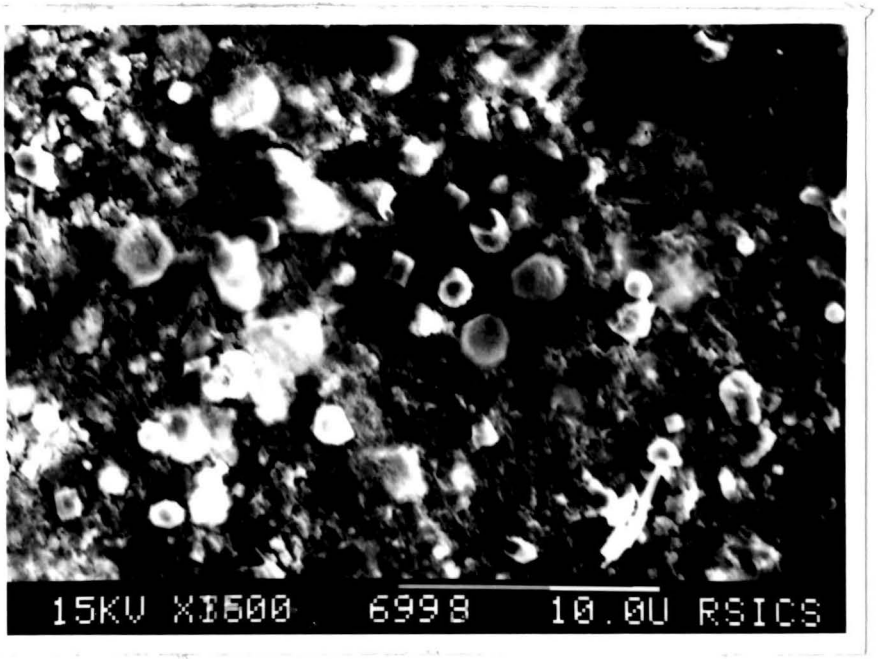

Fig. 4.9 : SCANNING ELECTRON MICROGRAPH OF $K_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$

RESULTS AND DISCUSSION

Synthesis and general considerations

Complex peroxo(phosphato)uranates(VI)

It is known from the familiar chemistry of uranium that UO_2^{2+} interacts with both O_2^{2-} and phosphate ligands[18] . However, both the peroxo and phosphato chemistries of UO_2^{2+} are quite complicated. We sought to develop a synthetic methodology for obtaining mixed ligand peroxo(phosphato) complexes of UO_2^{2+}. In view of our previous experience, three parameters, viz., the sequence of addition of the reactants, the reaction medium pH and the presence of an excess of H_2O_2 were ascertained to be strategically important. While the addition of alkali hydrogen phosphate was found to be necessary prior to that of H_2O_2, the reaction pH of *ca.*7 was conducive to the formation of the desired complex. A reverse sequence of addition led to the preponderance of binary peroxo compounds over the target species. It may be noted that the products obtained at pH values <7 did not produce a complex peroxophosphate of well defined composition, while those isolated at pH>7 were contaminated by excess of uranium contents. The use of excess of hydrogen peroxide, we believe, inhibited polymerization. The use of either AH_2PO_4 (A = NH_4, Na or K) or the corresponding A_2HPO_4 produces similar results. The elicit strategy worked well leading to a synthetic methodology for $(NH_4)_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$, $Na_3[UO_2(O_2)(PO_4)(H_2O)_2].2H_2O$ and $K_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$ in high isolated yields.

Regardless of the use of high concentration of H_2O_2, only monoperoxo complexes have been obtained under the experimental conditions maintained herein. A point worth commenting is that though phosphato complexes of UO_2^{2+} were rather gelatinous, the present products appear to be relatively more crystalline.

Complex peroxo(fluoro)uranates(VI)

Like phosphate and peroxide, both fluoride and peroxide have strong ability to coordinate with the metal centre[3]. Predecessors from this laboratory had reported in 1985[6] the reaction of AF (A = Na,K or NH_4) and H_2O_2 at pH 6.5-7 with UO_2^{2+} in presence of HF affording $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb). Problems encountered in the synthesis of these complexes have been elaborated in the introduction section of this Chapter.

In the present syntheses, following modifications have been made in order to make the procedure comparatively easier.

(i) Instead of $A_2U_2O_7$, $UO_2(NO_3)_2.6H_2O$ has been used directly, (ii) in place of a combination of HF and AF, AHF_2 (A=NH_4,Na or K) has been used, and (iii) the quantity of H_2O_2 has been reduced to a lower concentration ratio (vide Experimental).

The direct use of $UO_2(NO_3)_2.6H_2O$ has now helped reduce the extra preparation steps of $A_2U_2O_7$ (!) and similarly use of AHF_2 facilitated the fluorination of UO_2^{2+} without requiring an extra amount of hydrofluoric acid. A notable point is that lower molar ratio of H_2O_2 gave the desired results as against much higher

concentration used in the earlier work[6]. In this context, it is pertinent to state that an excess of H_2O_2 did not hamper the synthesis of the target species. Also, it has been observed that even if the molar ratio of UO_2^{2+} to AHF_2 was varied over a wide range i.e., 1:3 to 1:6, there was no change in the stoichiometry of the complexes obtained. This implies that peroxide coordination was independent of fluoride concentration. Adherence to the proper sequence of addition of the reagents (vide Experimental) is one of the essential requirements for successful synthesis of the desired products. Besides, pH of the reaction medium played a crucial role in the synthesis of the desired products.

Although a pH value of <7 favoured the coordination of F^- with UO_2^{2+} centre, the tendency of peroxide, O_2^{2-}, to coordinate with UO_2^{2+} centre diminished to a great extent affording only binary fluorocomplexes of UO_2^{2+}. Similarly, maintenance of a pH>7 did not lead to the coordination of fluoride. Since the starting material used in 1985[6] work had a dimeric uranium species ($U_2O_7^{2-}$), its cleavage leading to the formation of hydrated uranyl, $[UO_2(H_2O)_n]^{2+}$ was probably not possible in an aqueous solution alone. In the present methodology, however, the starting material in solution straightway undergoes solvation thereby producing hydrated uranyl species. Consequently, in presence of F^- and O_2^{2-}, some of the already coordinated H_2O molecules must have been substituted by F^- and O_2^{2-}, because of their stronger ligating ability thereby leading to the synthesis of complex species with hexa coordination of UO_2^{2+}, which is frequently encountered in many of the U(VI) complexes. An important

implication of the present observation is that the composition of the starting material *vis-a-vis* the genesis of a compound may be very vital in deciding the composition of the end product.

Characterisation and evaluation of structural features

Compounds $A_3[UO_2(O_2)(PO_4)(H_2O)_2].nH_2O$ (A = NH_4 or K, n = 4; A = Na, n = 2) are all yellow and insoluble in both water and organic solvents. Though they are stable in solid form, their aqueous suspensions on being treated with dil. H_2SO_4 not only dissolved the products but also liberated the active oxygen quantitatively. The peroxide contents of the compounds were determined by permanganometry and the results verified by iodometry. Phosphate complexes of UO_2^{2+} are generally gelatinous. Interestingly, however, the peroxo(phosphato) complexes are crystalline, though rather small in size. In order to get a clear view $K_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$, as a representative example, was subjected to scanning electron microscopy. The micrograph (SEM) as shown in Fig., 4.9 evidences for the crystalline nature of the compound as well as its homogeneity. While the compound is found to be homogeneous, the product seems to have hexagonal crystal morphology. The compounds all analysed very well and were diamagnetic in nature. The complexes are stable for a prolonged period. Their stability can be ascertained by the determination of active oxygen contents periodically as well as by recording the IR spectra.

Among the various physical methods used to delineate the structural motifs, vibrational spectroscopy is a powerful

technique. The systems under discussion in the present Chapter appear to be very interesting probes for their structural assessment by IR spectroscopic method as the ligands are sensitive to vibrational spectroscopy. Accordingly, the IR spectra of the new compounds were scanned repeatedly in order to ensure precision of the data.

The spectra were in order bearing signatures typical of an uranyl complex with the characteristic ν(U=O) band owing to translinked O=U=O at *ca.* 905 cm^{-1}. Similarly, the absorption pattern due to coordinated peroxide, O_2^{2-} was also clear. While the ν(O-O) ν_1 mode was observed at *ca.*890 cm^{-1}, the corresponding ν_2 and ν_3 modes appeared at *ca.* 610 and *ca.* 630 cm^{-1}, respectively. The pattern and the peak positions owing to the peroxo-ligand cause us to state that the dioxygen ligand (O_2^{2-}) is bonded to the metal centre in a triangular bidentate manner with its local symmetry being C_{2v}.

IR features at *ca.*970, *ca.* 1020, and at *ca.* 1120 cm^{-1} are rather characteristic of a chelated phosphato-ligand with their assignments being $\nu(PO_4)$ ν_3. We have a few occasions of dealing with phosphato complexes of metals [19,20] and these features resemble in size and shape those observed earlier, thereby limiting the scope of further discussion. The only point notable in this context is the absence of a band at *ca.* 2900 cm^{-1}. The band would be active if HPO_4^{2-} were present instead of PO_4^{3-}. In addition to all these absorptions, a medium intensity band at *ca.* 740 cm^{-1} was consistently observed in the spectrum of each of the compounds. This must be ascribed to the rocking mode of

coordinated water in line with the formulae. The)(O-H) and δ(H-O-H) were observed in their usual position i.e., *ca.* 3445 and 1640 cm^{-1}, respectively. Owing to competitive losses of active oxygen and water, no clear cut differentiation could be made between lattice and coordinated water from the results of pyrolysis experiments. However, the compound $(NH_4)_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$ when pyrolysed at *ca* 710°C attained a constant weight with a weight loss of 37.5%. The product thus obtained was identified to be uranyl pyrophosphate, $(UO_2)_2P_2O_7$. It may be stated that the afore mentioned experiment provides a newer route to the $(UO_2)_2P_2O_7$ compound.

Like the peroxophosphates discussed above, peroxofluoro complexes are also yellow crystalline solids insoluble in both water and organic solvents. These compounds are stable in the solid and when treated with conc. H_2SO_4, they dissolve rapidly with the evolution of active oxygen quantitatively. The peroxide contents of the compounds were determined by following similar procedures as used for peroxophosphato complexes. Insolubility of these compounds precluded their molar conductance measurements.

As in the case of peroxophosphato complexes described above, the peroxofluoro complexes have been structurally assessed by vibrational spectroscopy. The IR signatures of the compounds are very characteristic of the different ligands present in the complexes. While absorption at 900-890 cm^{-1} is due to ν(U=O)[translinked(O=U=O) group], those at 870-850 and at 300-350 cm^{-1} are due to ν(O-O) and ν(U-F) modes, respectively. The presence of a strong and sharp band at *ca.* 860 cm^{-1} attests

to the notion that the O_2^{2-} is coordinated to UO_2^{2+} centre in a triangular bidentate (C_{2v}) manner[21]. Somewhat broad nature of the ν(U-F) band indicates the possibility of the presence of a bridging fluoride as well. Also worth commenting here is on the physical properties, especially the solubility properties, of these compounds. The insolubility of these complexes may be attributed to a polymeric structure of the complexes through -U-F-U-F-U-or-U-O-O-U-O-O-. Appearance of a distinct band at *ca.* 740 cm^{-1} in the IR spectra of these complexes clearly demonstrates that some of the water molecules are coordinated to the UO_2^{2+} centre. This view was further supported by the pyrolysis study of $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$ and $K_2[UO_2(O_2)F_2(H_2O)_2].2H_2O$ at 110°C. While $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$ did not lose any weight at the chosen temperature, the $K_2[UO_2(O_2)F_2(H_2O)_2].2H_2O$ suffered a weight loss of 7.34 %, corresponding to the loss of $2H_2O$. Appearance of bands consistently at *ca.* 740 cm^{-1} in the IR spectra of the pyrolysed products and the results of their chemical analyses augment the above contention.

Reaction of $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$ with SO_2 solution

Reactions of different peroxo metal compounds were carried out by a number of groups, especially with organic substrates which yielded several newer transformations including epoxidation[7], hydroxylation and oxidation of hydrocarbons [22]. A few reactions with inorganic substrates were also conducted previously[9,10].

We have been interested in the reactions of coordinated peroxides with inorganic substrates like SO_2, CO_2,NO_2 etc. Our strategy was

to conduct such reactions in aqueous medium and to compare the results with those obtained from similar reactions conducted in an organic medium. In order to explore the possible reactivity profiles of these newly synthesised compounds towards $SO_2(g)$ as a representative substrate, the reaction of $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$ with $SO_2.xH_2O$ was carried out. The reaction product was isolated and characterised by elemental analyses and vibrational spectroscopy. The composition of the compound was found to be $(NH_4)_2[UO_2(SO_4)F_2].H_2O$. The motive behind conducting such a reaction was to ascertain wheather the redox reaction between coordinated peroxide and SO_2 produced a fluorosulfato complex. In line with the contention, reaction between $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$ and $SO_2.xH_2O$ was conducted. The reaction took place readily as evidenced by the dissolution of the complex peroxouranium compound.

The compound obtained (vide Experimental) was greenish-yellow in colour and microcrystalline in nature. It was readily soluble in water. Test of peroxide was negative implying that complete conversion of O_2^{2-} into SO_4^{2-} had taken place.

IR spectrum of the compound was rather straightforward showing distinct bands due to coordinated SO_4^{2-} and F^-. Although ν_1 mode of SO_4^{2-} was not observed, the ν_2, ν_3 and ν_4 absorption modes were clearly discernible. Bands at 1195, 1150 and 1050 cm^{-1} (split ν_3 band) suggest that SO_4^{2-} is coordinated to UO_2^{2+} centre in a bridging fashion. This finding was further supported by the X-ray crystallographic data on the corresponding potassium salt obtained earlier by another group[23]. Similarly, ν_4 mode was

also split into three distinct bands at 672,620 and 559 cm^{-1} respectively. The band at 440 cm^{-1} was ascribed to the ν_2 mode of coordinated SO_4^{2-}. Besides, distinct bands at 920 and 372 cm^{-1} were obtained due to ν(U=O)[(O=U=O)] and ν(U-F) modes, respectively. In addition, a broad band at 3440 cm^{-1} and a sharp band at 1645 cm^{-1} are the absorption due to ν(O-H) and δ(H-O-H),. respectively, implying that water of crystallisation is present in the compounds under discussion.

Conclusions

To conclude, the following points may be emphasised:
The results of investigations incorporated in this Chapter show that heteroligand peroxo-uranate(VI) complexes of the type $A_3[UO_2(O_2)(PO_4)(H_2O)_2].nH_2O$ (A = NH_4 or K, n = 4 and A = Na, n = 2) and $A_2[UO_2(O_2)F_2(H_2O)_2].nH_2O$ (A = NH_4, n = 0 and A = Na or K, n =2) could be synthesised under suitable experimental conditions providing newer examples of complex peroxouranates(VI). It is also evident that complex peroxofluorouranates (VI) can be easily synthesised from commercially available starting materials of the metal. Interestingly, both types of complexes appear to be thermally stable upto 150-170°C. This generally is not the case with other metal peroxo complexes. Typically $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$ reacts with SO_2 to provide $(NH_4)_2[UO_2(SO_4)F_2].H_2O$ implying that the coordinated dioxygen ligand is quite activated. Formation of the coordinated sulfate is believed to be through the insertion of SO_2 into the O-O bond of the coordinated peroxide.

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CHAPTER - V

COMPLEX PEROXOURANATES. SYNTHESIS AND ASSESSMENT OF STRUCTURE OF $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4,Na or K), STUDY OF THEIR REACTIVITY PROFILES WITH $SO_2.xH_2O$,CO_2(g) AND HF_2^- IN AQUEOUS MEDIUM AND AN ACCESS TO NEWER HETEROLIGAND DIPEROXO COMPLEXES OF UO_2^{2+} CONTAINING CO_3^{2-} AND 8-QUINOLINOL AS COLIGANDS

The intricacies involved in and the relevance of the research on peroxo chemistry of elements have been elaborated first in Chapter I and subsequently in Chapter IV. The inherent complexity associated with peroxo chemistry[1] of heavier elements, especially uranium, is presumably an inhibiting factor causing a relatively lesser progress in the area. A perusal of literature revealed that in contrast to monoperoxouranates (VI), such complexes with $U:O_2^{2-}$ ratio being 1:>1 have been far less dealt with. Although a host of heteroligand monoperoxouranates including those with

carbonate[2,3] oxalate[2,4], sulphate[2,4], fluoride[2,5] and several organic[6-11] ligands are known, similar complexes with $U:O_2^{2-}$ ratio of 1:>1 are not known so well. Albeit, the existence of binary complexes (with $U:O_2^{2-}$ ratio = 1:>1) in solution[12] and in solid [2,13] state were reported, no systematic approach to the synthesis of such complexes and isolation in the solid state was made in the earlier studies.

It is rather clear from our experience gained from the studies on peroxo chemistry of uranium(VI) that an access to a peroxo uranate of definite stoichiometry depends mainly on the control of pH of the reaction medium. Generally, an increase in the reaction medium pH results in a concomitant increase of peroxygenation of UO_2^{2+}. For example, mono, 1:1.5 type, di and triperoxouranates of definite stoichiometry could be accessed at a reaction medium pH of <8, 8-9, 10-11 and 14, respectively. The synthesis of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ ($U:O_2^{2-}$ = 1:1.5)[14] has been achieved very recently by conducting reactions at pH 8-9. As a logical extension, we have now been able to successfully synthesise diperoxo complexes by conducting reactions at pH 10. It is thus apparent that a choice of right pH is of paramount importance. Our major concern in the present context have been the following:

(i) to develop a new unique general methodology for obtaining diperoxo-dioxouranates(VI), (ii) to ascertain the number of water molecules present as coordinated or lattice, and also (iii) to look into the stability of different salts of the proposed complex. The point (iii) became relevant since an earlier report

described that while the sodium salt, $Na_2UO_6.nH_2O$ was stable, the potassium salt, $K_2UO_6.nH_2O$, was unstable. The ammonium salt did not have any reported existence. In what follows, the details of our endeavour to sorting out the identified problems, spectroscopically ascertain the modes of coordination of peroxide ligand to the metal centre and to investigate the reaction profiles of the compounds with polar inorganic substrates in aqueous medium and also to rationalise the reaction sequence by isolation of products at different stages of reactions. Besides, it was also necessary to explore the possibility of synthesising hitherto unreported heteroligand diperoxo complexes of UO_2^{2+} containing carbonate and 8-quinolinol as coligands. A point of synthetic difficulty related to heteroligand diperoxouranates(VI) is again the suitable pH for obtaining such complexes. This in turn restricts the choice of the coligands since many such ligands prefers an acidic or neutral reaction condition for their coordination with the UO_2^{2+} centre. Incidentally, carbonate and 8-quinolinol are known to sequester UO_2^{2+} at this pH thereby giving a hint that such species could be the ligands of choice. Therefore, in line with this contention reactions were conducted under specified conditions (vide Experimental) which enabled the synthesis of $Na_4[UO_2(O_2)_2(CO_3)].2H_2O$ and $(NH_4)_3[UO_2(O_2)_2Q].4H_2O$ (Q = 8-quinolinolate, C_9H_6ON). Additionally, it was also in our agenda to investigate the reaction profiles of the newly synthesised diperoxo complexes by conducting reactions with small inorganic substrates such as $SO_2.\ xH_2O$, $CO_2(g)$ and HF_2^-. It was also important to compare the results of reactivity studies with those obtained earlier by conducting the reaction of

$(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ with some of the similar substrates.

Accordingly, the Chapter under discussion presents an account of the synthesis of newer diperoxouranates, $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4, Na or K) followed by an investigation of their reactivity in aqueous medium with $SO_2.xH_2O$, $CO_2(g)$ and HF_2^-. Also, included in this Chapter are the syntheses of newer heteroligand diperoxouranates(VI) of the type, $Na_4[UO_2(O_2)_2(CO_3)].2H_2O$ and $(NH_4)_3[UO_2(O_2)_2Q].4H_2O$ (Q = 8-quinolinolate). The course of each reaction has been rationalised based upon isolation and characterisation of the products at different stages of the reactions.

EXPERIMENTAL

All chemicals used were of reagent grade quality.

(i) Synthesis of alkalimetal and ammonium dioxo(diperoxo) diaquouranate(VI), dihydrates, $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4, Na or K)

To a 1 g (1.99 mmol) of $UO_2(NO_3)_2.6H_2O$, 30 cm^3 (264.7 mmol) of 30% H_2O_2 was added. The mixture was stirred for 2 min followed by dropwise addition of aqueous ammonia (sp.gr 0.9) or 5% NaOH or KOH solution. The pH value of the solution was held at 10. At this pH a dark orange coloured solution was obtained. The solution was stirred for another 2 min and then the yellowish-orange micro-crystalline product was obtained by the addition of *ca.* 20 cm^3 of acetone under stirring. The product was isolated by filtration and purified by washing it 3 or 4 times with acetone. This was finally dried in *vacuo* over conc. H_2SO_4. The

yields were 0.75 g (85.2%) for $(NH_4)_2[UO_2(O_2)_2(H_2O)_2].2H_2O$, 0.7 g (77.6%) for $Na_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ and 0.65 g (67.4%) for $K_2[UO_2(O_2)_2(H_2O)_2].2H_2O$.

(ii) Synthesis of sodium dioxodiperoxo(carbonato)uranate(VI) dihydrate, $Na_4[UO_2(O_2)_2(CO_3)].2H_2O$

Powdered $UO_2(NO_3)_2.6H_2O$ (1 g,1.99 mmol) was first dissolved in water (20 cm^3) followed by a slow addition of 15% solution of NaOH with stirring until a yellow product ceased to appear. The solution was filtered off and the yellow product washed free from alkali. To a water (*ca.* 15 cm^3) suspension of this product was added 0.84 g (10 mmol) of $NaHCO_3$ (concentration ration of $U:CO_3^{2-}$ = 1:5) and the mixture was stirred for *ca.* 10 min. To it 30% H_2O_2 (25 cm^3, 220.5 mmol) was added and the stirring continued for a further period of 5 min. The pH of the solution was slowly raised to 10 by dropwise addition of 10% NaOH solution. This resulted into a clear yellowish orange solution. On addition of ice-cold acetone (*ca.* 30 cm^3) to the reaction solution, an oily mass was formed. It was separated by decantation and treated repeatedly with acetone until it turned into a microcrystalline solid. The compound was separated by filtration and then dried *in vacuo* over conc.H_2SO_4. The yield of the compound was 0.8g (77%).

(iii) Synthesis of ammonium dioxodiperoxo(8-quinolinolato)-uranate(VI)tetrahydrate, $(NH_4)_3[UO_2(O_2)_2(C_9H_6ON)].4H_2O$

A 1g (1.99 mmol) of $UO_2(NO_3)_2.6H_2O$ was dissolved in water (30 cm^3) and to it was added 30% H_2O_2 (25 cm^3, 220.5 mmol) and stirred well for *ca.* 5 min. To it was added a solution of 1.45 g

(10 mmol) of 8-quinolinol in 10 cm^3 of acetone. The mixture was stirred for another 10 min. The pH of this solution was then raised to 10 by dropwise addition of aqueous ammonia (sp.gr. 0.9) to obtain an orange coloured solution. The reaction solution was then treated with 20 cm^3 of acetone:ethanol (1:1 v/v) mixture. This led to the precipitation of an orange product. The reaction product was allowed to stand at room temperature for 15-20 min and then filtered off. The compound was washed 3 or 4 times with acetone:alcohol (1:1 v/v) mixture and finally dried *in vacuo* over conc. H_2SO_4. The Yield was 0.6 g (50%).

Reactivity

(a) Reactions of $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4,Na or K) with $SO_2.xH_2O$, ***an access to*** $(NH_4)_2[UO_2(SO_4)_2].H_2O$, $Na_2[UO_2(SO_4)_2].4H_2O$ ***and*** $K_2[UO_2(SO_4)_2].H_2O$

An amount of 0.5 g of the compound (1.13, 1.11 and 1.03 mmol each of NH_4,Na and K salts of diperoxouranates(VI),respectively) was taken separately in 100 cm^3 beaker and a 50 cm^3 of commercial grade SO_2 solution (5 to 6% aqueous solution) was added to each of them. The compound readily went into the solution. The pH of the solution recorded at this stage was 2. The solution was concentrated on a steam-bath until the volume was reduced to 20 cm^3. The concentrated solution was allowed to cool to ambient temperature and then the product was precipitated by the addition of acetone (*ca.* 20 cm^3). The product was washed 3 or 4 times with acetone and finally dried *in vacuo* over concentrated H_2SO_4.The yields were 0.5g (85.7%) for $(NH_4)_2[UO_2(SO_4)_2].H_2O$,

0.45g (80.9%) for $K_2[UO_2(SO_4)_2].H_2O$, and 0.5g (78%) for $Na_2[UO_2(SO_4)_2].4H_2O$.

(b) ***Reactions of*** $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ **(A = Na *or* K) *with*** $CO_2(g)$, ***an access to*** $A_2[UO_2(O_2)(CO_3)].2H_2O$ **(A = Na or K)**

Carbon dioxide (CO_2) gas generated by the action of concentrated HCl on $CaCO_3$ was allowed to pass through a train of fritted glass-scrubbers containing distilled water and finally through the reaction vessel (another fritted scrubber) containing aqueous suspension of 0.5g of the compound under study (1.1 and 1.03 mmol of Na and K salts respectively) for 2 to 3 h. Carbon dioxide reacted with the suspension of the insoluble diperoxo complexes and two phases distinctively separated out as a yellowish orange soluble portion and a pale yellow suspension. The soluble part was separated by filtration and the product of the soluble part was isolated either by evaporating on a steam-bath or by adding acetone. The yields were 0.18g (36.7%) for $Na_2[UO_2(O_2)(CO_3)].2H_2O$ and 0.19g (38.8%) for $K_2[UO_2(O_2)(CO_3)].2H_2O$

(c) Reactions of $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ **(A = NH_4 *or* Na) *with*** AHF_2 **(A = NH_4 or Na), *an access to*** $A_6[UO_2F_8].nH_2O$ **(A = NH_4, n = 0; A = Na, n = 2)**

A 0.5g of the compound (1.13 and 1.10 mmol of $(NH_4)_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ and $Na_2[UO_2(O_2)_2(H_2O)_2].2H_2O$, respectively) was taken in a 100 cm^3 polyethylene beaker and an excess of AHF_2 (1:5) U:F was added and then mixed well. About 10 cm^3 of distilled water was added and stirred well for 2 or 3 min

and then gently heated on a steam-bath till the compound completely dissolved. The solution was allowed to cool to room temperature and then the product was precipitated by the addition of a minimum quantity of acetone (*ca.* 5 cm^3). The product was allowed to settle for *ca.* 10 min and then filtered. The product was washed 3 or 4 times with acetone and finally dried *in vacuo* over conc. H_2SO_4. The yields of $(NH_4)_6[UO_2F_8]$ and $Na_6[UO_2F_8].2H_2O$ were 0.5g (83.5%) and 0.45g (68.3%), respectively.

RESULTS AND DISCUSSION

Alkali metal and ammonium dioxo(diperoxo)diaquouranate(VI) dihydrates, $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$

Synthesis

It is an acknowledged fact that uranium(VI) (UO_2^{2+}) readily reacts with H_2O_2 to afford a light yellow precipitate having a composition of $UO_4.nH_2O$ (n = 2 to 4). But if the pH of such a reaction is raised to 10, the complex, $UO_4.nH_2O$, passes into solution and a dark yellowish-orange colouration of the solution results. A spectrophotometric method[15] based upon this reaction is prevalent for the determination of U(VI) for quite sometime. On the basis of this knowledge and in line with our own strategy, mentioned earlier, we conducted similar reactions with the specific aim of isolating the product in the solid state. The reactions were conducted between $UO_2(H_2O)_n^{2+}$ (generated by dissolving $UO_2(NO_3)_2.6H_2O$) and H_2O_2 at pH 10 to afford the compound, $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4, Na or K) as obtained. The role of pH in the peroxo chemistry has been

emphasised already in Chapter IV as well as in the introduction of this Chapter. The pH adjustment was made by the addition of dilute ammonia or alkali solutions which also served as the source of the counter cations. The compounds are all yellow in colour and have been obtained as microcrystals. The products are diamagnetic and stable for days in solid form.

Characterisation and assessment of structure

Insolubility in water and in organic solvents precluded the molar conductance measurements on the complexes . Owing to a rather simple nature of the complex ions as well as vibrational spectral sensitivity of the oxo and peroxo ligands, the newly synthesised compounds constitute important vibrational spectroscopic probe, amenable to structural analysis. Significantly, IR spectra of these complexes showed strong band at 889-895 cm^{-1} due to U=O absorption. Similarly, a sharp band in the region 835-845 cm^{-1} for all these complexes can be attributed to the ν(O-O) ν_1 mode of coordinated O_2^{2-}. Apart from this, the consistent appearance of two medium intensity bands in the 615-645 cm^{-1} region (Table 5.3) attributable to the ν_2 and ν_3 modes of coordinated O_2^{2-} clearly demonstrate that O_2^{2-} groups are coordinated to the metal centre in a triangular bidentate (C_{2v}) manner. A notable point in this context is the small separation between the ν_2 and ν_3 modes which often resulted into a broad band, especially if the scanning in the region was fast. Incidentally, all the compounds possessed lattice as well as coordinated water thereby making the region at *ca.* 1620 cm^{-1} and at *ca.* 3450 cm^{-1} noncharacteristic for either type. The IR signatures in support

of the coordinated water was observed consistently in 710-723 cm^{-1} region due to the rocking mode of bonded water. The ν(O-H) and and δ(H-O-H) modes for water were observed in the expected regions for all the complexes. The ν(O-H) region, however, was complicated owing to the presence of both coordinated and lattice water. In addition, the occurrence of ν_1 and ν_3 modes of NH_4^+ in the region where ν(O-H) also appears, makes the pattern further complicated in the case of $(NH_4)_2[UO_2(O_2)_2(H_2O)_2].2H_2O$. However, the ν_4 mode of NH_4^+ was observed at 1400 cm^{-1}. This is unambiguous because no other absorption was expected. Laser Raman (LR) spectra of these complexes were recorded on solid. Raman spectroscopy is a very diagnostic technique for ascertaining structural motifs of peroxo complexes. A notable point in this context is that owing to an extensive fluorescence, many uranyl complexes do not produce good LR spectra. Incidentally, in the present cases when the argon laser line at 4880 Å was used well shaped signals were observed. The LR signals in the ranges, 850-855 cm^{-1} and 812-815 cm^{-1} have been attributed to ν(U=O)[trans-linked O=U=O] and ν(O-O) ν_1, respectively. A lower value of the ν(O-O) ν_1 mode (present case) in comparison with that of the monoperoxo complexes (as discussed in chapter IV) of the metal[3] signifies a decrease in the O-O bond order of the bonded peroxo ligand with the increase in the number of peroxo groups coordinated with the UO_2^{2+} centre. This suggests *inter-alia* that removal of further 2pπ density from O_2^{2-} to uranyl core appears to have taken place in the complexes. Fortunately, the observance of band positions at still lower value for triperoxouranate, $Na_4[UO_2(O_2)_3].9H_2O$[16]

augments the above given interpretation.

Having achieved the synthesis of binary diperoxo complexes, our attention was turned to heteroligand diperoxo complexes of uranium.

Sodium dioxodiperoxo(carbonato)uranate(VI)dihydrate, $Na_4[UO_2(O_2)_2(CO_3)].2H_2O$(1)and ammonium dioxodiperoxo(8-quinolinolato)uranate(VI) tetrahydrate, $(NH_4)_3[UO_2(O_2)_2(C_9H_6ON)].4H_2O$ (2)

Synthesis

In keeping with the elicit strategy, the reactions of UO_2^{2+} with HCO_3^- or 8-quinolinol (QH, C_9H_7ON) and hydrogen peroxide were conducted at pH 10. The strategy apparently worked well leading to the development of a methodology for the synthesis of the complexes $[UO_2(O_2)_2(CO_3)]^{4-}$ and $[UO_2(O_2)_2Q]^{3-}$ (Q = 8-quinolinolate, C_9H_6ON) and isolation as their sodium(1) and ammonium (2) salts,respectively. The counter cations (Na^+ or NH_4^+) were derived from the corresponding alkali that were used for maintaining the appropriate pH of the reaction solutions. In order to avert polymerisation an excess of hydrogen peroxide was employed. The reactions were monitored by isolation of the products at different pH values (between 7 and 10) followed by chemical determination of the active oxygen contents and recording of the IR spectra. The compounds isolated at PH>11 did not correspond to the desired stoichiometry, instead they were found to contain much higher amounts of uranium. The complexes 1 and 2 are important additions to the few examples of complex diperoxouranates(VI)[2]

Characterisation and structural assessment

The yellowish-orange $Na_4[UO_2(O_2)_2(CO_3)].2H_2O$ (1) and the orange $(NH_4)_3[UO_2(O_2)_2Q].4H_2O$(2) are stable with the former being soluble. While the insolubility of 2 precluded its molar conductance measurements, the solution electrical conductivity of 1 was recorded to be 450 $\Omega^{-1}cm^2mol^{-1}$. The result is in order with the formulation. The structures of the compounds have been assessed by vibrational spectroscopy. The common features of the IR and Raman spectra of 1 and 2 are bands due to ν(U=O) [trans-linked O=U=O], ν(O-O) ν_1, ν(U-O_2) ν_2 and ν(U-O_2) ν_3 observed at *ca* 895, *ca.* 840, *ca.* 610 and *ca.* 585 cm^{-1}, respectively. A striking feature of the spectra is the position of the peroxo stretch ν(O-O) ν_1. A lower value of the ν(O-O) ν_1 mode (present case) in comparison with that of the monoperoxo complexes (*cf.ca.*870 cm^{-1}) of the metal[3] signifies a decrease in the O-O bond order of the bonded peroxoligand with the increase in the number of peroxo groups coordinated with the UO_2^{2+} centre as interpreted earlier in this section.

In addition to those discussed above, the IR spectrum of 1 displayed bands (vide Experimental) typical of coordinated carbonate with feature well comparable to that of the corresponding monoperoxocarbonato complexes of UO_2^{2+}. A large separation between ν_1[A_1 ν(C-O)] at 1585 cm^{-1} and ν_5[B_2, ν(C-O) + δ(O-C-O)] at 1340 cm^{-1} modes of CO_3^{2-} is notable. Furthermore, the ν_1 mode was found to be Raman active with a strong signal at 1570 cm^{-1}. These provide clear cut evidences in support of the occurrence of a chelated carbonate in the complex. The IR

spectrum of the complex 2 shows, besides the UO_2^{2+} and coordinated peroxo modes, bands due to coordinated 8-quinolinolate ligand,Q with the pattern comparing very well with that reported [17,18] for 8-quinolinolato coordinated systems. The 8-quinolinolato related peak positions also appear to be very similar to those observed recently for a complex peroxovanadium(V) species[19] containing a chelated Q ligand. Apart form these, two more bands at *ca.* 1640 m and *ca.* 3460 m,br were observed in each of the spectra. These absorptions are typical of the δ(H-O-H) and ν(O-H) modes of uncoordinated water[20].

Table 5.1: Analytical data of $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4, Na or K), $A_2[UO_2(SO_4)_2].nH_2O$ (A = NH_4 or K, n = 1; A = Na, n = 4), $A_2[UO_2(O_2)(CO_3)].2H_2O$ (A = Na or K), $(NH_4)_6[UO_2F_8]$ and $Na_6[UO_2F_8].2H_2O$

Compounds	Analysis [a] (%)				
	A or N	U	O_2^{2-}	SO_4^{2-} or C	F
$(NH_4)_2[UO_2(O_2)_2(H_2O)_2].2H_2O$	5.98 (6.33)	54.1 (53.83)	12.51[+] (14.47)	-	-
$Na_2[UO_2(O_2)_2(H_2O)_2].2H_2O$	10.43 (10.17)	52.6 (52.65)	12.0[+] (14.15)	-	-
$K_2[UO_2(O_2)_2(H_2O)_2].2H_2O$	15.92 (16.14)	50.19 (49.15)	12.62[+] (13.21)	-	-
$(NH_4)_2[UO_2(SO_4)_2].H_2O$	5.62 (5.42)	46.81 (46.1)	-	36.59 (37.21)	-
$Na_2[UO_2(SO_4)_2].4H_2O$	7.46 (7.92)	41.53 (41.0)	-	33.39 (33.11)	-
$K_2[UO_2(SO_4)_2].H_2O$	13.89 (13.97)	44.39 (42.60)	-	34.98 (34.38)	-
$Na_2[UO_2(O_2)(CO_3)].2H_2O$	10.92 (10.35)	54.18 (53.6)	7.89 (7.2)	2.67 (2.7)	-
$K_2[UO_2(O_2)(CO_3)].2H_2O$	15.82 (16.42)	49.88 (49.97)	6.95 (6.72)	2.56 (2.52)	-
$(NH_4)_6[UO_2F_8]$	16.0 (15.84)	43.56 (44.89)	-	-	29.9 (28.66)
$Na_6[UO_2F_8].2H_2O$	24.1 (23.14)	40.17 (39.94)	-	-	26.13 (25.5)

[a] Calculated values are in parenthesis

[+] A low value of peroxide may be attributed to the loss of peroxide during its quantitative estimation.

Table 5.2 : Analytical data of $Na_4[UO_2(O_2)_2CO_3].2H_2O$ and $(NH_4)_3[UO_2(O_2)_2(C_9H_6ON)].4H_2O$

Compounds	Analysis[a] (%)				
	A or N	U	O_2^{2-}	C	H
$Na_4[UO_2(O_2)_2(CO_3)].2H_2O$	17.79 (17.62)	44.92 (45.60)	12.15 (12.26)	2.33 (2.30)	-
$(NH_4)_3[UO_2(O_2)_2(C_9H_6ON].4H_2O$	8.86 (9.27)	40.34 (39.38)	10.20 (10.59)	17.46 (17.88)	4.27 (4.34)

[a] Calculated values in parenthesis

Table 5.3: Structurally significant IR and LR bands of $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4, Na or K), $A_2[UO_2(SO_4)_2].nH_2O$ (A = NH_4 or K, n = 1; A = Na, n = 4), $A_2[UO_2(O_2)(CO_3)].2H_2O$ (A = Na or K), $(NH_4)_6[UO_2F_8]$ and $Na_6[UO_2F_8].2H_2O$

Compounds	IR(cm^{-1})	LR(cm^{-1})	Assignments	
$(NH_4)_2[UO_2(O_2)_2(H_2O)_2].2H_2O$	895 s	850	ν(U=O) (O=U=O)	
	835 w,br	812	ν(O-O) ν_1	C_{2v}
	621 m	-	ν(U-O_2) ν_3	C_{2v}
	635 m	-	ν(U-O_2) ν_2	C_{2v}
	3434 m	-	ν(O-H)	
	1641 m	-	δ(H-O-H)	
	720 m	-	$\rho_r(H_2O)$	
	1402 m	-	ν(N-H) ν_4	
$Na_2[UO_2(O_2)_2(H_2O)_2].2H_2O$	890 s	852	ν(U=O) (O=U=O)	
	840 w, br	815	ν(O-O) ν_1	C_{2v}
	615 m	-	ν(U-O_2) ν_3	C_{2v}
	645 m	-	ν(U-O_2) ν_2	C_{2v}
	3450 m	-	ν(O-H)	
	1640 m	-	δ(H-O-H)	
	710 m	-	$\rho_r(H_2O)$	

Table 5.3 (Contd.)

$K_2[UO_2(O_2)_2(H_2O)_2].2H_2O$	889 s	855	ν (U=O) (O=U=O)
	845 w	819	ν (O-O) ν_1
	617 m	-	ν (U-O_2) ν_3
	639 m	-	ν (U-O_2) ν_2
	3438 m	-	ν (O-H)
	1638 m	-	δ (H-O-H)
	723 m	-	ρ_r (H_2O)
$(NH_4)_2[UO_2(SO_4)_2].H_2O$	920 s	-	ν (U=O) (O=U=O)
	980 m	-	ν_1
	441 m	-	ν_2
	1150 s	-	ν_3
	1050 s	-	ν_3
	1220 s	-	ν_3
	672 s	-	ν_4
	620 s	-	ν_4
	559 s	-	ν_4
			ν S-O
	3441 m	-	ν (O-H)
	1640 m	-	δ (H-O-H)
	1400 s	-	ν (N-H) ν_4

Table 5.3 (Contd.)

$Na_2[UO_2(SO_4)_2].4H_2O$	921 s	-	ν (U=O) (O=U=O)
	981 m	-	ν_1
	445 m	-	ν_2
	1145 s	-	ν_3
	1050 s	-	
	1230 s	-	
	665 s	-	ν_4
	610 s	-	
	580 s	-	
	3462 s	-	ν (O-H)
	1635 m	-	δ (H-O-H)
$K_2[UO_2(SO_4)_2].H_2O$	921 s	-	ν (U=O) (O=U=O)
	985 m	-	ν_1
	445 m	-	ν_2
	1145 s	-	ν_3
	1020 s	-	
	1230 s	-	
	650 s	-	ν_4
	615 s	-	
	575 s	-	
	3449 m	-	ν (O-H)
	1640 m	-	δ (H-O-H)

ν (S-O)

Table 5.3 (Contd.)

$Na_2[UO_2(O_2)(CO_3)].2H_2O$	895 s	-	ν(U=O)(O=U=O)
	865 s	-	ν(O-O) ν_1
	645 m	-	ν(U-O_2) ν_3
	615 m	-	ν(U-O_2) ν_2
	1580 s	-	ν(C-O) $\nu_1(A_1)$
	1355 m	-	[ν(C-O)+δ(O-C-O)] $\nu_5(B_2)$
	3475 m	-	ν(O-H)
	1640 m	-	δ(H-O-H)
$K_2[UO_2(O_2)(CO_3)].2H_2O$	900 s	-	ν(U=O)(O=U=O)
	860 s	-	ν(O-O) ν_1
	665 w	-	ν(U-O_2) ν_3
	619 m	-	ν(U-O_2) ν_2
	1559 s	-	ν(C-O) $\nu_1(A_1)$
	1344 s	-	[ν(C-O)+δ(O-C-O)] $\nu_5(B_2)$
	3459 m	-	ν(O-H)
	1640 m	-	δ(H-O-H)
$(NH_4)_6[UO_2F_8]$	890 s	-	ν(U=O)(O=U=O)
	347 s,br	-	ν(U-F)
	1410 s	-	ν(N-H) ν_4
$Na_6[UO_2F_8].2H_2O$	895 s	-	ν(U=O)(O=U=O)
	365 s,br	-	ν(U-F)
	3459 m	-	ν(O-H)
	1645 m	-	δ(H-O-H)

Table 5.4: Structurally significant IR and LR bands of $Na_4[UO_2(O_2)_2(CO_3)].2H_2O$ and $(NH_4)_3[UO_2(O_2)_2(C_9H_6ON)].4H_2O$

Compounds	IR(cm^{-1})	LR(cm^{-1})	Assignments
$Na_4[UO_2(O_2)_2(CO_3)].2H_2O$	890 s	900	ν(U=O)(O=U=O)
	840 s,br	843	ν(O-O) ν_1
	615 w	607	ν(U-O_2) ν_2
	580 m	585	ν(U-O_2) ν_3
	1585 s	1580	ν(C-O) $\nu_1(A_1)$
	1335 m	-	[ν(C-O)+δ(O-C-O)] $\nu_5(B_2)$
	1640 w,br	-	δ(H-O-H)
	3467 m,br	-	ν(O-H)
$(NH_4)_3[UO_2(O_2)_2(C_9H_6ON)].4H_2O$	900 s	905	ν(U=O)(O=U=O)
	840 m	840	ν(O-O) ν_1
	608 m	610	ν(U-O_2) ν_2
	595 m	585	ν(U-O_2) ν_3

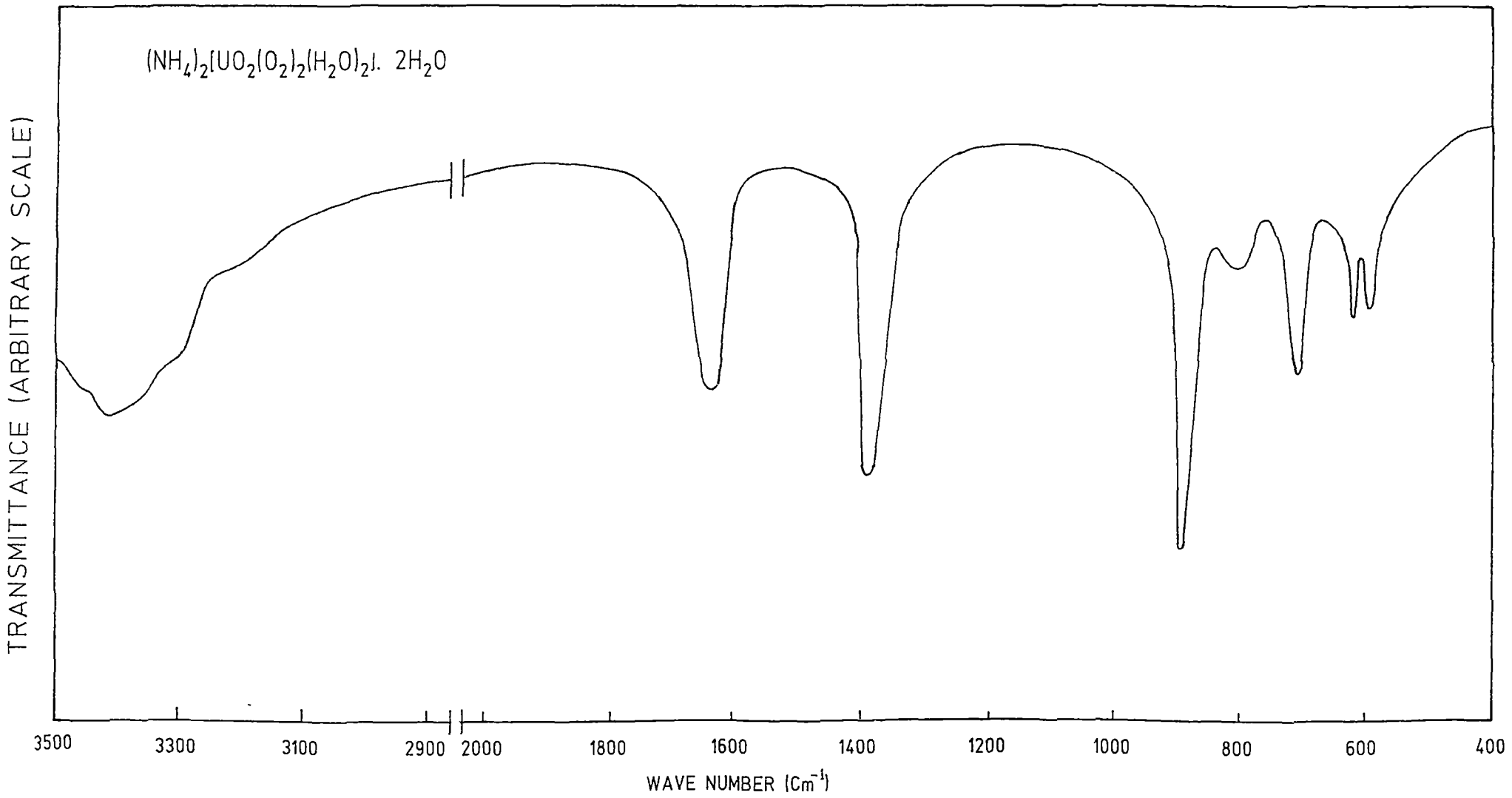


Fig. 5.1 : IR SPECTRUM

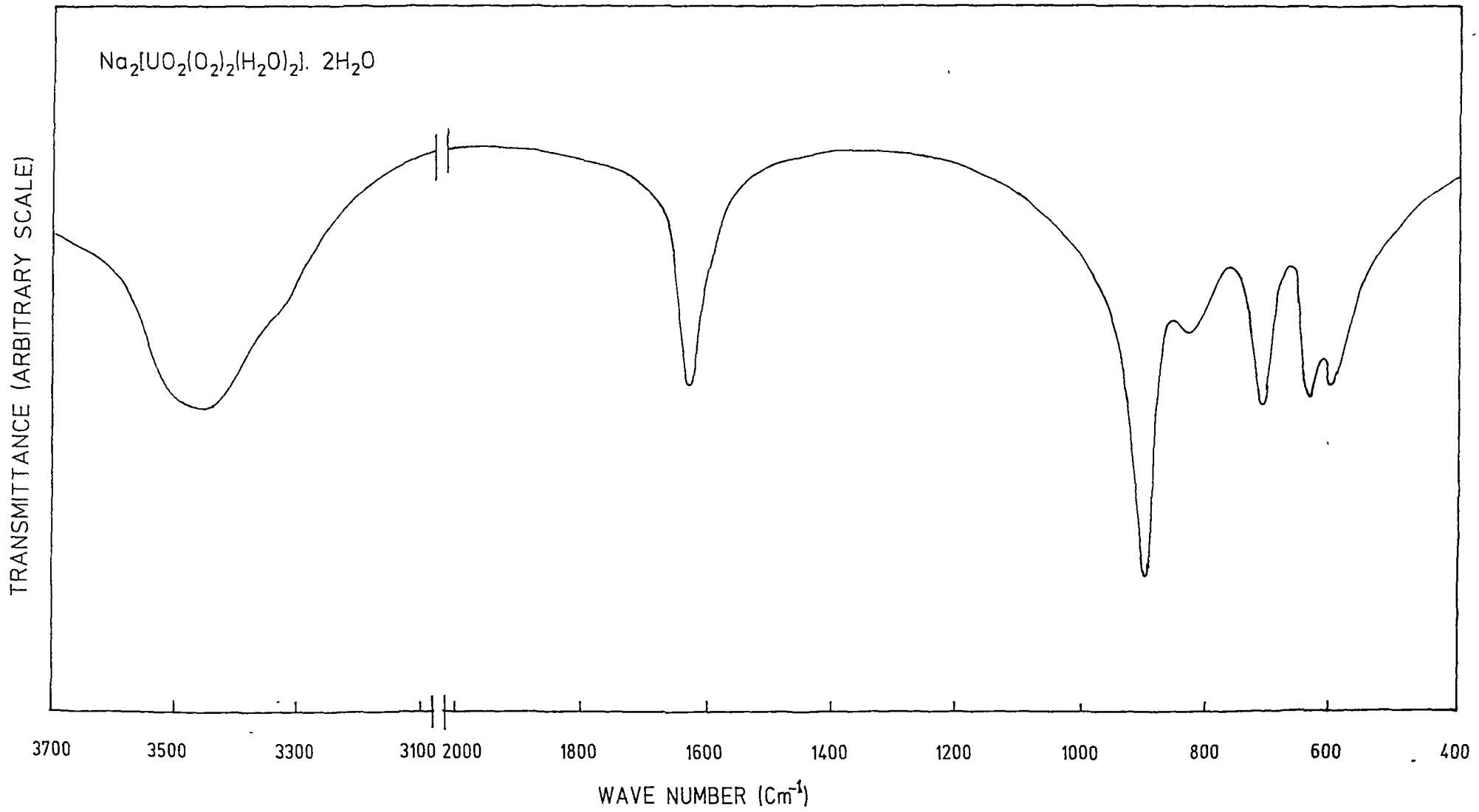


Fig. 5.2 : IR SPECTRUM

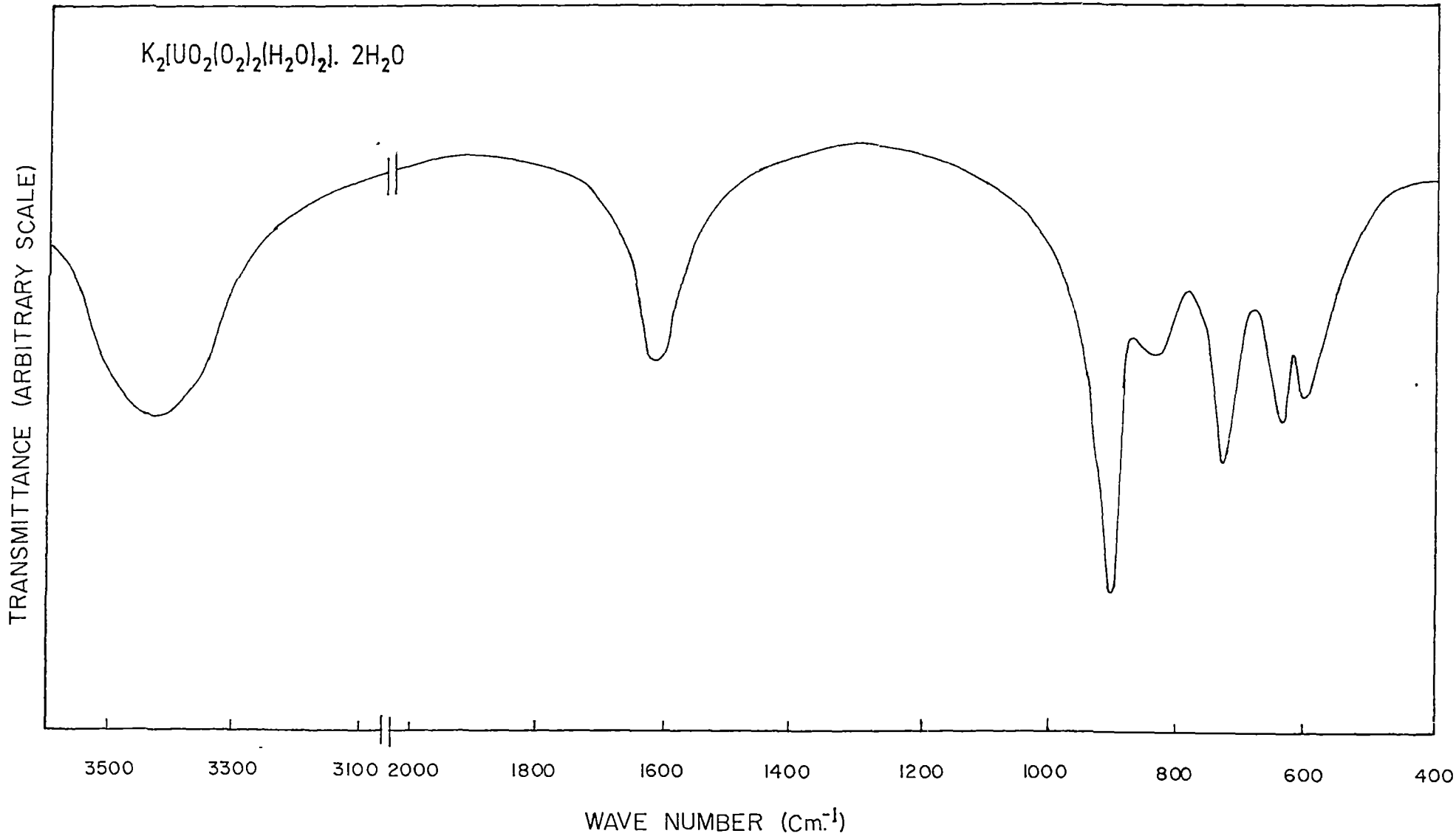


Fig. 5·3 : I R SPECTRUM

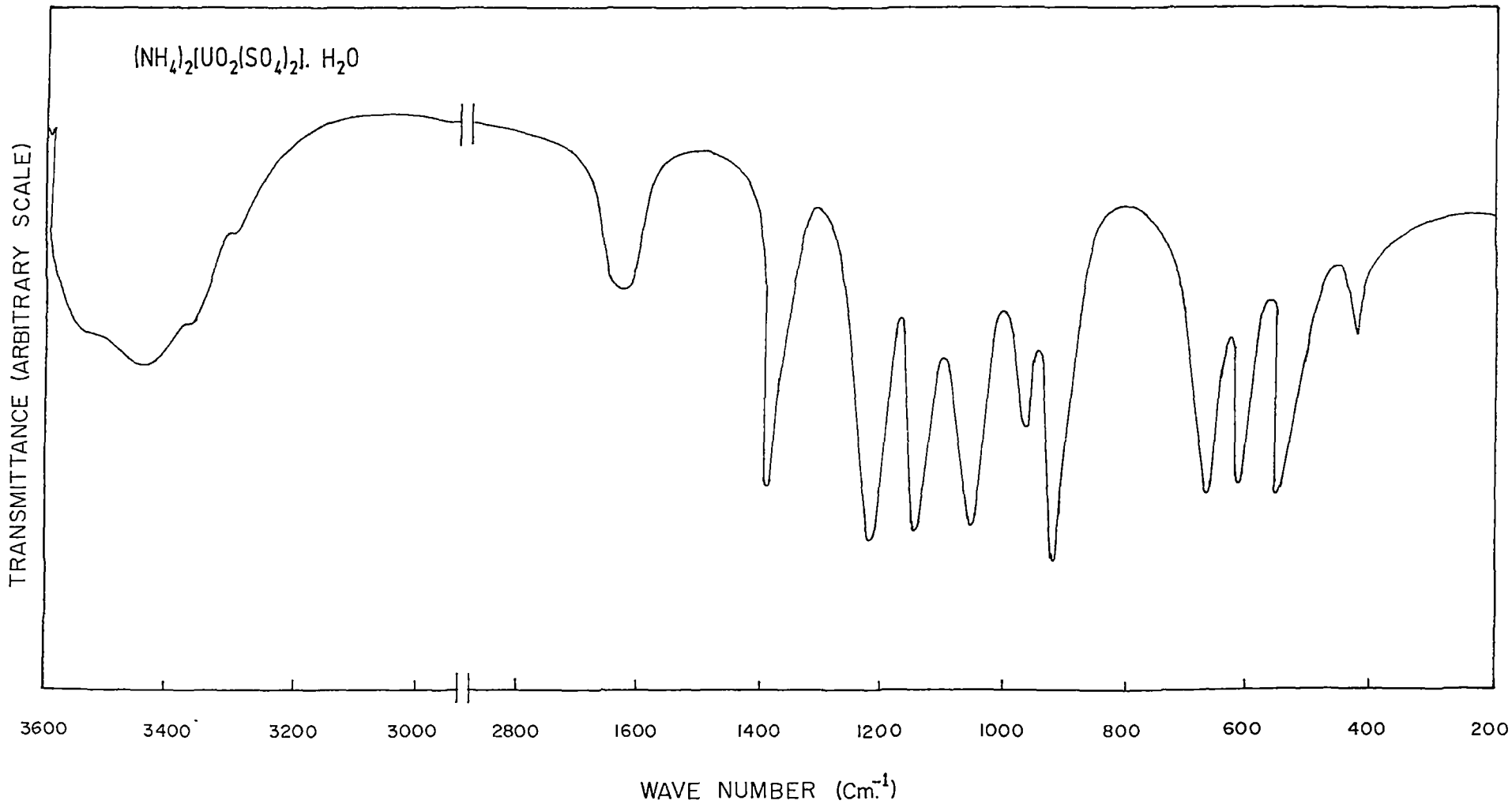


Fig. 5.4 : IR SPECTRUM

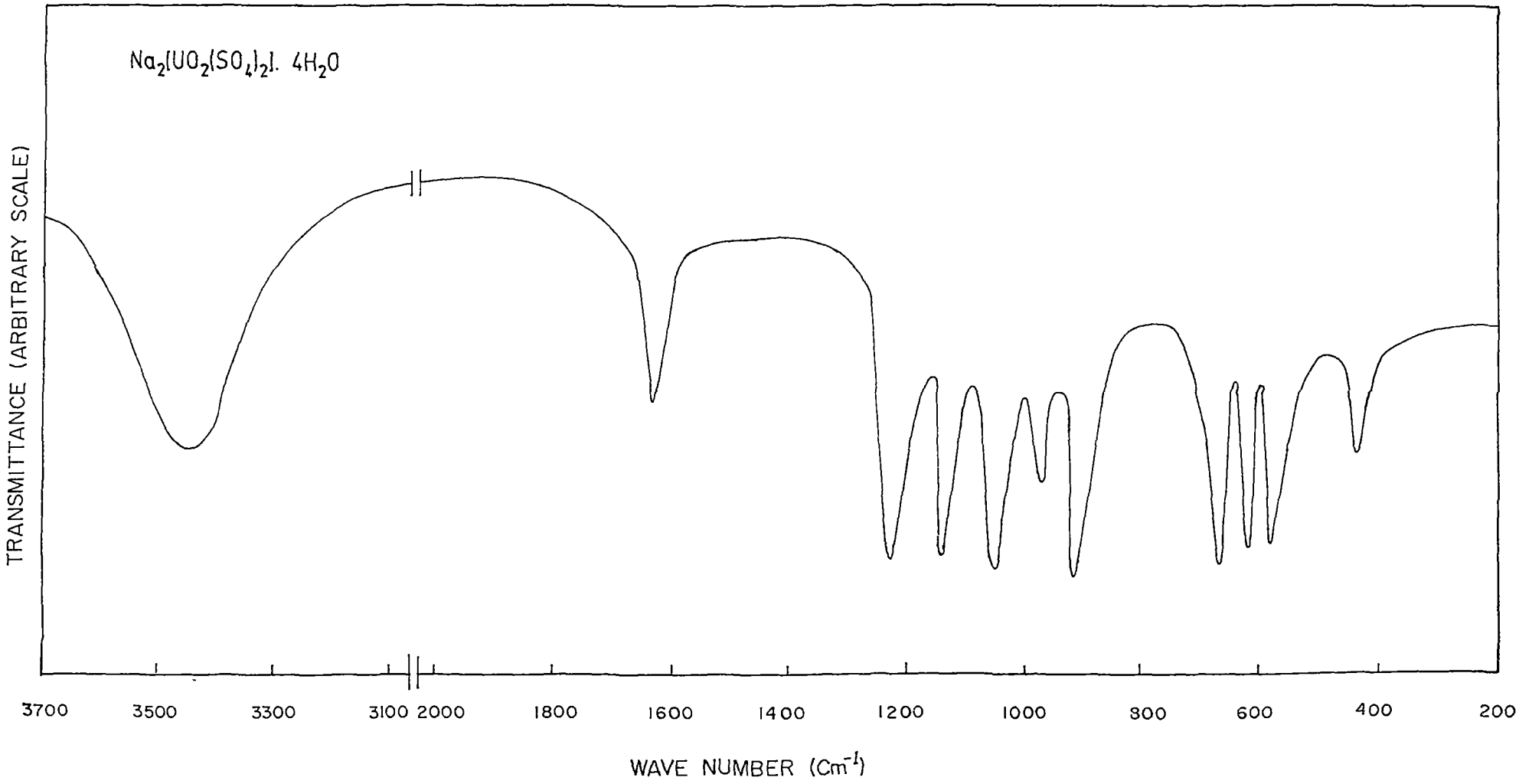


Fig. 5·5 : IR SPECTRUM

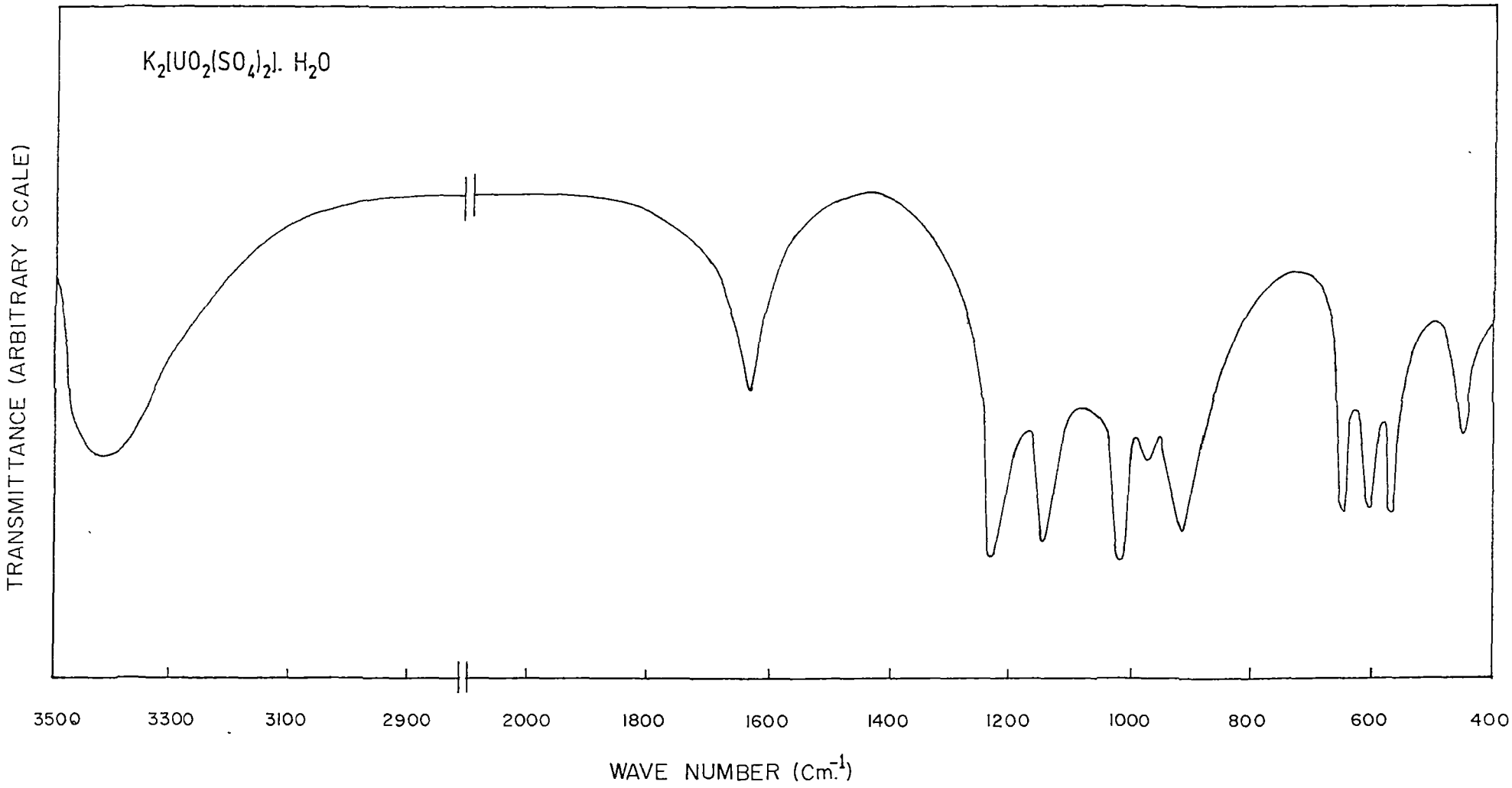


Fig.5·6: IR SPECTRUM

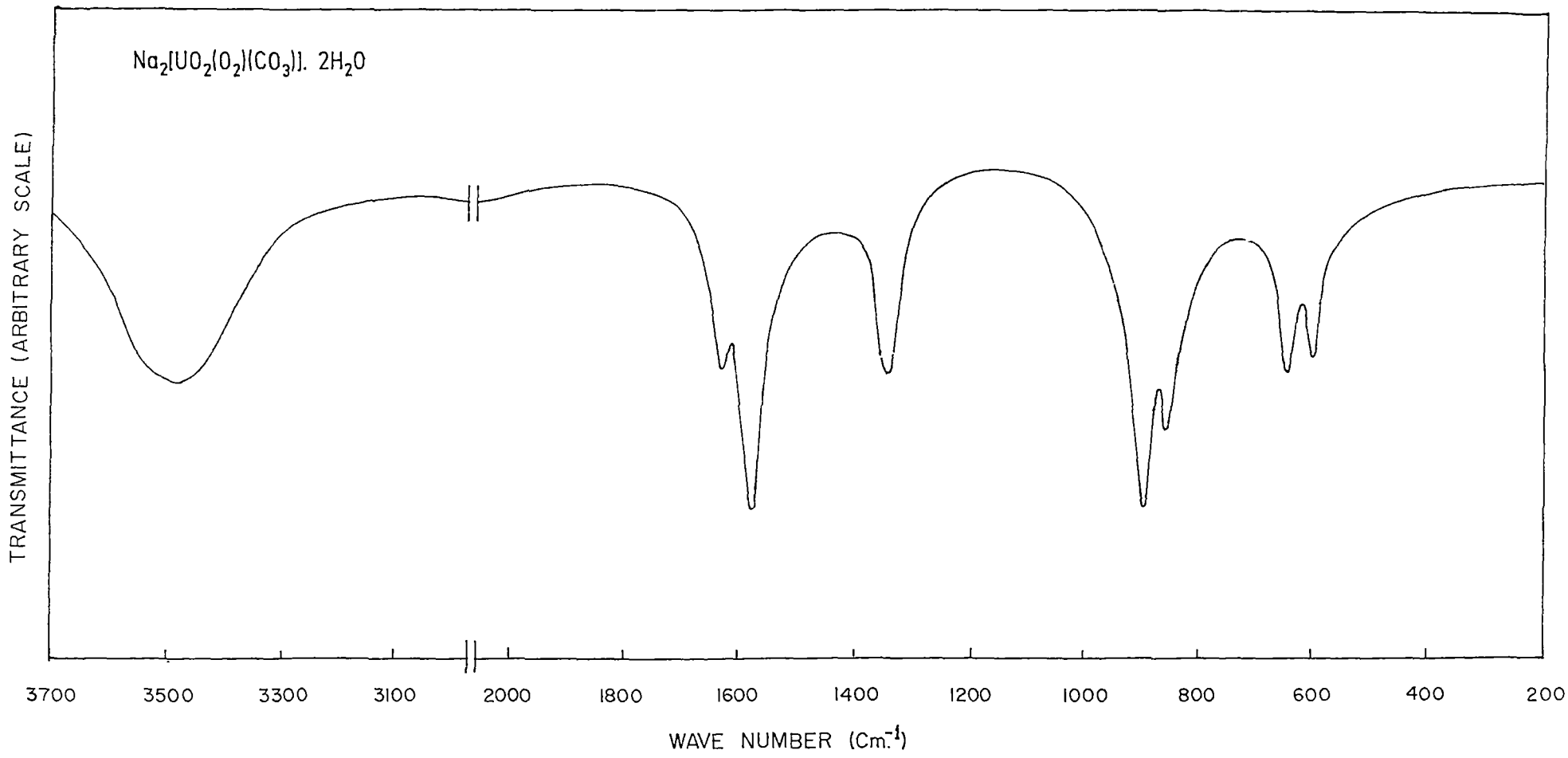


Fig. 5·7: IR SPECTRUM

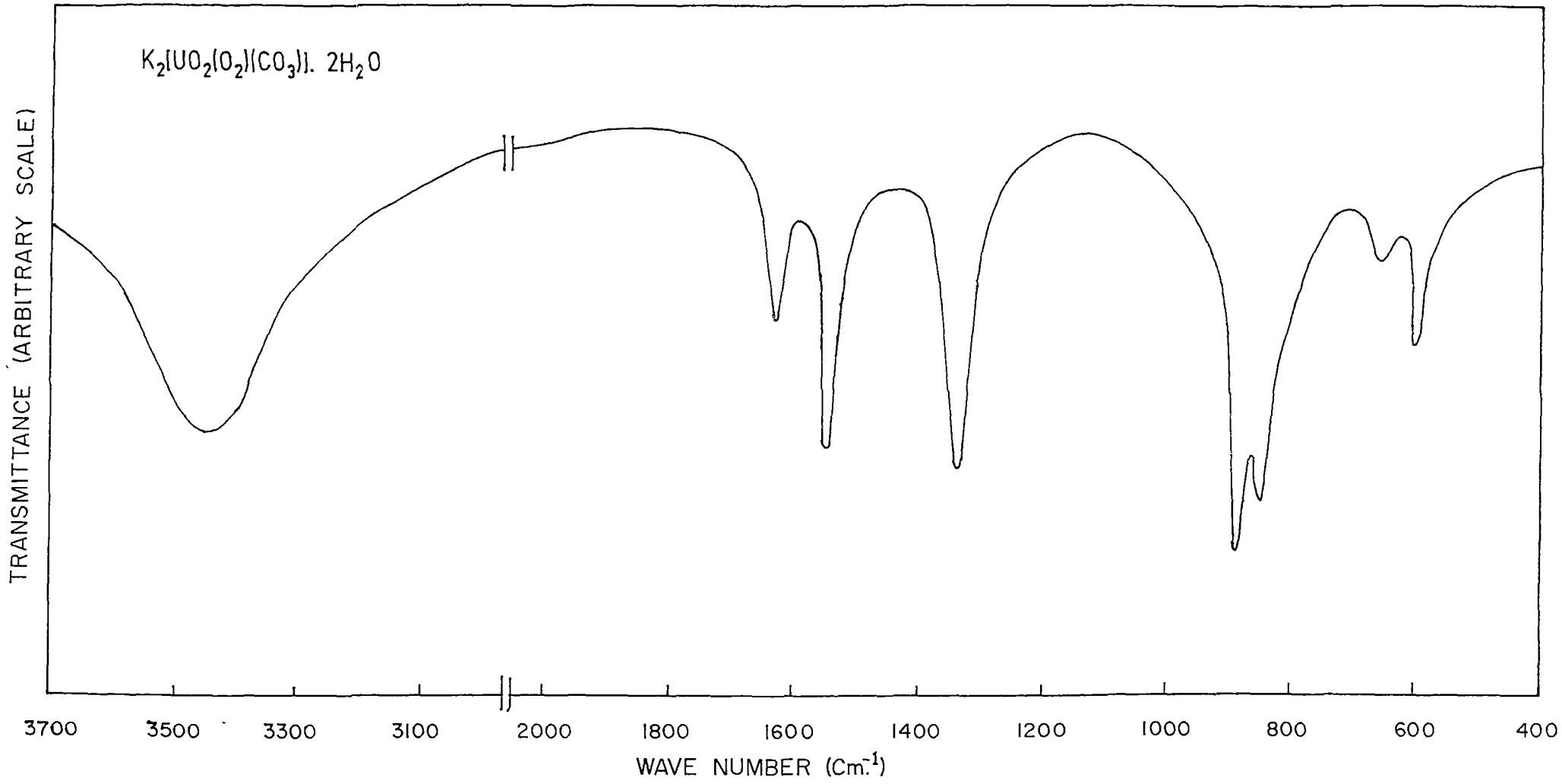


Fig. 5.8 : I R SPECTRUM

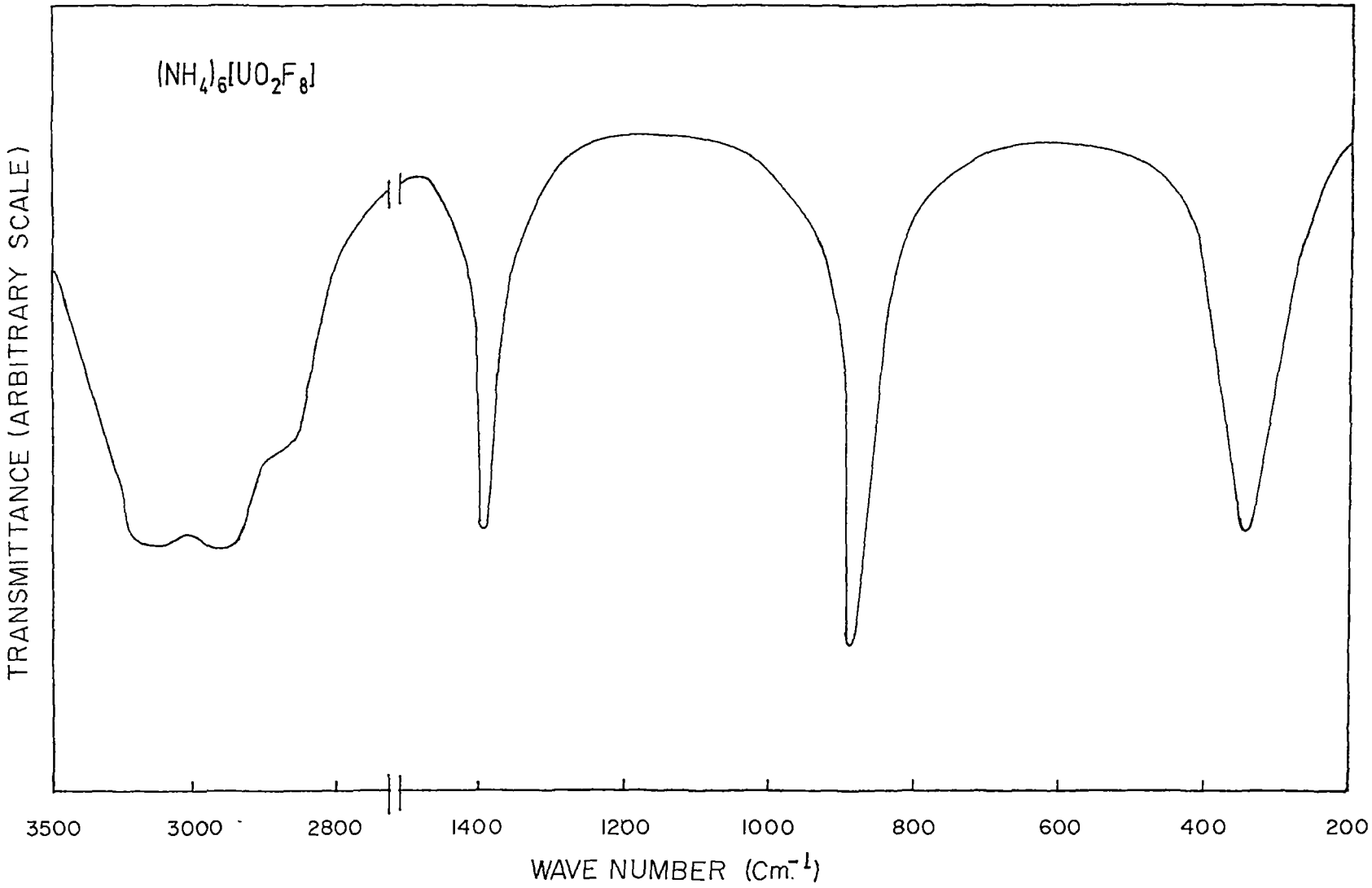


Fig. 5·9: IR SPECTRUM

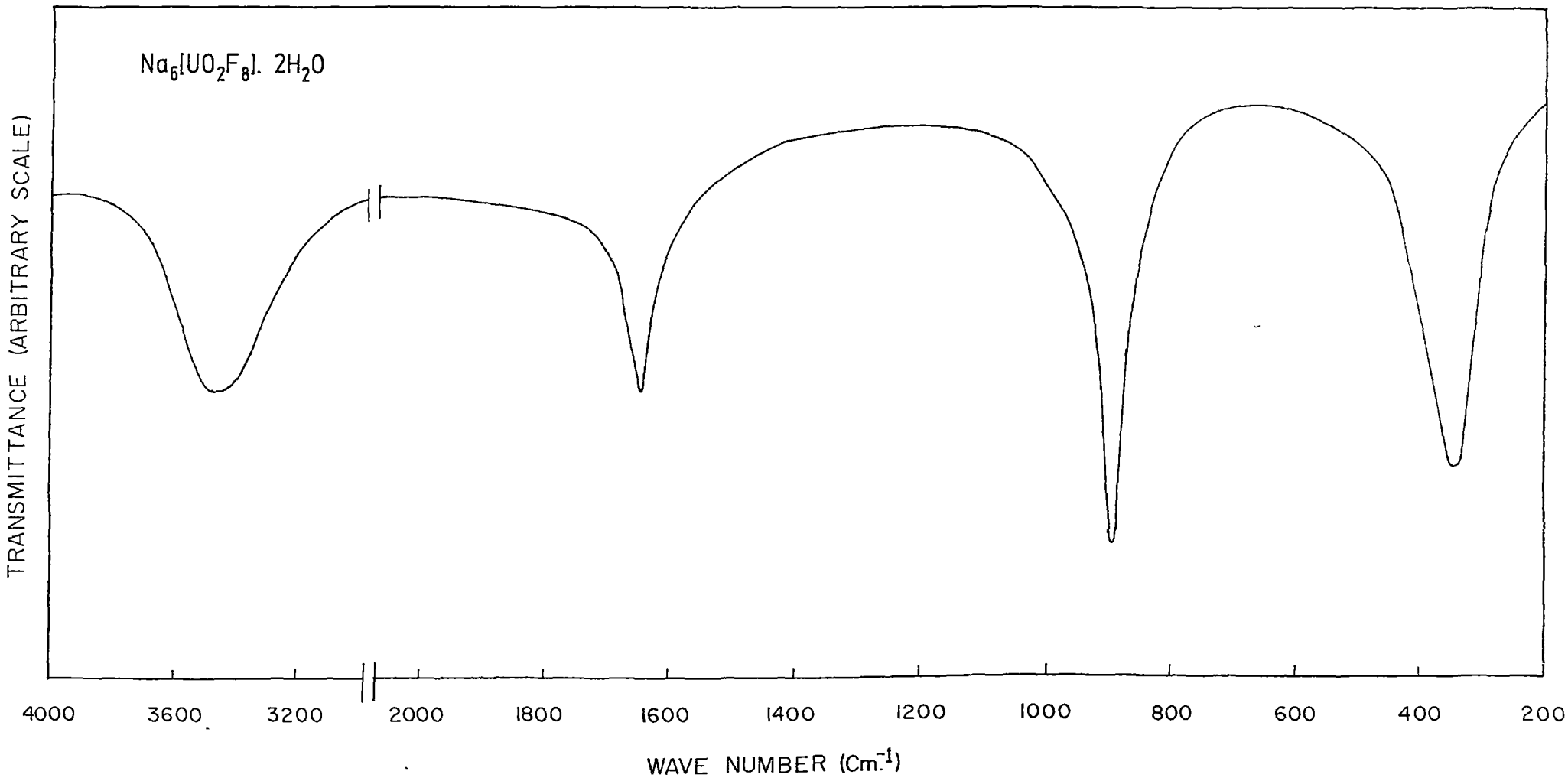


Fig. 5·10 : IR SPECTRUM

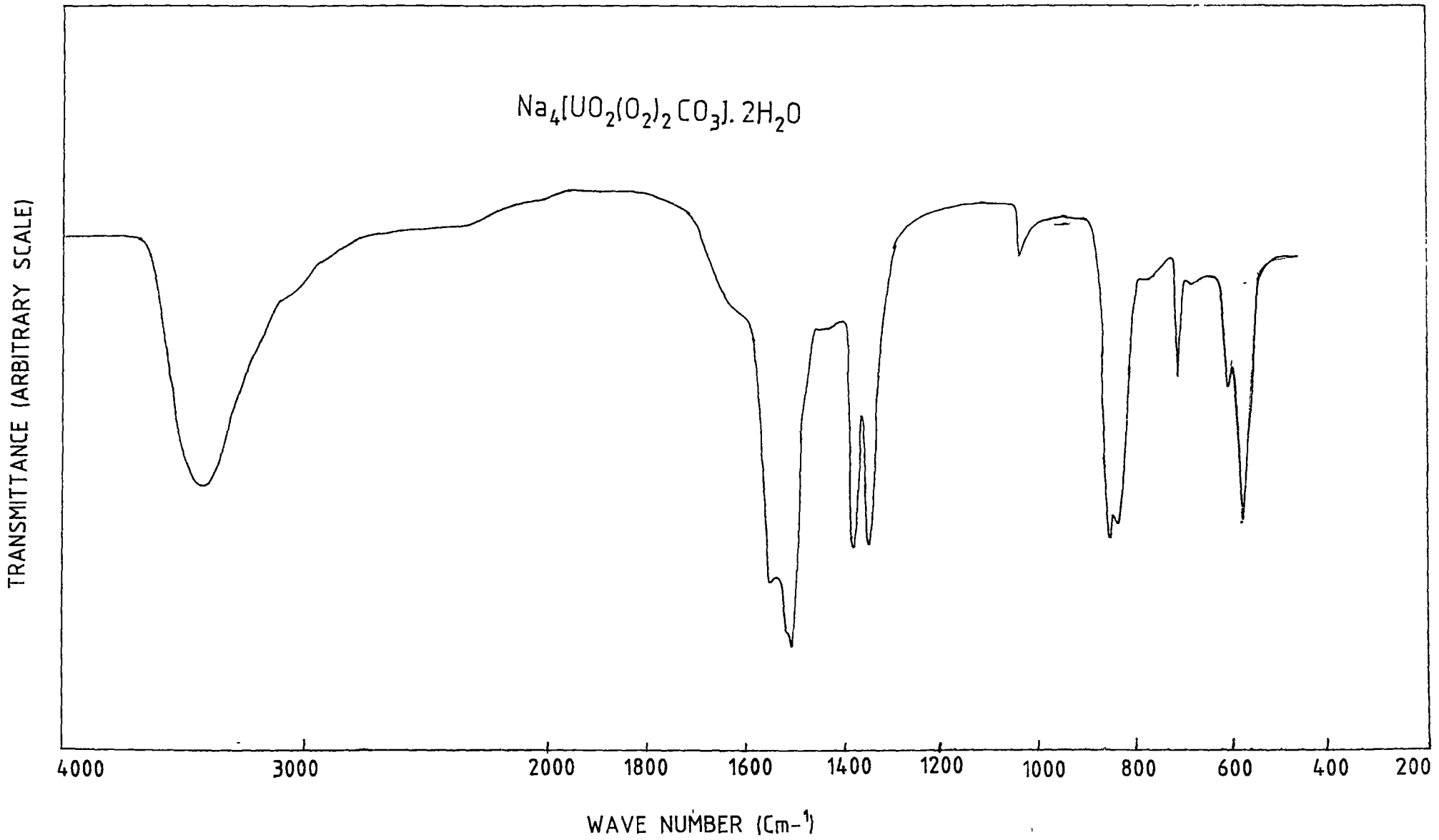


Fig. 5.11 : IR SPECTRUM

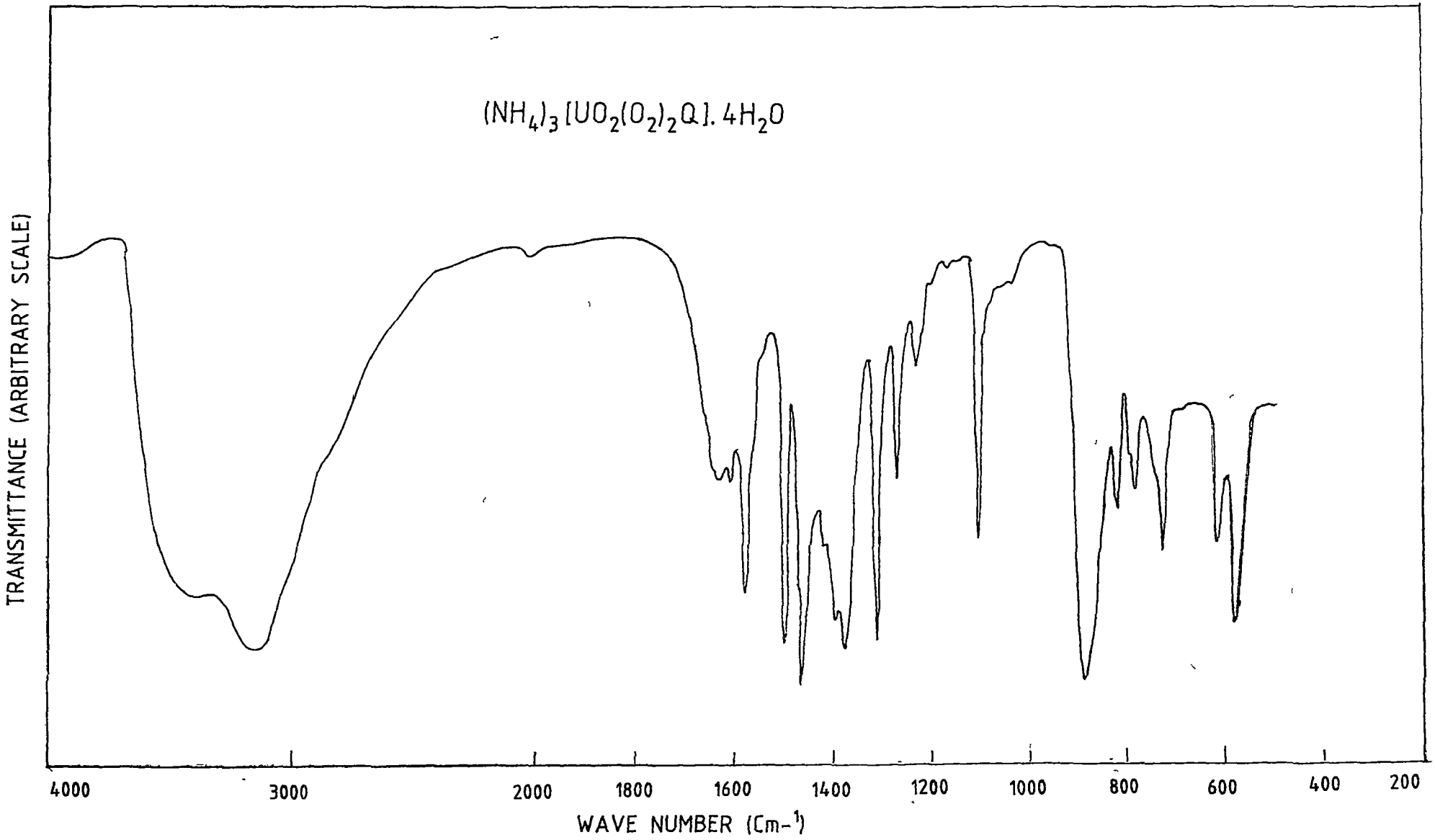


Fig. 5.12 : IR SPECTRUM

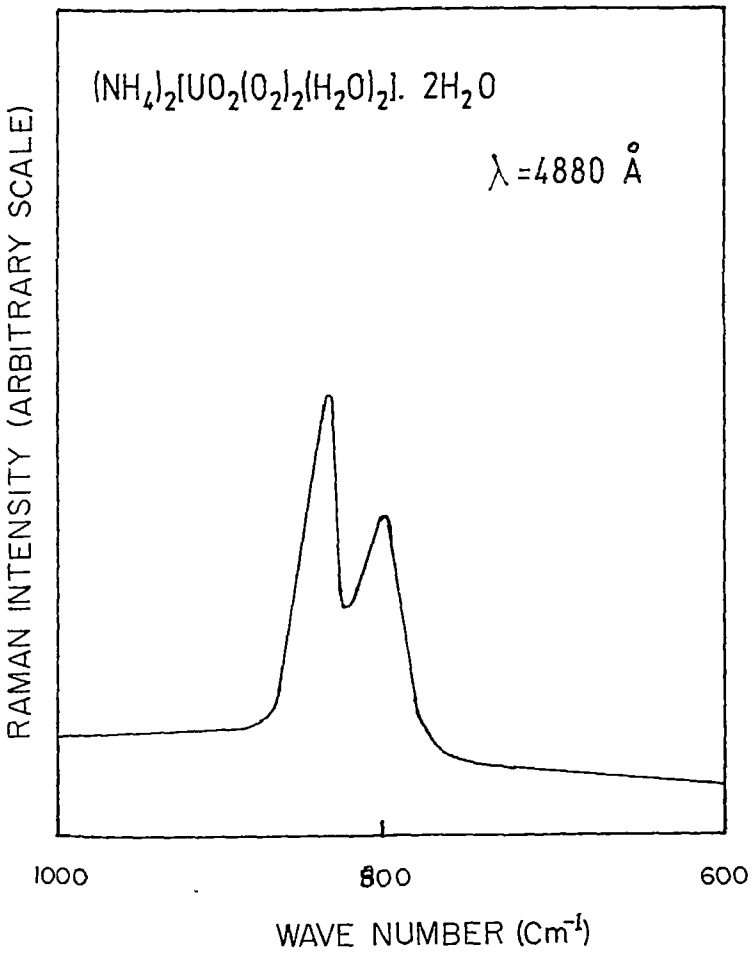


Fig.5·13: LASER RAMAN SPECTRUM

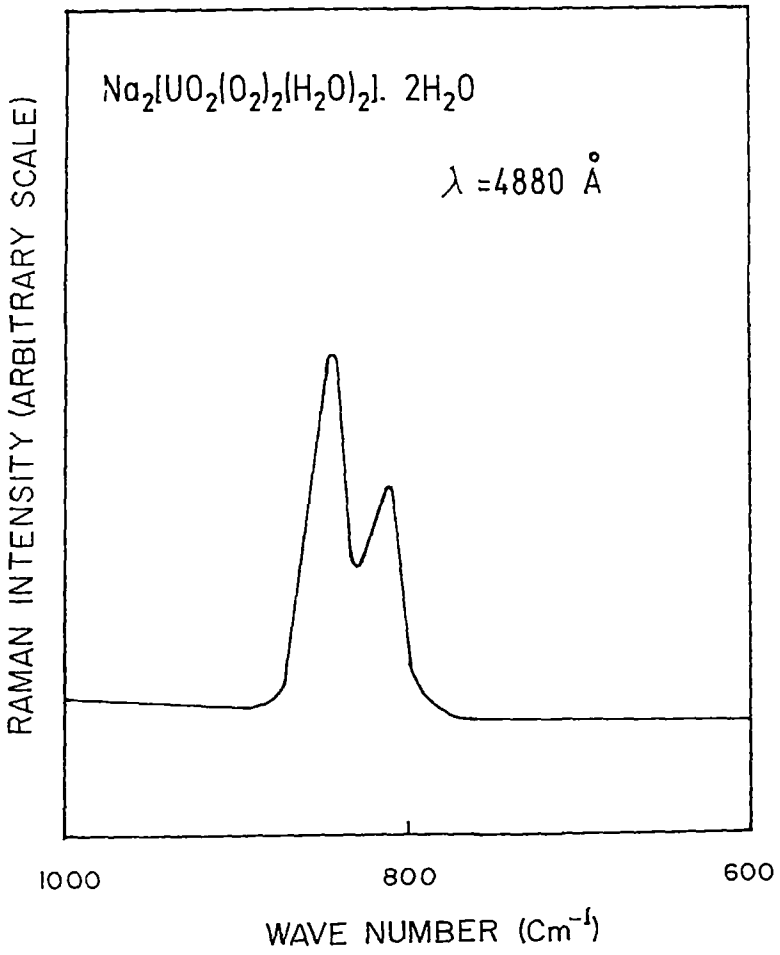


Fig.5·14: LASER RAMAN SPECTRUM

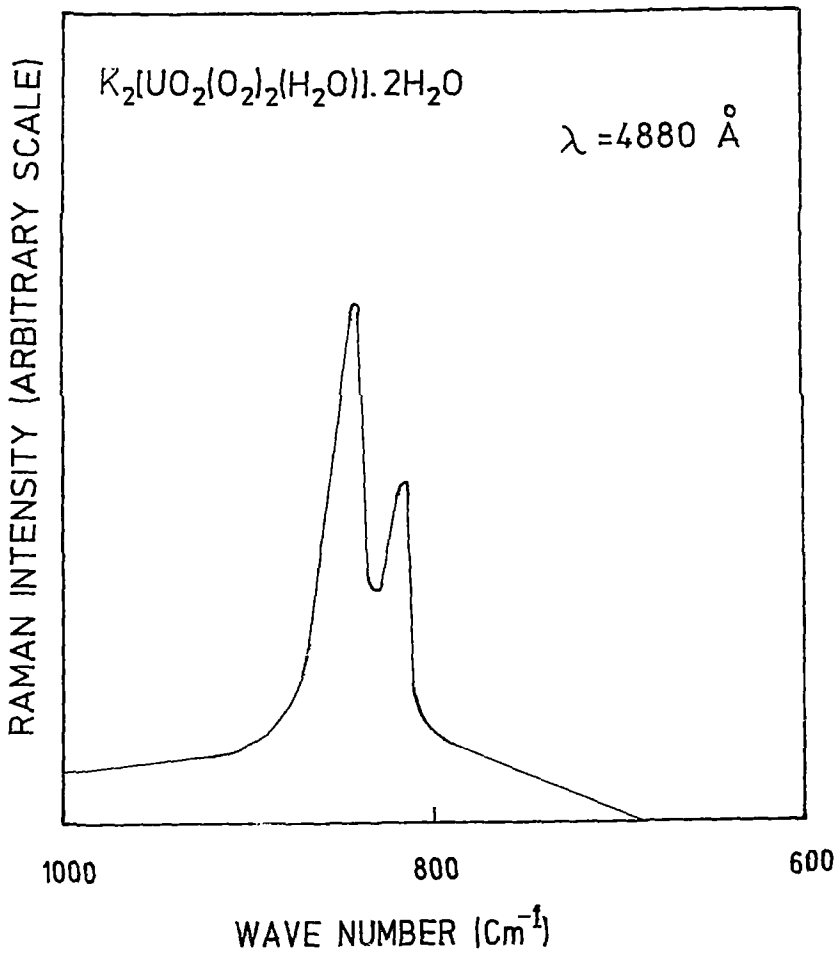


Fig. 5.15 : LASER RAMAN SPECTRUM

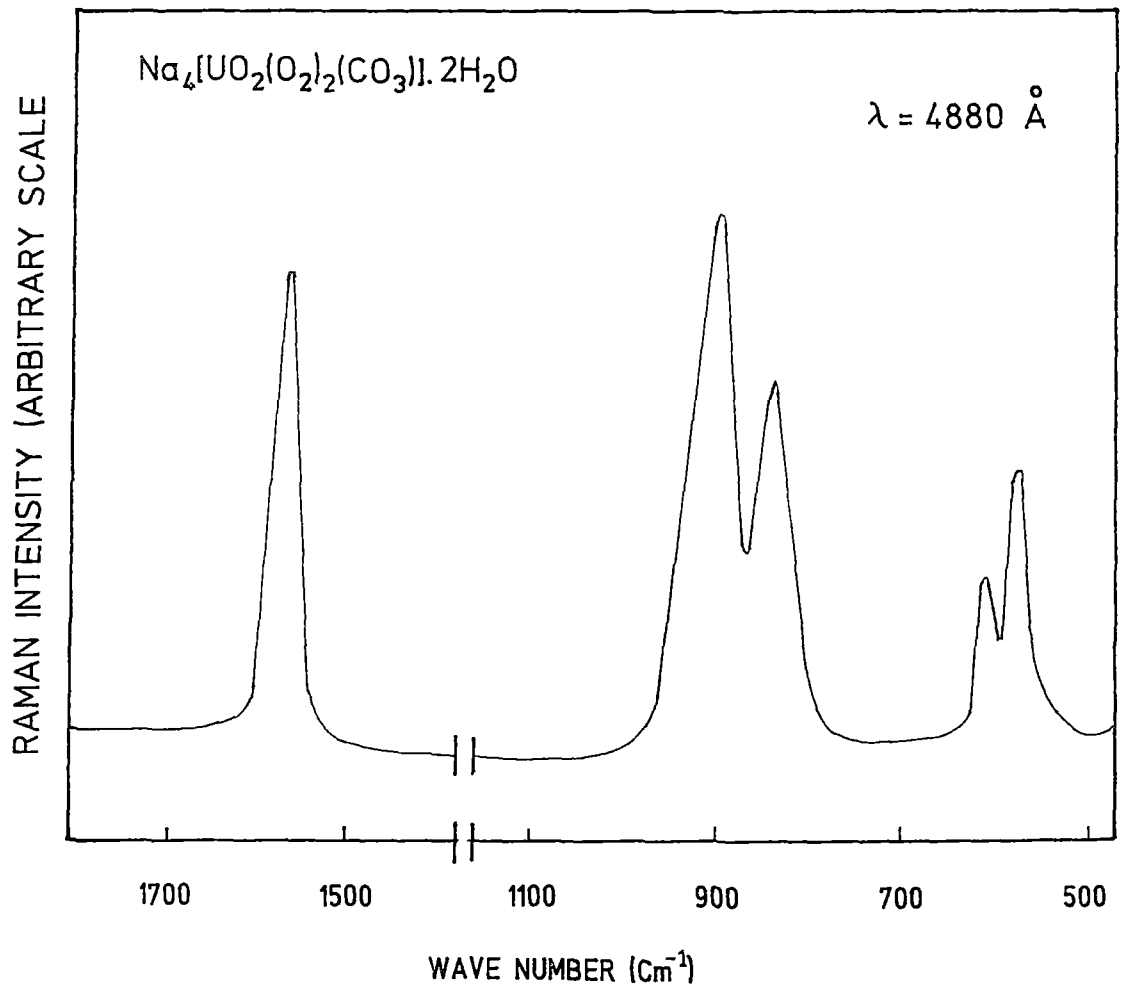


Fig. 5.16 : LASER RAMAN SPECTRUM

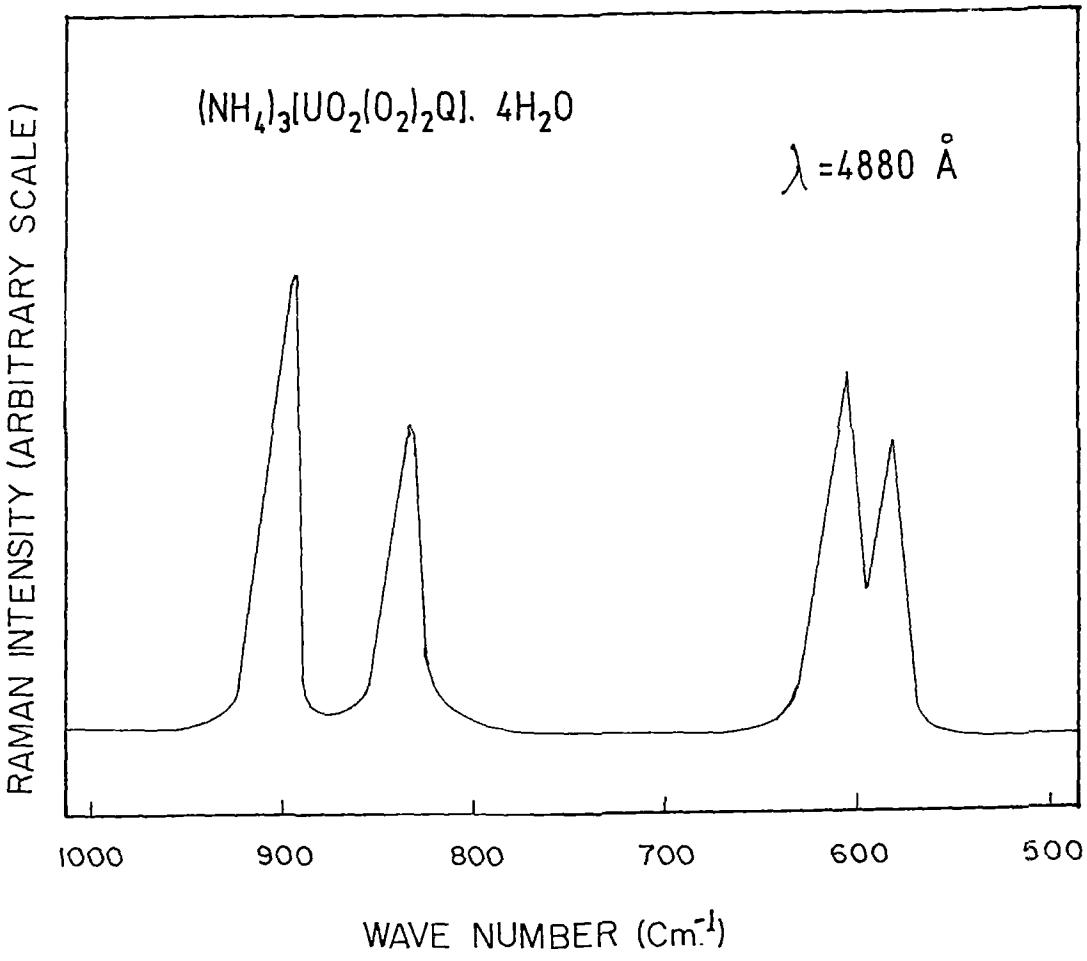
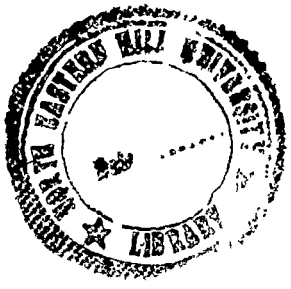


Fig.5·17 : LASER RAMAN SPECTRUM

Investigation of reactivity profiles of $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4, Na or K) with $SO_2.xH_2O$, $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = Na or K) with $CO_2(g)$ and $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4 or Na) with HF_2^-

(i) Reactions of $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4, Na *or* K) *with* $SO_2.xH_2O$

Peroxometal complexes exhibit a variety of reactions[21]. Relatively recent studies from this laboratory on the reactivity of peroxocomplexes of vanadium[22] and uranium[14] towards $SO_2(g)$ have shown that peroxo groups in these complexes got activated to different extents thereby allowing the isolation of different products at different stages of reaction. As a sequel to this endeavour, it was necessary to explore the reactivity profiles of the newly synthesised complexes with the similar substrates. Unlike the earlier studies on reactivity of $SO_2(g)$ on complex peroxouranate (1:1.5 $U:O_2^{2-}$ ratio) where SO_2 gas was reacted with the peroxo complex in solution, the present study was conducted using SO_2 solution (5-6%, aqueous solution). It may be recalled that in an earlier investigation on reactivity of $SO_2(g)$ with the peroxouranate, $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$, a well known peroxouranate(VI), $UO_2(O_2).4H_2O$ was obtained as an intermediate which ultimately underwent further reaction to produce $[UO_2(SO_4)_2]^{2-}$. In the present case, to the contrary, no isolable intermediate was formed and straightway newer sulphatouranates(VI) of definite stoichiometry was produced. On reacting $SO_2.xH_2O$ with the complexes $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4, Na or K) separately, the compounds first dissolved in the reaction medium. From the



solution, isolation of the product was facilitated by working up of the reaction at 100°C on a steam-bath. The pH of the reaction medium was recorded to be 2 at this stage. The product isolated after concentrating had no peroxide in it but contained sulphate as ascertained from a combination of chemical analyses and vibrational spectroscopy. The results of both chemical and physical studies characterised the compounds to be $A_2[UO_2(SO_4)_2].H_2O$ (A = NH_4 or K) and $Na_2[UO_2(SO_4)_2].4H_2O$, respectively. The sulphato complexes were diamagnetic in conformity with the presence of hexavalent uranium. Unlike in the case of peroxovanadate (V)[22] no reduction of the metal centre took place. Thus, in view of the above observation and in conjunction with the results of similar reactions described in the preceding section, it may sound logical to state at least empirically that the number of sulphates, attached to the metal centre, obtained from such reaction is proportional to the number of coordinated peroxide in the parent compound.

All the sulphato complexes are soluble in water and stable, as evidenced by both instantaneous and time dependent solution molar conductance data (*ca.*240-250 $\Omega^{-1}cm^2mol^{-1}$). The results are also in agreement with a 2:1 electrolytic nature of the compounds. The IR spectra provided clear evidence in support of the formulation of the complex species. While ν(U=O) (trans-linked O=U=O) for all the sulphato complexes was observed at 920 cm^{-1}, the characteristic ν_3 and ν_4 modes of coordinated sulphate were found to be split into three bands each in the region 1020-1230 cm^{-1} and 559-672 cm^{-1}, respectively .The splitting pattern is in

line with the lowering of symmetry of SO_4^{2-} form T_d to C_{2v}. Since one of the three split bands of ν_3(S-O) frequencies appeared at relatively higher wave numbers (>1200 cm^{-1}), it is believed that the SO_4^{2-} ligands in the compounds are coordinated to the UO_2^{2+} centre in a chelated manner[23]. As all the sulphato complexes were highly fluorescent, LR spectra did not provide any information. The IR spectrum also exhibited pattern characteristic of lattice water, while the ν (N-H) mode of NH_4^+ occurred at 1400 cm^{-1} for the ammonium salt.

(ii) Reactivity of $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ **(A = Na *or* K) *with*** CO_2**(g)**

Having conducted the reactions of the chosen compounds with $SO_2.xH_2O$, it was considered important to investigate similar reactions involving a much softer substrate e.g., CO_2. In an earlier report[14] from this laboratory, the reactivity pattern of CO_2(g) with $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$ was demonstrated. The product isolated after the prolonged passage of CO_2(g) through the suspension of the peroxo complex was dicarbonato complex of UO_2^{2+}. Incidentally, the course of the reaction of CO_2(g) was similar to that of the corresponding SO_2 reaction. In the present investigation, the complex $A_2[UO_2(O_2)_2(H_2O)].2H_2O$ interacted with CO_2 producing first $UO_2(O_2).4H_2O$ as an intermediate. As CO_2(g) has no redox character, the reaction was found to be very slow as expected.

After a prolonged (*ca.* 2h) passage of CO_2(g) through the suspension of the diperoxouranates, two distinct phases got separated out. While one was a yellowish-orange solution, the

other was a pale yellow precipitate. (The pH of the solution at this stage was 5). These were separated by filtration. The product from the solution was isolated by ethanol addition (vide Experimental). While the product isolated from the solution analysed as $A_2[UO_2(O_2)(CO_3)].2H_2O$ (A = Na or K), the one from the insoluble part assayed as $UO_2(O_2).4H_2O$. It may be mentioned *in passing* that the afore mentioned reactions provide a new route for obtaining heteroligand peroxocarbonatouranate(VI).

Incidentally, the bubbling of $CO_2(g)$ for a still longer duration (i.e., *ca.* 4h) did not bring about any change to the compositions of the complexes, $A_2[UO_2(O_2)(CO_3)].2H_2O$ (A = Na or K), and $UO_4.4H_2O$ formed after 2h as described above. This implies *inter-alia* that one of the two coordinated peroxides is relatively more activated. A plausible explanation of these observations may be that there occurs a competitive reaction between the thermodynamically more stable $UO_2(O_2).4H_2O$ and $A_2[UO_2(O_2)(CO_3)].2H_2O$ as evidenced by the poor yield of the latter compared to the former. It may be relevant to comment in this context that in view of what have been observed, the reactivity pattern of $CO_2(g)$ towards diperoxouranates(VI) is quite different from that of $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$. This might be attributable to higher degree of peroxygenation of the metal.

The peroxo(carbonato)uranates(VI) $A_2[UO_2(O_2)(CO_3)].2H_2O$ (A = Na or K) are yellowish-orange in colour. The NH_4^+ salt could not be isolated for reasons not discernible at the moment. The solution electrical conductances of these complexes are in the range, 210-250 $\Omega^{-1}cm^2\ mol^{-1}$ attesting the formulation of the complexes.

The IR spectra of the monoperoxo(carbonato)uranates(VI), $A_2[UO_2(O_2)(CO_3)].2H_2O$ (A = Na or K) provided evidence for trans-linked O=U=O, chelated peroxide, and carbonate (Table 5.3). Noteworthy is the large separation between the [$\nu_1(A_1)$,ν(C-O)] and [$\nu_5(B_2)$ ν(C-O) + δ(O-C-O)] modes appearing in the range 1559-1580 and 1344-1355 cm^{-1}, respectively. This indicates that carbonate is coordinated to the UO_2^{2+} centre as a chelated ligand[24]. The features originating from coordinated carbonate match well with other carbonato complexes dealt with earlier in this laboratory[3,14].

(iii) Reactivity of $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ *with* AHF_2 (A = NH_4 *or* Na)

On completion of the reactions of diperoxouranates with $SO_2.xH_2O$ and CO_2(g), it was considered worthwhile to know wheather the highly neucleofile, F^- reacted with highly peroxygenated diperoxouranates(VI) and if it were so, what would be the profiles of the reactions and what would be the product. With these being the aim, reaction of fluoride, taken in the form of acid fluoride,HF_2^-, was conducted with diperoxouranates(VI). A facile reaction took place between the chosen compounds and HF_2^-, which led to an easy access to the hitherto unreported fluorouranates(VI), $[UO_2F_8]^{6-}$. No reaction was observed with binary alkali fluorides such as AF (A = Na or K) demonstrating that an acidity of the reaction medium is needed for such reactions to occur. AHF_2 was conducive to meeting the two requirements i.e., supply of fluoride and acidity. This way the synthesis of a newer fluoro complex (Na or K salts) having an

unusual coordination number 8 for UO_2^{2+} was achieved. Although such a coordination number is quite uncommon among known complexes of UO_2^{2+} but is not unprecedented[25]. However, we considered it relevant to mention that the binary fluoro complex triad i.e. $[UO_2F_6]^{4-}$, $[UO_2F_7]^{5-}$ and $[UO_2F_8]^{6-}$, did not have any precedence in literature. While $[UO_2F_6]^{4-}$ and $[UO_2F_7]^{5-}$ have been very recently reported from our laboratory, $[UO_2F_8]^{6-}$ species is introduced now (present work).

The two salts, $(NH_4)_6[UO_2F_8]$ and $Na_6[UO_2F_8].2H_2O$ are light yellow in colour and soluble in water. The solution electrical conductances of these compounds have been measured. The values were 650 and 700 Ω^{-1} cm^2 mol^{-1}, respectively, attesting the formulations as assigned on the basis of elemental analysis. The IR spectra of fluorouranates, $(NH_4)_6[UO_2F_8]$ and $Na_6[UO_2F_8].2H_2O$ are very simple. The presence of a sharp band at *ca.* 900 cm^{-1} and those in the range, 347—365 cm^{-1} can be assigned to trans-linked O=U=O group and O_2U-F group, respectively. Somewhat sharp nature of the ν(U-F) band causes us to state that the fluoride is coordinated to the UO_2^{2+} centre. The two bands at 3440 and 1640 cm^{-1} in the spectra of Na^+ salt resemble in their shape and positions those of the ν(O-H) and δ(H-O-H) modes respectively of uncoordinated water. Similar to those observed for sulphatouranates, the bands were not properly developed in the LR spectra of the compounds owing to high fluorescence.

Conclusions

Further evidence for the importance of reaction pH for the formation and successful isolation of peroxouranates(VI) has been provided and methodology has been developed for the synthesis of diperoxouranates(VI) of the formula, $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4, Na or K). A plausible interpretation for the shift of ν(O-O) *as a function of an increase in the number of coordinated* peroxide (O_2^{2-}) has been advanced. Hopefully, this should be generalised in future.

Investigation of some aspects of reaction chemistry of $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = NH_4,Na or K) with inorganic substrates, viz., $SO_2.xH_2O$, CO_2(g), or HF_2^-, has contributed to the knowledge of reaction chemistry of peroxo-uranium(VI) complexes in addition to providing an unprecedented fluorocomplex of UO_2^{2+}, i.e., $[UO_2F_8]^{6-}$. The results of the present studies enlarges the scope for further research in this area.

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CHAPTER - VI

DEVELOPMENT OF A SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF URANIUM USING A NEW REAGENT, GUAIACOL*

In the course of syntheses and physico-chemical studies of complex uranates[1-5] in our laboratory and as a part of our intrinsic interest in the reaction of uranium with various phenolic derivatives, it was observed that o-hydroxyanisole, commonly known as guaiacol, instantaneously reacted with uranium(VI) in methanol under weakly alkaline conditions to give a yellowish-orange coloured chelate suitable for spectrophotometric determination of uranium at ppm levels. It was therefore decided to explore the suitability of this new reagent for the determination of the metal in solution.

The reagent guaiacol, to the best of our knowledge, has not been used for the determination of uranium so far. However, owing to

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the presence of potential donating groups in ortho position in the benzene ring (OCH_3 and OH groups at 1 and 2 positions, respectively of the benzene ring), it has got ability to form stable charge transfer complexes with appropriate metal ions. Its complex formation with Fe^{3+} and subsequent spectrophotometric determination of the metal ion in solution was reported[6]. In character, it resembles resorcinol which is also known to form similar complex[7] with UO_2^{2+}.

Uranium, being a chromogenic element, forms complexes with innumerable ligands displaying some or the other colour shades in solution. Accordingly, a number of photometric methods by using different reagents, have been known for its determination[8]. Among the reagents used for the determination of uranium, mention may be made of hydrogen peroxide[9] thiocyanate[10], ferrocyanide[11], resorcinol[7], sulfosalicylic[12] acid, pyrogallol[13], azide[14], ascorbic acid[15], ammonium thioglycolate[16], acetylacetone[17], 8-hydroxyquinoline[18], morin[19], dibenzoylmethane[20], arsenazo-III[21] pyridylazonaphthol[22] and its derivatives[23-25]. Of these reagents, arsenazo-III, dibenzoylmethane and morin are quite sensitive although not sufficiently selective. Certain derivatives of pyridylazonaphthol, especially bromoderivative, 2-(5-Br-PADAP)[26], [2(5-bromo-2-pyridylazo)5-diethylaminophenol), although most sensitive for spectrophotometric determination of uranium(VI) ($\varepsilon = 7.4 \times 10^4 l.mol^{-1}cm^{-1}$), can not be directly applied to rock samples because of poor selectivity.

In the present investigation, guaiacol has been proposed as a new reagent for spectrophotometric determination of uranium(VI). The main thrust of our present research is to test the efficacy of this new reagent for uranium determination and also to find out its suitability for application to real samples.

Detailed studies pertaining to the development of a new method (spectrophotometric) for uranium determination have been the subject matter of the present Chapter. Also highlighted are the advantages of the new method in terms of reproducibility, stability of the complex and operational simplicity. The reagent is easily available and nontoxic.

EXPERIMENTAL

Reagent grade chemicals were used throughout the investigation.

Guaiacol in methanol, 10% (v/v)

10 cm^3 of guaiacol was dissolved in methanol and the volume was made up to 100 cm^3 with methanol. The solution once made is stable for 1 week.

Uranyl Nitrate hexahydrate, 0.01 M

A 0.5 g of $UO_2(NO_3)_2.6H_2O$ was dissolved in distilled water in a 100 cm^3 volumetric flask and the volume was made up to the mark with distilled water. Uranium content of the stock solution was ascertained gravimetrically[27]. Appropriate dilute solutions were then prepared from this solution.

Tributylphosphate, 25% (v/v) in hexane

25 cm^3 of TBP (previously washed with sodium hydroxide)was dissolved in 50 cm^3 of hexane and then diluted to 100 cm^3 with hexane.

Ammonium nitrate, 60% (m/v) in water

A 60 g of NH_4NO_3 was dissolved in 50 cm^3 of distilled water and the solution was diluted to 100 cm^3 with distilled water.

Ethylenediamine tetra acetic acid, disodium salt, 1%

A 1.0g of disodium salt of ethylenediamine tetraacetic acid was dissolved in 100 cm^3 of distilled water.

Ammonia solution

Aqueous ammonia (density 0.9g cm^{-3}) was diluted with an equal volume of distilled water and it was used for pH adjustment.

Apparatus

Already described in Chapter II

Reaction conditions

Absorption spectra

Two solutions, one containing known amounts of U(VI) and guaiacol, and the other containing only guaiacol, both at pH 8.0, were prepared. The absorption spectra of the complex against the reagent blank and the reagent blank against methanol were recorded in the wavelength region, 330-450nm.

Effect of pH

Solutions containing known amounts of U(VI) and guaiacol were prepared in the pH range of 1.5-8.0 and the absorbances measured at 352 nm.

Effect of reagent concentration

Two sets of solutions, one set containing a fixed amount of U(VI) and varying amounts of guaiacol, and the other set containing only guaiacol (corresponding blank) were prepared at pH 8.0. The absorbances were measured at 352 nm against the corresponding reagent blank.

Adherence to Beer's law

Solutions containing a fixed amount of the reagent and varying amounts of U(VI) were prepared at pH 8.0 and the absorbances were measured at 352 nm.

Effect of foreign ions

Solutions containing 100 µg of U(VI), a 1000 fold excess of guaiacol, and varying amounts of foreign ions were prepared and the absorbances measured against the corresponding reagent blank at 352 nm. The total volume of the solution in direct measurements was 10 cm^3 and that in the extractive system was 25 cm^3.

Choice of solvents

As guaiacol was insoluble in water, the present study could not be conducted in an aqueous medium. Experiments involving solvents like chloroform, carbon tetrachloride, hexane, benzene, ethyl alcohol and methylalcohol etc. in which guaiacol was soluble, were conducted and the most satisfactory results were obtained with methanol as the solvent. A 40:60 (v/v) water:methanol medium gave equally satisfactory results.

Recommended procedures

1. Direct determination

Place 2 cm^3 of aliquot containing 5 to 800 µg of U(VI) into a 10 cm^3 volumetric flask and add 5 cm^3 of 10% guaiacol solution in methanol. Adjust the pH of the solution to 8.0 with a few drops of dilute ammonia solution and make up the volume to the mark with guaiacol solution in methanol. Stopper the flask, shake it and then keep aside for 5 min. Prepare a reagent blank similarly without using uranium and measure the absorbance of the complex against the reagent blank while covering the cuvettes. Deduce the amount of uranium from previously prepared calibration graph.

2. Extraction Spectrophotometric determination

Take an aliquot containing 15 to 800 µg of U(VI) in the presence of interfering ions into a 100 cm^3 separating funnel. Add to it 1 cm^3 of 1% EDTA, 25 cm^3 of 60% NH_4NO_3 solution and 5 cm^3 of 25% TBP in hexane. Shake the mixture for 2 min and keep for phase separation. Remove the aqueous phase, wash the organic phase with

distilled water and discard the aqueous phase. Add 15 cm^3 of guaiacol solution in methanol and adjust the pH of this solution to 8.0 with ammonia solution. Shake it for a few seconds. Yellowish-orange colour develops immediately. Transfer the methanol-TBP solution to a 25 cm^3 volumetric flask and make up the volume to the mark with methanol. Stopper the flask, shake it and then set aside for 5 min. Measure the absorbance of the solution at 352 nm against a similarly prepared reagent blank while covering the cuvettes. Prepare a calibration graph between the amounts of uranium taken and the corresponding absorbances by taking 15 to 800 µg of U(VI) and carrying through the procedure.

RESULTS

Absorption spectrum

The absorption spectrum of the complex is shown in Fig.6.1. From the figure it is evident that the complex has a maximum absorption (λ_{max}) at 352 nm. The absorption due to the reagent is negligibly small at this wavelength. However, a reagent blank was employed in further experiments.

Effect of pH

It was found that the absorbance remained constant in the pH range of 6.5 to 8.0. The absorption above this pH decreased because of precipitation of uranium as $U_2O_7^{2-}$. Many buffer systems like pyridine, monoethanolamine and hexamine were tried separately but none gave satisfactory results. A dilute ammonia solution was found to be most effective for pH adjustment.

Effect of reagent concentration

The absorbance increased with increasing amount of the reagent, guaiacol, and became constant when the reagent was present in a large excess(about 1000 fold molar excess over Uranium)

Adherence to Beer's law, molar absorptivity, Sandell's sensitivity and stability of the complex

Beer's law was found to be obeyed over a wide range i.e., 5 to 1200 µg U in 10 cm^3 of the solution (Fig. 6.2). The molar absorptivity and Sandell's sensitivity were found to be 3.75×10^3 $l.mol^{-1}cm^{-1}$ and 0.063 µg cm^{-2}, respectively. The colour of the complex was stable for more than 72 hours.

Composition of the complex

In order to find out the stoichiometry of the complex formed, Job's method of continuous variation was adopted (Table 6.1). From the results (Fig. 6.3) it was evident that the metal U(VI): Ligand (guaiacol) ratio was 1:2. Tentative structure of the complex is shown in Fig. 6.4.

Effect of diverse ions

To find out the effect of foreign ions on the colour development and subsequent determination of uranium(VI), recovery of 100µg of U(VI) in presence of different concentrations of interfering ions (by separate set of experiments) was found out. Results for <2% error in the determinations are shown in Table 6.2.

Precision and accuracy

The RSD (relative standard deviation) was found to be ±1.92% for nine replicate determinations of 200µg uranium(VI) over a period of nine consecutive days. The results are shown in Table 6.3. The accuracy of the method was found to be ±1.1% in the range of 200 to 800 µg of U(VI). The results are shown in Table 6.4. Statistical analyses were made based upon the results obtained from a series of solutions containing uranium in the range of 200 to 800 µg, because the corresponding absorbances fall in the region of least photometric error of absorbance measurements on the instrument.

DISCUSSION

The reagent guaiacol, works very satisfactorily for quantitative determination of uranium in solution. However, when the metal occurs in a sample in which interfering elements are present, for instance, a rock sample containing uranium, it is essential to selectively extract the metal ion prior to its spectrophotometric determination owing to the fact that no spectrophotometric method for uranium determination can directly be applied to rock sample solution. This is also true for the present method. For the present case, the extraction is achieved from either a neutral or a slightly acidic solution by a tributylphosphate (TBP) solution in hexane. The extraction is carried out in the presence of ammonium nitrate and disodium salt of EDTA. While ammonium nitrate acts as a salting out agent, the disodium salt of EDTA masks the interfering ions by complexation. It has been found that 1 cm^3 of 1% solution of EDTA disodium salt enables

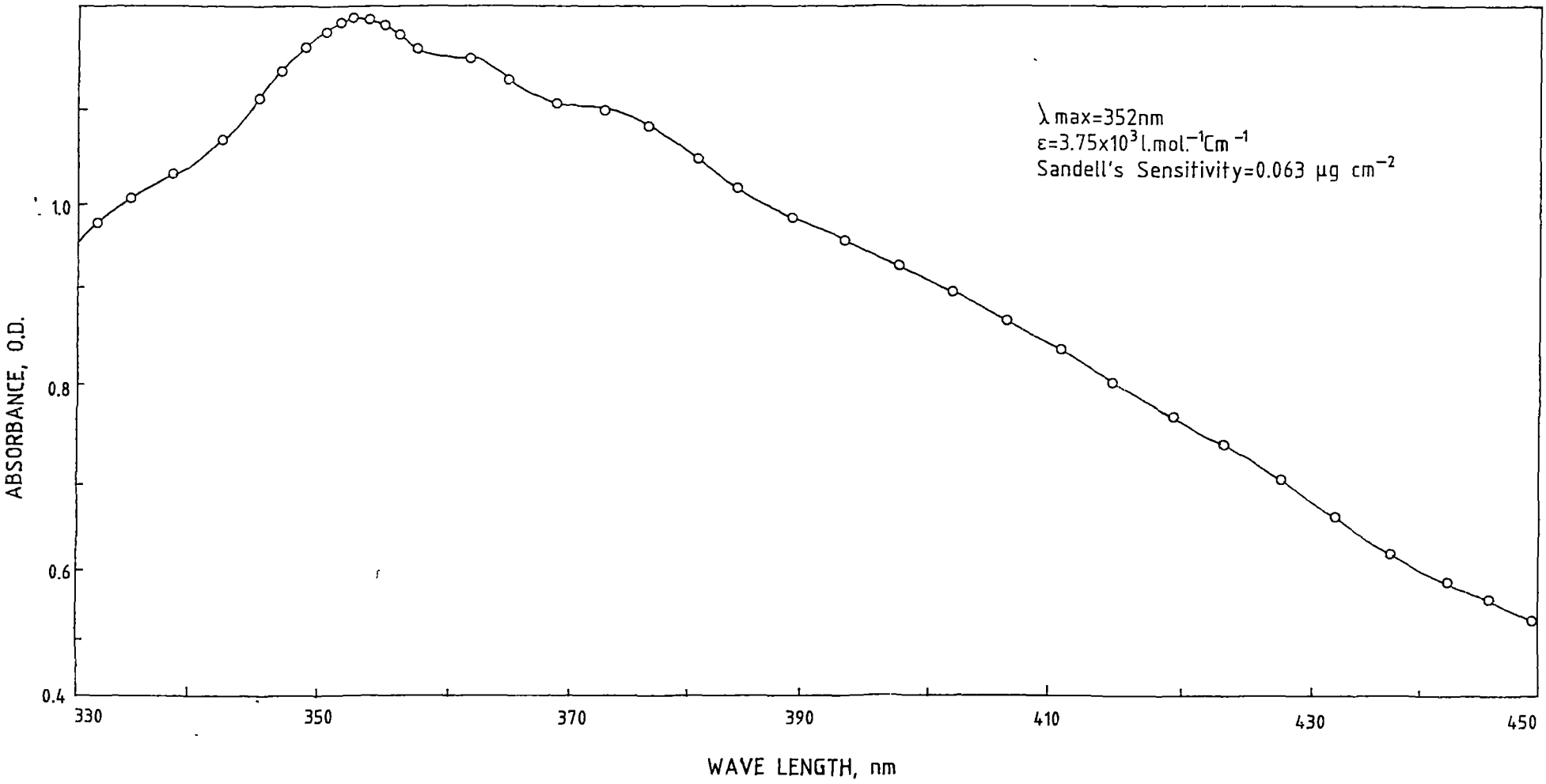


Fig.6.1: ABSORPTION SPECTRUM OF THE COMPLEX AGAINST REAGENT BLANK.(800µgU/10ml)

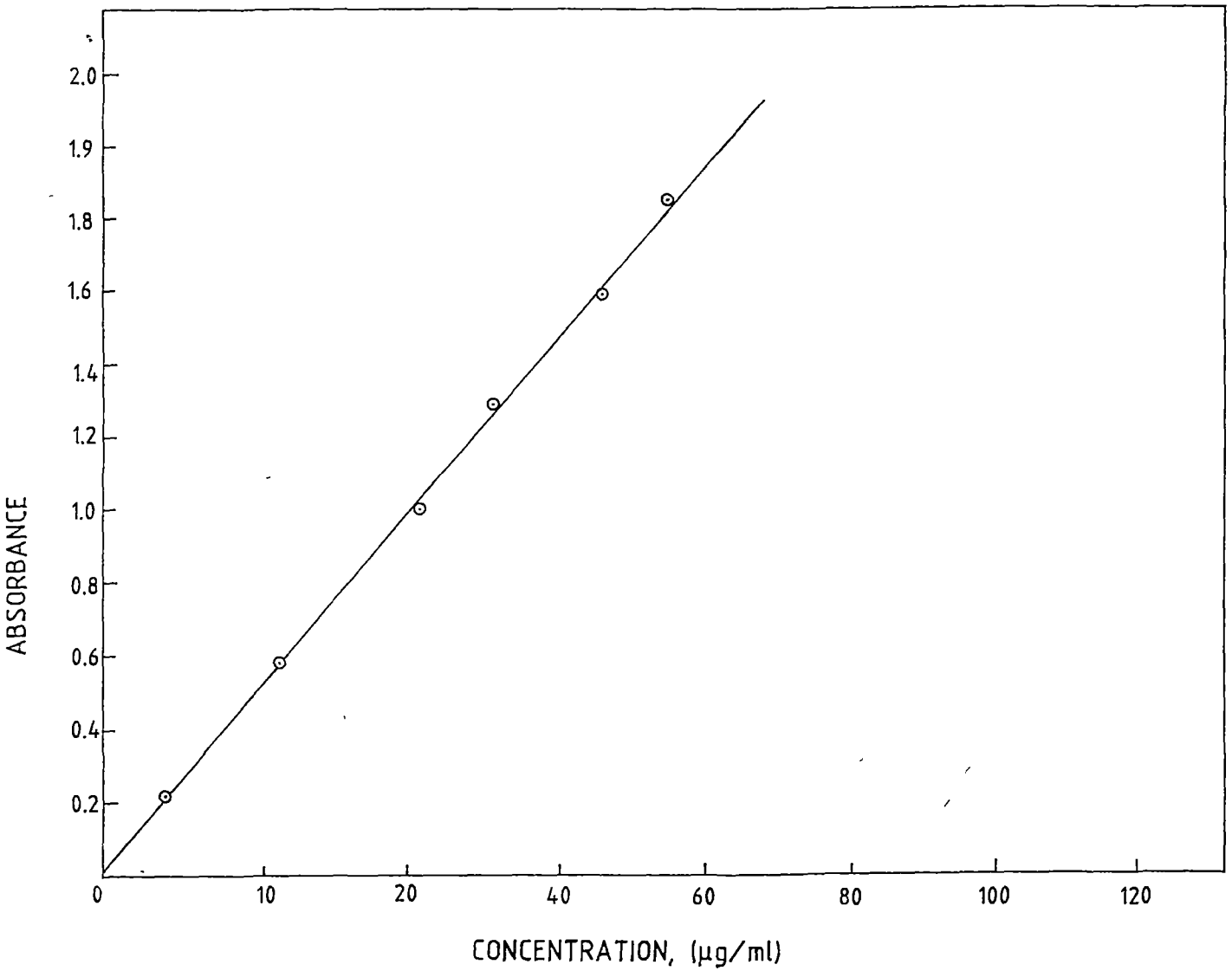


Fig. 6.2: PLOT OF ABSORBANCE Vs. CONCENTRATION (ADHERANCE TO BEER'S LAW)

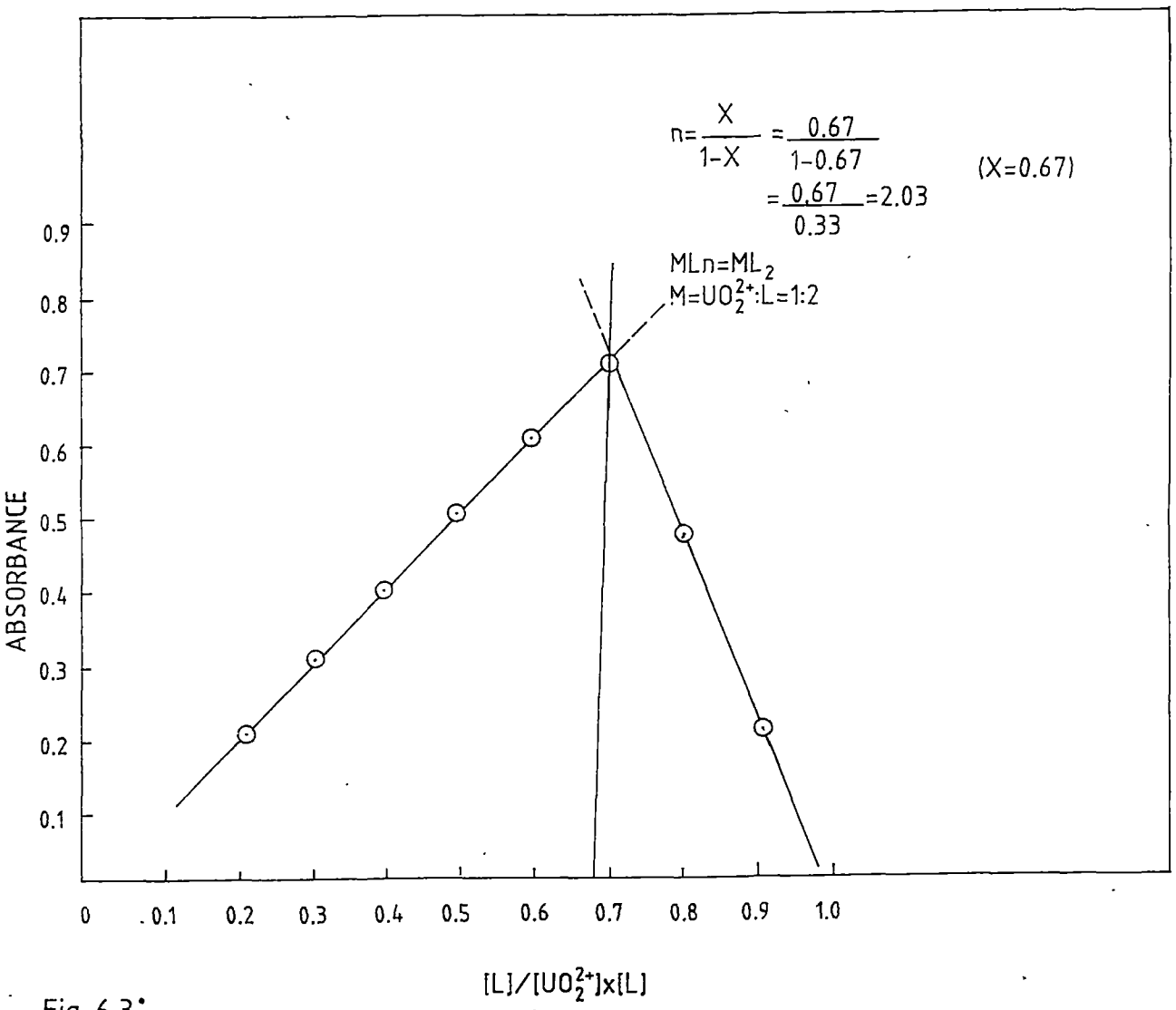
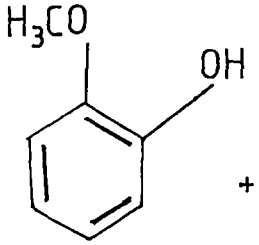
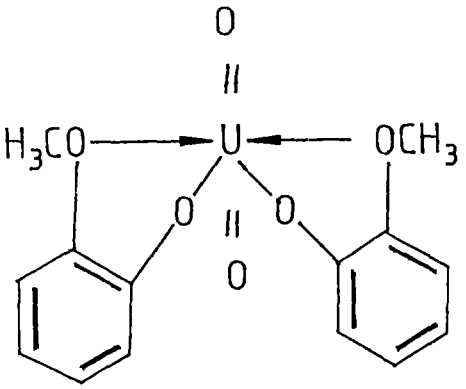


Fig. 6.3:
PLOT BETWEEN ABSORBANCE Vs. MOLE FRACTION OF LIGAND (GUAIACOL) IN TOTAL CONCENTRATION (JOB'S METHOD OF CONTINUOUS VARIATION)

(i) $UO_2^{2+} + 2C_7H_8O_2 \xrightarrow[6-8]{pH} (C_7H_7O_2)_2UO_2$

(Guaiacol)

(ii) 2  + $UO_2^{2+} \xrightarrow[6-8]{pH}$ 

(Guaiacol) (Chelate)

Fig. 6.4 : (i)Reaction Scheme, (ii)Tentative structure of the Chelate.

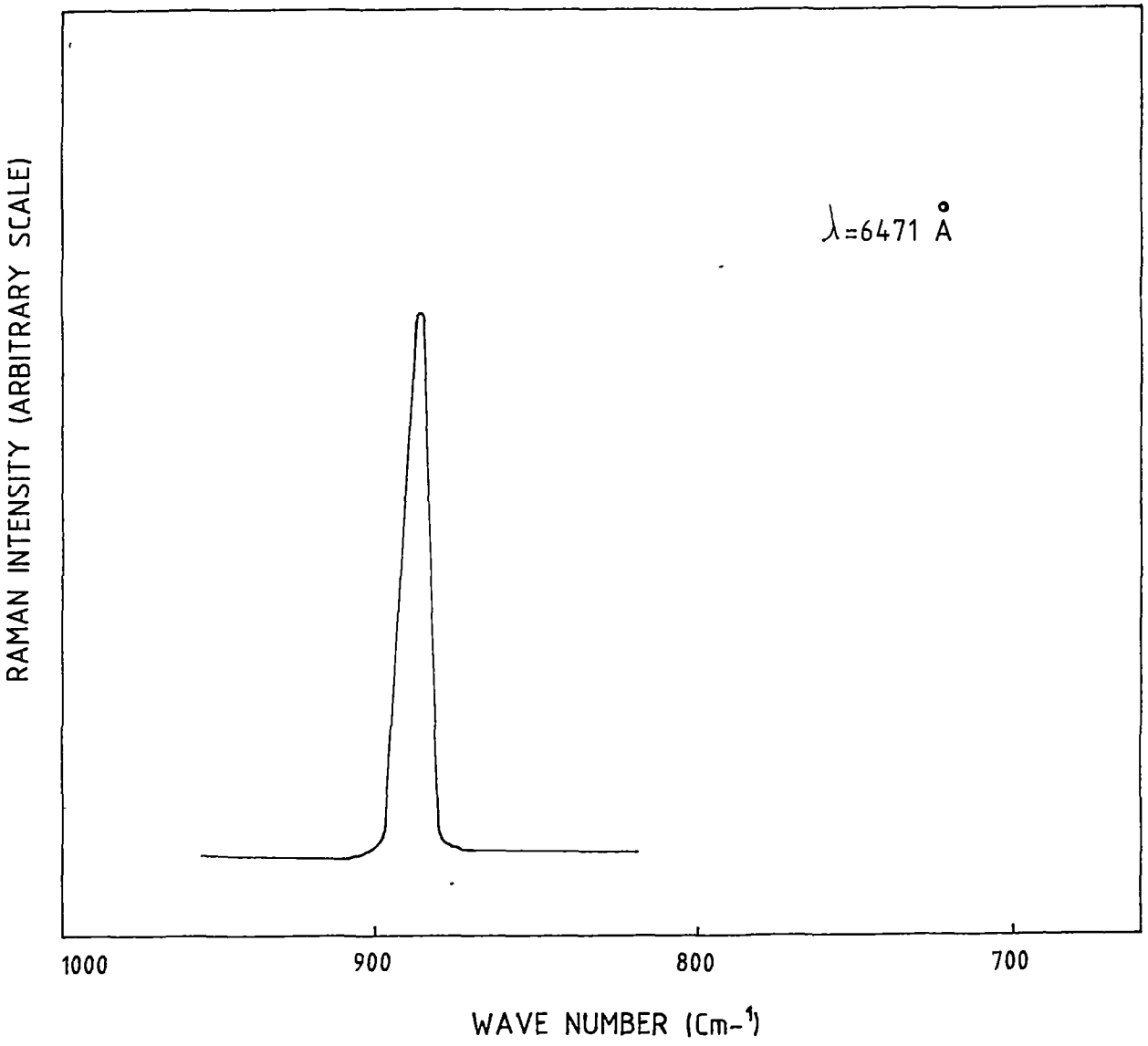


Fig. 6.5 : RAMAN SPECTRUM

masking of the usual interferents. It is worth mentioning that the above mentioned extraction procedure permits a very satisfactory determination of the metal content down to a concentration of 15 μg per 25 cm^3 of solution in the presence of most metals generally occurring in rock samples. It is recommended that for the determination of U(VI), the spectrophotometric experiments should be done in the presence of the extractant containing TBP since a quantitative stripping off of the metal may not be possible. It may be mentioned that an excess of the reagent is needed to determine the metal. This implies that the complex formed is rather weak. The novelty of the new extraction spectrophotometric method for uranium determination lies in the fact that the extraction is performed from neutral solution where the sequestering ability of EDTA is found to be maximum for most of the interfering elements especially Fe^{3+} which is a potential interferent unless otherwise EDTA is used. This observation has been recorded in contrast to other TBP extraction procedures mentioned in literature, most of which extracts U(VI) from a moderately high acidic solution. Another important observation was that a concentration of EDTA more than 1 cm^3 of 1% solution decreased the sensitivity of the method for uranium(VI) determination probably owing to the onset of EDTA complexation of U(VI) with increased concentration of EDTA.

Application of the method

In order to ascertain the efficacy of the new procedure, the method was applied to six different rock samples. First uranium

was separated from the sample solution as prescribed in procedure 2 and then the method was applied to determine the uranium content.

The rock sample solution was prepared by repeated treatment of 1.0 g of the sample (200 mesh) on a platinum dish with hydrofluoric and nitric acids. Organic matter was removed by fuming the residue with perchloric acid. About 1 cm^3 of HNO_3 and 25 cm^3 of distilled water were added to the residue and digested for 15 min. The solution was filtered through Whatman No.1 filter paper and the filtrate stored. The residue, if any, was fused with Na_2O_2 in nickel curcible and then extracted with dilute nitric acid solution. This extract was mixed with the filtrate. The solution was neutralised with dilute ammonia solution. A suitable aliquot was used to determine U(VI) following procedure 2 as mentioned in this Chapter. Results obtained by this method were compared with those obtained from fluorimetric and radiometric analyses of the sample under study. The results agree very well, as shown in Table 6.5.

Laser Raman spectroscopic study of the complex

LR spectrum of the solution used for determination of the metal in procedure 1, recorded at room temperature, showed a strong signal at 905 cm^{-1} (Fig.6.5). Because of large polarisability changes involved in the U=O bond, the band appeared as a strong one evidencing the occurrence of a trans-linked O=U=O centre[1] in the complex, as expected.

Conclusions

The new method is suitable for the determination of U(VI) in rock samples assaying more than 0.01% U_3O_8. High precision and accuracy permit routine determinations of uranium in rock samples using this method. Although the sensitivity of this method is not too high, it is comparable to those of $K_4Fe(CN)_6$[11], KSCN[10] and 8-quinolinol [18] and better than those of mercaptoacetate[16] and H_2O_2[9] methods.

Table 6.1: Job's method of continuous variation for the determination of the composition of the complex

UO_2^{2+} = 7 mmol											
L(Guaiacol) = 7 mmol											
cm^3 of UO_2^{2+}	0	1	2	3	4	5	6	7	8	9	10
cm^3 of L	10	9	8	7	6	5	4	3	2	1	0
O.D.	-	0.29	0.46	0.71	0.61	0.50	0.43	0.30	0.21	-	-
Mole fraction of Metal	-	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	-	-
Mole fraction of ligand	-	0.90	0.80	0.70	0.60	0.50	0.40	0.30	0.20	-	-

Table 6.2:Effect of diverse ions on the determination of 10 ppm of uranium(VI) in solution

Sl.No.	Ion	Tolerance Limits,ppm[a]	
		Direct Method	Extraction Method
1.	Acetate	4000	200
2.	Chloride	1000	1000
3.	Chlorate	200	200
4.	Citrate	500	500
5.	Bromide	2000	100
6.	Nitrate	1000	1000
7.	Phosphate	*	70
8.	Sulphate	50	50
9.	Tartrate	100	100
10.	Thiocyanate	100	100
11.	Aluminum	20	500
12.	Antimony(V)	*	100
13.	Barium(II)	200	1000
14.	Beryllium(II)	*	100
15.	Calcium(II)	200	500
16.	Cadmium(II)	*	200
17.	Cerium(III)	10	50
18.	Cerium(IV)	*	5
19.	Chromium(III)	20	40
20.	Chromium(VI)	*	10

Table 6.2 (Contd.)

21	Cobalt(II)	*	500
22.	Copper(II)	*	100
23.	Gold(II)	*	200
24.	Iron(III)	*	2000
25.	Lanthenum(III)	*	500
26.	Lead(II)	*	500
27.	Manganese(II)	*	500
28.	Magnesium(II)	500	500
29.	Molybdenum(VI)	20	30
30.	Nickel(II)	30	300
31.	Niobium(V)	15	50
32.	Potassium	2000	1000
33.	Sodium	2000	1000
34.	Strontium	200	1000
35.	Tantalum	*	40
36.	Tin(IV)	*	25
37.	Thorium(IV)	10	500
38.	Titanium(IV)	*	30
39.	Tungsten(VI)	*	40
40.	Vanadium(V)	*	75
41.	Yttrium(III)	*	500
42.	Zirconium(IV)	10	800
43.	Zinc(III)	*	100
44.	EDTA	2500	2500

[a] for less than 2% error.

* could not be applied because of interference

Table 6.3: Precision of U(VI) determinations (Uranium taken = 200µg)

Sample No.	U(VI) determined, µg	Mean µg	RSD %
1.	203.77		
2.	199.36		
3.	193.71		
4.	203.14		
5.	198.11	200.13±3.84	1.92
6.	194.96		
7.	203.77		
8.	201.25		
9.	203.14		

X_i	$\bar{X}$	$(X_i-\bar{X})$	$(X_i-\bar{X})^2$	$\Sigma(X_i-\bar{X})^2$
203.72		+3.636	13.220	
199.36		-0.774	0.599	
193.71		-6.424	41.267	
203.14		+3.006	9.036	
198.11	200.134	- 2.024	4.096	118.439
194.96		-5.170	26.720	
203.77		+3.636	13.220	
201.25		+1.116	1.245	
203.14		+3.006	9.036	

$\sigma = [\Sigma(X_i-X)^2/(n-1)]^{1/2}$ $\sigma = [118.439/(9-1)]^{1/2} = 10.8829/2.828 =$

RSD = (σ x 100)/Mean RSD = (3.848 x 100)/200.134 = 1.92%

Table 6.4 : Accuracy of uranium determinations

Sample No.	Amount taken µg	Amount determined µg	Deviation %
1.	200	197.90	-1.05
2.	400	403.47	+0.87
3.	600	597.87	-0.35
4.	800	803.49	+0.43

Table 6.5: Determination of uranium in rock samples (Average of 5 replicate determinations)

Sample No.	$\%U_3O_8$		
	New method	Fluorimetric Method	Radiometric Method
1.	3.37	3.40	3.35
2.	0.26	0.29	0.28
3.	0.33	0.34	0.35
4.	0.20	0.17	0.19
5.	0.42	0.41	0.41
6.	0.20	0.18	0.21

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LIST OF PUBLICATION

1. Complex Fluoroberyllates. Synthesis and Physicochemical Characterization of Mixed-Fluoro Complexes of Beryllium Containing Hydrogenoxalate ($HC_2O_4^-$), Glycinate, and Dihydrogenphosphate ($H_2PO_4^-$) as Coligands
   Mihir K.Chaudhuri, Nashreen S.Islam and Pranab K.Tarafder
   Bull.Chem.Soc.Jpn., 1992,65,522.

2. Guaiacol as an New Reagent for the Spectrophotometric Determination of Uranium
   P.K.Tarafder, G.V.Ramanaiah, M.K.Chaudhuri
   J.Radioanal. Nucl.Chem.,Letters, 1991,154,331.

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GUAIACOL AS A NEW REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

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Guaiacol, i.e. o-hydroxyanisole, gives a distinct color reaction with U(VI) suitable for spectrophotometric determination of the metal. The complex formed in the reaction has an absorption maximum at 352 nm. Optimum pH for the color development ranges from 6.5 to 8.5. The molar absorptivity and Sandell's sensitivity of the method were found to be 3.75×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$ and 0.063 $\mu g \cdot cm^{-2}$, respectively. Many anions and cations do not interfere up to 100 ppm. The method has been made very specific by selective extraction of U(VI) with TBP from a mixture of different cations and anions in the presence of 60% NH_4NO_3 as salting out agent followed by developing the color in the non-aqueous phase by adding guaiacol in methanol at pH 6.5 to 8.5. An amount as low as 30 µg of uranium(VI) per 10 ml of the solution could be satisfactorily determined with an RSD of $\pm$2.0%. The method was applied to rock samples after U(VI) had been extracted from a sample solution into 25% TBP in hexane. Results obtained by the new method compare very well with those of conventional fluorimetric and radiometric assays. The features of the method include excellent precision, rapidity, good selectivity, and ease of performance.

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INTRODUCTION

Uranium is a chromogenic element and therefore a number of photometric methods using different reagents have been known for its determination. Among the reagents used for the determination of uranium, mention may be made of hydrogen peroxide[1], thiocyanate[2], ferrocyanide[3], resorcinol[4], sulfosalicylic acid[5], pyrogallol[6], azide[7], ascorbic acid[8], ammonium thioglycollate[9], acetylacetone[10], 8-hydroxyquinoline[11], morin[12], dibenzoylmethane[13], and arsenazo-III[14,15]. Of these reagents dibenzoylmethane, morin, and arsenazo-III are quite sensitive although not sufficiently selective. Others are neither selective nor sensitive. In the course of syntheses and physicochemical studies of complex uranates[16-19] in our Laboratory and as part of our interest in the reaction of uranium with various phenolic derivatives, it was observed that o-hydroxyanisole, commonly known as guaiacol, rapidly reacted with uranium(VI) in methanol under slightly alkaline conditions to give a yellowish-orange color suitable for spectrophotometric determination of uranium on ppm level. It was therefore decided to explore its applicability for determination of the metal. The efficacy of guaiacol as a reagent for spectrophotometric determination of uranium is reported in this paper. Also highlighted are the advantages of the new method in terms of reproducibility, stability of the complex, and operational simplicity. The reagent is easily available and non-toxic.

EXPERIMENTAL

Preparation of reagents

Reagent grade chemicals were used throughout the investigation.

10% v/v guaiacol in methanol: dissolve 10 ml of guaiacol in methanol and make up the volume to 100 ml with methanol. The solution once made is stable for 1 week.

0.01M $UO_2(NO_3)_2.6H_2O$: Dissolve 0.5 g of $UO_2(NO_3)_2.6H_2O$ in distilled water in a 100 ml volumetric flask and fill up with distilled water. Uranium content of the stock solution was ascertained gravimetrically[20]. Prepare appropriate dilute solutions from this solution.

25% v/v tributylphosphate in hexane: dissolve 25 ml of TBP (previously washed with sodium hydroxide) in 50 ml of hexane and dilute to 100 ml with hexane.

60% m/v NH_4NO_3 in water: Dissolve 60 g of NH_4NO_3 in 50 ml of distilled water and dilute the solution to 100 ml with distilled water.

1.0% EDTA: Dissolve 1.0 g of disodium salt of ethylenediaminetetraacetic acid in 100 ml of distilled water.

Ammonia solution: Aqueous ammonia (density 0.9 g cm^{-3}) was diluted with an equal volume of distilled water and used for pH adjustment.

Apparatus: An ELICO pH meter model LI-120 equipped with combination electrodes was used for pH measurements.

Varian (634-S) double beam digital spectrophotometer equipped with 1.0 cm quartz cuvettes was used for ab-

sorbance measurements. Laser Raman spectra were recorded on a SPEX Ramalog model 1403 spectrometer.

Reaction conditions

Absorption spectra: Two solutions, one containing known amounts of U(VI) and guaiacol, and the other containing only guaiacol both at pH 8.0, were prepared.

The absorption spectra of the complex against the reagent blank and the reagent blank against methanol were recorded in the wavelength region of 330-450 nm.

Effect of pH: Solutions containing known amounts of U(VI) and guaiacol were prepared in the pH range of 1.5-8.0 and the absorbances measured at 352 nm.

Effect of reagent concentration: Two sets of solutions, one set containing a fixed amount of U(VI) and varying amounts of guaiacol, and the other set containing only guaiacol (corresponding blank) were prepared at pH 8.0. The absorbances were measured at 352 nm against the corresponding reagent blank.

Adherence to Beer's Law: Solutions containing a fixed amount of the reagent and varying amounts of U(VI) were prepared at pH 8.0 and the absorbances were measured at 352 nm.

Effect of foreign ions: Solutions containing 100 µg of U(VI), a 1000 fold excess of guaiacol, and varying amounts of foreign ions were prepared and the absorbances measured against the corresponding reagent blank at 352 nm. Total volume of the solution in direct measurement was 10 ml and that in extractive system was 25 ml.

Choice of solvents: As guaiacol is insoluble in water, the present study could not be conducted in an aqueous medium. Experiments involving solvents like

chloroform, carbon tetrachloride, hexane, benzene, ethyl alcohol, methyl alcohol etc., in which guaiacol is soluble, were conducted and the most satisfactory results were obtained with methanol as the solvent. A 40:60 water:methanol medium gave equally satisfactory results.

Recommended procedures

1. Direct determination

Take 2 ml aliquot containing 5 to 800 µg of U(VI) into a 10 ml volumetric flask and add 5 ml of 10% guaiacol solution in methanol. Adjust the pH of the solution to 8.0 with a few drops of dilute ammonia solution and make up the volume to the mark with guaiacol solution in methanol. Prepare a reagent blank similarly without using uranium and measure the absorbance of the complex against the reagent blank. Deduce the amount of uranium from a previously prepared calibration graph.

2. Extractive spectrophotometric determination

Take an aliquot containing 15 to 800 µg of U(VI) in the presence of interfering ions into a 100 ml separating funnel. Add to it 1 ml of 1% EDTA, 25 ml of 60% NH_4NO_3 solution and 5 ml of 25% TBP in hexane.

Shake the mixture for 2 min and keep for phase separation. Remove the aqueous phase, wash the organic phase with distilled water and discard the aqueous phase. Add 15 ml of guaiacol solution in methanol and adjust the pH of this solution to 8.0 with ammonia solution. Shake it for a few seconds. Yellowish-orange color develops immediately. Transfer the methanol-TBP solution to a 25 ml volumetric flask and make up the volume to the mark with methanol. Measure the absorbance at 352 nm

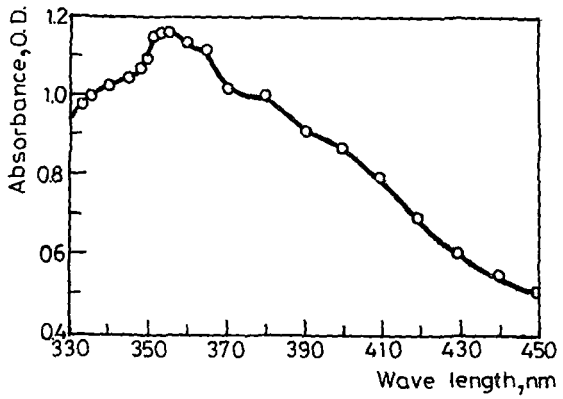

Fig. 1. Absorption spectrum of the complex against reagent blank (methanol)

against a similarly perepared reagent blank. Prepare a calibration graph between the amount of uranium taken and the corresponding absorbance by taking 15 to 800 µg of U(VI) and carrying through the procedure.

RESULTS

Absorption spectrum: The absorption spectrum of the complex is shown in Fig. 1. From the figure it is evident that the complex has a maximum absorption at 352 nm. The absorption due to the reagent is negligibly small at this wavelength. However, a reagent blank was employed in further experiments.

Effect of pH: It was found that the absorbance remained constant in the pH range of 6.5 to 8.0. The absorption above this pH decreased because of precipitation of uranium as $U_2O_7^{2-}$. Many buffer systems like pyridine, monoethanolamine and hexamine were tried separately but dilute ammonia was found to be the most effective.

Effect of reagent concentration: The absorbance increased with increasing amount of the reagent, guaiacol, and became constant when the reagent was present in a large excess (above 1000-fold molar excess over uranium).

Adherence to Beer's Law, molar absorptivity and stability of the complex: Beer's law was found to be obeyed in the range of uranium(VI) concentrations from 5 to 1200 µg per 10 ml of the solution. The molar absorptivity was found to be 3.75×10^3 $l.mol^{-1}.cm^{-1}$ and the color was stable for 72 h.

Composition of the complex: The metal [U(VI)] :Ligand [guaiacol] composition was found to be 1:2 by Job's method of continuous variation.

Effect of foreign ions: In order to verify the effect of foreign ions on the newly developed method, the efficacy of the reagent was tested separately in the presence of a number of ions.

- In the direct method, the amount in ppm shown against each ion did not cause any interference with the determination of 10 ppm uranium(VI) in a solution. Al(III) (20), Ce(III) (10), Cr(III) (20), Mo(VI) (20), Ni(II) (30), Mn(II) (30), Ba(II), Ca(II) and Sr(II) (200), Th(IV) (10), Zr(10), Nb(V) (15), ClO_4^-(200), Cl^-(1000), Br^-(2000), NO_3^-(1000), SO_4^{2-}(50), $S_2O_3^{2-}$(500), SCN^-(100), acetate(4000), BrO_3^-(1000), citrate(500), tartrate(100), EDTA(2500).
- In an extractive system, for the determination of 10 ppm of U(VI), the following concentrations of different foreign ions (ppm) did not interfere. Th(500), Zr(800), Fe(III) (2000), Cr(III) (40), Cr(VI) (10), Ce(III) (50), Ce(IV) (5), Cu(II) (100), Pb (500), Cd (200), Zn (100), Nb (50), Ta (40), Na (1000), K (1000), Ca (500), Mg(500), La (500), Ba(II) and

TABLE 1

Precision of U(VI) determination
(uranium taken = 200 μg)

Sample No.	U(VI) determined, μg	Mean, μg	RSD, %
1	203.77		
2	199.36		
3	193.71		
4	203.14	200.13 ± 3.84	1.92
5	198.11		
6	193.71		
7	203.77		
8	201.25		
9	203.14		

Sr(II) (1000), Yt(500), W(VI) (40), V(V) (75), Al(III) (500), Ti(IV) (30), Mn(II) (45), Co(II) (500), Ni(II) (300), Au (200), Sb(V) (100), Be (100), Sn(IV) (25), Cl^- (1000), SO_4^{2-} (50), NO_3^- (1000), Br^- (100), PO_4^{3-} (70), acetate (200), tartrate (100), EDTA (2500), NO_2^- (50), SCN^- (100).

These results make us to state that the new reagent is quite effective.

Precision and accuracy: The RSD was found to be ±1.92% from nine replicate determinations of 200 μg uranium(VI) over a period of 9 consecutive days. The results are shown in Table 1. The accuracy of the method was found to be ±1.1% in the range of 200 to 800 μg of U(VI). The results are shown in Table 2. Statistical analyses were made based upon the results obtained from a series of solutions containing uranium in the range of 200 to 800 μg, because the corresponding absorbances fall in the region of lowest, photometric error of absorbance measurements of the instrument.

TABLE 2

Accuracy of uranium determination

Sample No.	Amount taken, µg	Amount determined, µg	Deviation, %
1	200	197.90	-1.05
2	400	403.47	+0.87
3	600	597.87	-0.35
4	800	803.49	+0.43

DISCUSSION

The reagent, guaiacol, works very satisfactorily for quantitative determination of uranium in solution. However, when the metal occurs in a sample in which interfering ions are present, for instance, a rock sample containing uranium, it is necessary to perform a selective extraction of the metal prior to its spectrophotometric determination. The extraction is achieved from either a neutral or a slightly acidic solution by a tributyl phosphate (TBP) solution in hexane. The extraction is carried out in the presence of ammonium nitrate and disodium salt of EDTA. While ammonium nitrate acts as a salting out agent, the disodium salt of EDTA traps the interfering ions by complexation. It has been observed that 1 ml 1% solution of EDTA disodium salt enables masking of the usual interferences. It is notable that the above mentioned extraction procedure permits a very satisfactory determination of the metal content down to a concentration of 15 µg per 25 ml of solution in the presence of most of the cations generally occurring in rock samples. It is recommended that for the determination of U(VI), the spectrophotometric experiments should be done in the presence of the extractant containing TBP since a quantitative stripping off of

the metal may not be possible. A point worth mentioning is that an excess of the reagent is needed to determine the metal. This implies that the complex formed is rather weak.

Application of the method: In order to ascertain the efficacy of the new procedures, the method was applied to six different rock samples. First uranium was separated from the sample solution as prescribed in procedure 2 and then the method was applied to determine the uranium content.

The rock sample solution was prepared by repeated treatment of 1.0 g of the sample (200 mesh) on a platinum dish with hydrofluoric and nitric acids. Organic matter was removed by fuming the residue with perchloric acid. About 1 ml of HNO_3 and 25 ml of distilled water were added to the residue and digested for 15 min. The solution was filtered through Whatman no. 1 filter paper and the filtrate stored. The residue, if any, was fused with Na_2O_2 in a nickel crucible and then extracted with dilute nitric acid solution. This extract was mixed with the filtrate. The solution was neutralized with dilute ammonia solution. A suitable aliquot was used to determine U(VI) following procedure 2 as given in this paper. Results obtained by this method were compared with those obtained from fluorimetric and radiometric analyses of the sample under study. The results agree very well, as is shown in Table 3.

Laser Raman spectrum of the solution used for determination of the metal in procedure 1, recorded at room temperature, showed a strong signal at 905 cm^{-1}. Because of large polarizability changes involved in the U-O bond, the band appeared as a strong one evidencing the occurrence of a trans-linked O=U=O center[16] in the complex, as expected.

TABLE 3

Determination of uranium in rock samples.
(Average 5 replicate determinations)

Sample No.	% U_3O_8		
	New method	Fluorimetric method	Radiometric method
1	3.37	3.40	3.35
2	0.26	0.29	0.28
3	0.33	0.34	0.35
4	0.20	0.17	0.19
5	0.42	0.41	0.41
6	0.20	0.18	0.21

CONCLUSION

The new method is suitable for the determination of U(VI) in rock samples assaying more than 0.01% U_3O_8. High precision and accuracy permit routine determination of uranium in rock samples using this method. Although the sensitivity of this method is not too high, it is comparable to those of the $K_4Fe(CN)_6$[3], KSCN[2] and 8-quinolinol[11] methods and better than those of the mercaptoacetate[9] and H_2O_2 methods[1].

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Complex Fluoroberyllates. Synthesis and Physicochemical Characterization of Mixed-Fluoro Complexes of Beryllium Containing Hydrogenoxalate ($HC_2O_4^-$), Glycinate, and Dihydrogenphosphate ($H_2PO_4^-$) as Co-Ligands

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Synthesis of novel mixed complex fluoroberyllates of the types $M_2[BeF_3(HC_2O_4)]\cdot H_2O$ ($M=NH_4$ or Na) $K_2[BeF_3(HC_2O_4)]$, $M_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$ ($M=NH_4$ or Na), and $M_2[BeF_2(H_2PO_4)_2]$ ($M=NH_4$ or K) has been achieved from the reaction of $Be(OH)_2$ with MF and the corresponding co-ligands viz., oxalic acid, glycine and orthophosphoric acid, at pH ca. 2. Vibrational spectroscopic evidences have been provided in respect of co-ordinated F and the ligands $HC_2O_4^-$, $NH_2CH_2COO^-$, or $H_2PO_4^-$. IR spectra of ammonium salt of the complexes demonstrate the presence of hydrogen bonding.

The chemistry of fluoroberyllium compounds is gaining fast momentum probably due to many unusual properties which make some of them highly useful industrially.[1] Notable applications are, for instance, in the manufacture of glass,[1,2] as coating materials, and in nuclear technology.[1] Biological implications of beryllium fluorocomplex are also documented in literature.[3] Significantly some fluoroberyllates are known to be ferroelectric.[4,5] Unfortunately, however, there is only a very limited accessibility of such compounds, especially mixed fluoroberyllates.

For a number of years we have been trying our hands in the field of fluoro and mixed fluoro metal compounds for a variety of reasons.[6] The interesting properties and applications of fluoroberyllium species[1-5,7] prompted us to undertake studies on fluoro chemistry of the metal.

The main concerns were to identify appropriate co-ligands, improvise practical routes to newer mixed fluoroberyllates, and isolate and characterize the compounds. We considered this to be important to provide new materials amenable to physical studies. Another important aim was to demonstrate the new synthesis directly from $Be(OH)_2$. This would reduce the extra steps involved in the preparation of BeF_2, a commonly used starting material for fluoroberyllates.[1] The co-ligands have been drawn from the anions of a dicarboxylic acid, $HC_2O_4^-$, an aminocarboxylic acid, $NH_2CH_2COO^-$ and a tribasic acid, $H_2PO_4^-$, such that target species are obtained.

The synthesis of new compounds of the types $M_2[BeF_3(HC_2O_4)]\cdot H_2O$ ($M=NH_4$, Na, or K) $M_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$ ($M=NH_4$ or Na) and $M_2[BeF_2(H_2PO_4)_2]$ ($M=NH_4$ or K) and the results of some physicochemical studies on them constitute the subject matter of the present report.

Experimental

The chemicals used were analytical reagent grade products. Infrared spectra were recorded on a Perkin Elmer Model 983 spectrophotometer and Laser Raman (LR) spectra on an instrument described earlier.[8] The pH values of the reaction solutions were measured with an Elico model LI 120 pH meter and also with indicator paper (BDH).

Synthesis. Ammonium and Sodium Trifluoro(hydrogenoxalato)beryllate Monohydrate, $M_2[BeF_3(HC_2O_4)]\cdot H_2O$ ($M=NH_4$ or Na) and Potassium Trifluoro(hydrogenoxalato)-beryllate, $K_2[BeF_3(HC_2O_4)]$. To a slution of $BeSO_4\cdot 4H_2O$ (1.0 g, 5.65 mmol) in water (150 cm³), dilute NaOH solution was added slowly with continuous stirring. The precipitate of $Be(OH)_2$ was filtered and washed 5 to 6 times with water. $Be(OH)_2$ was transferred into a polyethylene beaker. To it were added water (10 cm³) and 16.95 mmol each of solid MF ($M=NH_4$, Na or K) and $H_2C_2O_4\cdot 2H_2O$ with stirring.

The mixture was heated on a steam bath for ca. 20 min to obtain a clear solution. The pH of the solution was recorded to be 2. The reaction solution was allowed to cool and to this ethanol was added to precipitate the product. The product was filtered and washed 3 to 4 times with ethanol and dried in vacuo over conc. H_2SO_4. Yield 1 g (85%) for $(NH_4)_2[BeF_3(HC_2O_4)]\cdot H_2O$, 1.1 g (88.7%) for $Na_2[BeF_3(HC_2O_4)]\cdot H_2O$ and 1.25 g (95%) for $K_2[BeF_3(HC_2O_4)]$.

Ammonium and Sodium Trifluoro(glycinato)beryllate Monohydrate, $M_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$ ($M=NH_4$ or Na). To an aqueous suspension of $Be(OH)_2$, obtained from $BeSO_4\cdot 4H_2O$ (1.0 g, 5.66 mmol) in a similar way to that described in the preceding synthesis, were added water (10 cm³) and 16.95 mmol each of MF ($M=NH_4$ or Na) and glycine with continuous stirring. The mixture was heated over a steam bath for ca. 30 min. The pH of the reaction solution was 2–2.5. The solution was cooled to room temperature. Addition of ethanol to this afforded a white microcrystalline product. The compound was separated by filtration, washed 4 to 5 times with ethanol and dried in vacuo over conc. H_2SO_4. Yield 1 g (91%) for $(NH_4)_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$ and 1 g (87%) for $Na_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$.

Ammonium and Potassium Bis(dihydrogenphosphato)di-fluoroberyllate $M_2[BeF_2(H_2PO_4)_2]$ ($M=NH_4$ or K). To an aqueous suspension of $Be(OH)_2$ obtained from $BeSO_4\cdot 4H_2O$ (1.0 g, 5.66 mmol) as mentioned above was added 16.95 mmol of MF ($M=NH_4$ or K) and 22.64 mmol of orthophosphoric acid (sp. gr. 1.75 g cm⁻³) under stirring. The mixture was heated over a steam bath for ca. 20 min and a clear solution was obtained. The pH of the solution was recorded to be 2.

Addition of ethanol to this solution afforded a white microcrystalline product. The compound thus obtained was filtered and washed 3 to 4 times with ethanol and dried in vacuo over conced H_2SO_4. Yield 1.3 g (83%) for $(NH_4)_2[BeF_2(HPO_4)_2]$ and 1.5 g (83%) for $K_2[BeF_2(HPO_4)_2]$.

Elemental Analysis. Beryllium was estimated gravimetrically.[9a] The fluoride content was determined gravimetrically as lead chlorofluoride.[9b] Oxalate was determined volumetrically with standard $KMnO_4$ solution.[9c] Phosphate estimation was accomplished gravimetrically[9d] and the results checked spectrophotometrically.[9e] Carbon, hydrogen, and nitrogen were determined by micro analytical methods at the Micro Analytical Laboratories, North Eastern Hill University, Shillong, India. While sodium content was ascertained by flame photometric method, the potassium was estimated by both flamephotometry as well as atomic absorption spectrophotometry.

Results and Discussion

Synthesis of fluoroberyllate complexes generally uses beryllium fluoride, BeF_2.[1] Its preparation requires high temperature[1,10] and since the compound is hygroscopic careful handling is recommended. In order to avert these difficulties as well as to demonstrate the efficacy of $Be(OH)_2$ as a source of the metal center, each of the new synthesis was carried out with a freshly prepared beryllium hydroxide sample. Two points were of interest in the present context viz. (i) asymmetry of the metal center and (ii) the occurrence of hydrogen bonding. While any mixed fluoroberyllate would fulfil the first condition, selection of an appropriate coligand is important to achieve the second point of contention. To reach the destination the chosen coligands were identified and synthetic reactions conducted at pH values of 2—2.5 of the reaction medium. Thus under the present reaction conditions $Be(OH)_2$ reacted with MF and oxalic acid to afford $M_2[BeF_3(HC_2O_4)]\cdot H_2O$ (M=NH_4 or Na) and $K_2[BeF_3(HC_2O_4)]$, in contrast to $M_2[BeF_2(C_2O_4)]$ (M=Na or K) and $K_2[Be_2F_6(C_2O_4)]\cdot H_2O$ reported in literature.[7] An acidic condition (pH 2) has, seems to us, favored $HC_2O_4^-$ formation which then coordinated to the metal center to produce trifluoro(hydrogenoxalato)beryllate, as obtained. Significant is the rarity, though not unprecedented,[11,12] of hydrogenoxalato as a ligand.

A glycinium fluoroberyllate $(NH_2CH_2COOH)_3H_2BeF_4$ was reported quite some time ago.[13] The compound which is a glycine adduct is very interesting because of its ferroelectric properties. Our interest was to develope glycine coordinated fluoroberyllates. This has been now possible through a direct interaction of $Be(OH)_2$ with alkali fluoride and glyH. It is believed that at pH 2–2.5, a coordinatively unsaturated fluoroberyllate was formed which then accommodated glycinate in its coordination sphere to provide $M_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$ (M=NH_4 or Na). Incidentally the experimental condition was conducive to the formation of glycinate ion enabling it to co-ordinate as an anionic ligand. The sequence of addition of the ligands i.e., MF followed by glycine is important since a reverse order did not yield the desired compound.

The dissociation of phosphoric acid, H_3PO_4, is highly pH dependent and it has been well established that the acid generates $H_2PO_4^-$ at pH below 4.[14] Based upon this knowledge strategy was worked out and the reaction conducted at pH 2 as described (see Experimental) to obtain $M_2[BeF_2(H_2PO_4)_2]$ (M=NH_4 or K). In this way an access to a number of novel mixed fluoroberyllate complexes could be made to provide materials for further research on their physical properties. The methods are direct and do not require BeF_2, thus offering many advantages.

Characterization and Assessment of Structure. The newly synthesized compounds are white micro-crystalline products stable for a prolonged period. In contrast to the insolubility of $M_2[BeF_3(HC_2O_4)]$ and $M_2[BeF_2(H_2PO_4)_2]$ the salts of fluoroglycinatoberyllate, $[BeF_3(NH_2CH_2COO)]^{2-}$, are highly soluble and stable in aqueous medium. The stability is attested by molar conductance lying between 232 and 238 $\Omega^{-1}cm^2mol^{-1}$. The values are also in agreement with a 2:1 electrolytic nature of each of them.

The common features of vibrational spectra of the compounds are the presence of two bands, one each at ca. 800s and at 380 m cm^{-1} which have been assigned to the ν(Be-F) and δ(F-Be-F) modes of coordinated fluoride.[1] Laser Raman signals at ca. 800 and ca. 385 cm^{-1} compliment the assignments. In addition, consequent upon the presence of O-donor ligands in all the three types of complexes the ν(Be-O) mode has been observed consistently at ca. 920 cm^{-1}. Pertinent is to mention that similar observations were made in the spectra of $BeCl_2$ complexes containing O-donor ligands.[1,15] A comparison of this result with that of chlorocompounds of the metal clearly indicates that change of halides does not have a significant effect on the Be-O band positions. Apart from the common features discussed above, each type of the complexes displays a pattern typical of itself. The most significant in the context of vibrational spectra of $M_2[BeF_3(HC_2O_4)]$ is an evidence for the occurrence of HC_2O_4 as the co-ligand. Though such examples are far less encountered, a strong band at 1630 cm^{-1} seems to be the distinctive feature.[12] The $K_2[BeF_3(HC_2O_4)]$ complex was chosen as a representative example for it did not contain H_2O. Both IR and I.R. spectra of this compound clearly showed intense signals at 1630 cm^{-1} (Table 1) supporting the contention. Fortunately, this band was also observed in the IR spectra of other two salts of the complex causing it to be a representative feature of the complexes under discussion. In addition, the IR frequencies at ca. 1670 [ν_{asym}(COO)] and ca. 1340 [ν_{sym}(COO)] were observed due to the coordination of HC_2O_4 through its carboxylate group, as expected.[16] Thus the vibrational spectroscopy adduced clean support to the formulation.

Glycine has different ways of coordination with a

Table 1 Analytical Data for the Complexes of Beryllium and Structurally Significant IR Bands of $M_2[BeF_3(HC_2O_4)]\cdot H_2O$ (M=NH_4 or Na) $K_2[BeF_3(HC_2O_4)]$ $M_2[BeF_3(NH_2CH_2COO)]\cdot H_2O$ (M=NH_4 or Na), and $M_2[BeF_2(H_2PO_4)_2]$ (M=NH_4 or K)

Compounds	Analysis/%								IR	Assignments
	Be	M	F	C_2O_4	PO_4	C	H	N		
$(NH_4)_2[BeF_3(HC_2O_4)]\cdot H_2O$	4 23		27 38	41 63	—	11 18	5 19	12 95		
	(4 31)		(27 25)	(42 08)		(11 48)	(5 31)	(13 40)	818 s,br	ν(Be F)
									347 m,br	δ(F-Be F)
									911 s	ν(Be-O)
									3450 s	ν(O-H)
									1657 s	δ(H O H)
									1668 s	ν_{asym}(COO)
									1310 m	ν_{sym}(COO)
									725 w	δ(CO_2)
$Na_2[BeF_3(HC_2O_4)]\cdot H_2O$	4 14	21 12	25 64	39 85		10 85	1 32			
	(4 11)	(21 0)	(26 02)	(40 18)		(10 97)	(1 38)		810 s,br	ν(Be F)
									545 m,br	δ(F Be-F)
									920 s	ν(Be-O)
									3445 s	ν(O H)
									1650 s	δ(H-O-H)
									1670 s	ν_{asym}(COO)
									1310 m	ν_{sym}(COO)
									720 w	δ(CO^{-2})
$K_2[BeF_3(HC_2O_4)]$	3 86	34 11	24 95	38 19		10 19				
	(3 86)	(33 52)	(24 44)	(37 74)		(10 30)			818 s,br	ν(Be-F)
									396 m,br	δ(F-Be F)
									911 s	ν(Be-O)
									1672 s	ν_{asym}(COO)
									1338 m	ν_{sym}(COO)
									719 w	δ(CO^{-2})
$(NH_4)_2[BeF_3(NH_2CH_2COO)]$ H_2O	4 70		29 18			12 89	7 21	20 80		
	(4 64)		(29 35)			(12 37)	(7 28)	(21 64)	802 s,br	ν(Be F)
									363 m,br	δ(F-Be F)
									930 s	ν(Be O)
									1610 s	ν(COO)
									3440 s	ν(OH)
									1657 s	δ(H O H)
$Na_2[BeF_3(NH_2CH_2COO)]\cdot$ H_2O	4 24	23 11	28 14			11 94	2 75	6 81		
	(4 41)	(22 54)	(27 93)			(11 77)	(2 97)	(6 87)	822 s,br	ν(Be F)
									363 m,br	δ(F-Be F)
									930 s	ν(Be O)
									1615 s	ν(COO)
									3438 s	ν(O-H)
									1629 s	δ(H-O H)
$(NH_4)_2[BeF_2(H_2PO_4)_2]$	3 38		13 55		70 15			9 88		
	(3 26)		(13 73)		(68 50)			(10 13)	810 s,br	ν(Be-F)
									372 m,br	δ(F Be F)
									922 s	ν(Be O)
									1104 s br	coord
									2854 w br	H_2PO_4
$K_2[BeF_2(H_2PO_4)_2]$	2 78	23 89	11 21		59 24					
	(2 83)	(24 53)	(11 92)		(59 46)				815 s,br	ν(Be F)
									373 m,br	δ(F-Be-F)
									926 s	ν(Be O)
									1108 s br	coord
									2922 w br	H_2PO_4

metal center and various possible modes of coordination can be ascertained from IR spectroscopic studies[17] The distinctive features in respect of coordinated glycine ligand in the present case is the consistent appearance of a band at ca 1610 cm^{-1}, well separated from the δ(H O H) mode (1645 cm^{-1}) of lattice water This observation as well as the absence of any absorption around 1700 cm^{-1} cause us to state that the co ligand occurs in its ionic form and attaches itself with the beryllium center through its carboxylic oxygen The band at 1615 cm^{-1} has been assigned to COO stretching mode[17] of coordinated glycinate

The IR spectral pattern of metal phosphato complexes are in general rather complicated owing the peak broadening and poor resolution The spectra of $M_2[BeF_2(H_2PO_4)_2]$ complexes exhibited a medium intensity band

at ca. 1108 and a broad weak absorption at ca. 2850 cm^{-1} attributable to the presence of phosphates. These bands are rather typical of coordinated hydrogenphosphato ligand[18] and are in conformity with the formulation.

A notable general feature of IR spectra of all the compounds, dealt with in this report, is the broadening of both ν(Be-F) and δ(F-Be-F)modes. This is a clean reflection of a definite possibility of intramolecular hydrogen bonding in each of the compounds.

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