SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF HETEROLIGAND-PEROXYVANADATE(V) AND FLUORONICKELATE(II) COMPLEXES AND DIRECT SYNTHESIS OF BIS(ACETYLACETONATO)NICKEL(II) DIHYDRATE AS WELL AS THE ISOLATION OF $\alpha,\alpha,\beta,\beta$-TETRA-ACETYLETHANE AS THE OXIDATION PRODUCT OF ACETYLACETONE

ABSTRACT

ZAVEI HIESE
DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES
NEHU

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

To

THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG
INDIA

NOVEMBER 1985

101892

[illegible]
Acc. No. 101892
Acc. by
Class by
19/8/87
Sub. Heading by
Cata. by
Transcribed by

26/9/89

D.S
547.5
HIE

ABSTRACT

Synthesis and Physico-Chemical Studies
of
Heteroligand-Peroxyvanadate(V) and Fluoronickelate(II) Complexes
And
Direct Synthesis of Bis(acetylacetonato) nickel(II) Dihydrate
as well as
the Isolation of $\alpha,\alpha,\beta,\beta$ - Tetra-acetylethane as the Oxidation Product of Acetylacetone

Abstract

The above mentioned thesis is based on the results of studies which involved the syntheses and assessment of structures of some heteroligand diperoxyvanadate(V) and heteroligand triperoxyvanadate(V) complexes of the type $[VO(O_2)_2CO_3]^{3-}$, $[VO(O_2)_2en]^{-}$ (en = ethylenediamine), and $[V(O_2)_3CO_3]^{3-}$, and syntheses and physico-chemical studies of alkali tetrafluoronickelates(II), $A_2[NiF_4]$, and alkali trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$ (A = alkali metal or NH_4^+). Further, the thesis describes the direct synthesis of bis(acetylacetonato) nickel(II) dihydrate, $Ni(C_5H_7O_2)_2 . 2H_2O$, as well as the isolation of $\alpha,\alpha,\beta,\beta$ -tetra-acetylethane as the oxidation product of acetylacetone, as obtained from the reaction of nickel(III) with $C_5H_8O_2$ (acacH). The subject matter of the thesis has been distributed over eight Chapters.

Chapter 1 presents a brief introduction pertaining to the work embodied in the thesis. It highlights (i) the importance of and the interest in the studies of peroxy-vanadium chemistry in general and

heteroligand peroxy-vanadium compounds in particular , and (ii) the problems associated with the reported methods of syntheses of fluoro compounds of nickel and of bis(acetylacetonato) nickel(II) dihydrate, $Ni(C_5H_7O_2)_2.2H_2O$. Another piece of a problem, as emphasised in this Chapter, is the lack of a firm evidence regarding the oxidation product of acetylacetone which is formed in its reaction with a higher-valent transition metal species. This Chapter also projects the scope of work on the afore-mentioned aspects.

Details of the methods of elemental analyses, and the instruments/equipment used for characterization and structural assessment of the newly synthesized compounds constitute the basis of Chapter 2.

Chapter 3 of the thesis describes the first synthesis and structural assessment of alkali oxodiperoxymonocarbonatovanadate(V) trihydrates, $A_3[VO(O_2)_2CO_3].3H_2O$ (A = Na or K). The synthesis of $A_3[VO(O_2)_2CO_3].3H_2O$ has been achieved by reacting vanadium pentoxide, V_2O_5, with alkali carbonate, A_2CO_3 (A = Na or K), maintaining V : CO_3^{2-} ratio of 1 : 1.5, and an excess of 30% H_2O_2 at pH ca 7. Compounds were precipitated with ethanol. $A_3[VO(O_2)_2CO_3].3H_2O$ compounds were diamagnetic, and the molar conductances, recorded at 7°C, were found to be in order (ca 370 $\Omega^{-1}cm^2mol^{-1}$). The occurrence of terminal $V=O$, and the presence of triangular bidentate peroxide (O_2^{2-}), and chelated bidentate carbonate, CO_3^{2-}, ligands in the complex $[VO(O_2)_2CO_3]^{3-}$ ion have been ascertained from infrared and Laser Raman spectroscopic studies. Alkali diperoxymonocarbonatovanadate(V) trihydrates are stable at room temperature, however, they start decomposing at ca 100°C.

Chapter 4 deals with the synthesis and physico-chemical studies of a new series of heteroligand peroxyvanadate(V) compounds, alkali monokis-(ethylenediamine)oxodiperoxyvanadate(V), $A[VO(O_2)_2(en)]$ ($A = Na$, K or NH_4 ; en = ethylenediamine). It has been shown that vanadium pentoxide reacts with aqueous hydrogen peroxide and ethylenediamine at pH 9, adjusted by the addition of alkali hydroxide or aqueous ammonia, to afford the lemon-yellow coloured, diamagnetic $A[VO(O_2)_2(en)]$ ($A = Na$, K or NH_4) compound in a very high yield. The corresponding 2,2 - bipyridyl (bipy) and 1,10-phenanthroline (o-phen) complexes requires the maintenance of pH 4-5 for their successful syntheses. The new compounds have been characterized on the basis of the results of chemical analyses, molar conductance and magnetic susceptibility measurements, and infrared and Laser Raman spectroscopic studies. The $A[VO(O_2)_2(en)]$ compounds dissolve in water without decomposition, and are comparatively more stable than the corresponding $A_2[VO(O_2)_2X]$ ($X = F^-$ or Cl^-) compounds. An analysis of the results of spectroscopic (IR and Raman) studies suggests the presence of a terminally bonded $V=O$ group. The results also provide unequivocal evidences for the occurrence of triangularly bonded peroxide (O_2^{2-}) groups and a chelated ethylenediamine ligand. The complex species $[VO(O_2)_2(en)]^-$ most probably has a pentagonal bipyramidal structure as often encountered in the peroxy-metal chemistry.

Chapter 5 of the thesis contains the results of studies involving the synthesis, characterization and assessment of structure of alkali triperoxymonocarbonatovanadate(V) trihydrates, $A_3[V(O_2)_3CO_3]\cdot3H_2O$ ($A = Na$ or K). The blue $A_3[V(O_2)_3CO_3]\cdot3H_2O$ compounds have been synthesized from the reaction of V_2O_5 with alkali carbonate, A_2CO_3, and

30% hydrogen peroxide in the molar ratio of V_2O_5 : A_2CO_3 : H_2O_2 as 1 : 3 : 49, followed by the addition of alkali hydroxide, AOH (A = Na or K) at an ice-water temperature, until a deep blue colouration was developed; the compounds were precipitated, from the reaction solution, by adding ethanol. The $A_3[V(O_2)_3CO_3]\cdot 3H_2O$ compounds, which decompose in water at ambient temperatures precluding molar conductance measurements, are all diamagnetic. The results of infrared and Laser Raman (LR) spectroscopic studies of the compounds confirmed the complete absence of $V{=}O$. IR and LR spectral results also showed that the peroxide groups are bonded to the vanadium(V) centre in a triangular bidentate (C_{2v}) manner, and the carbonate (CO_3^{2-}) ligand binds the metal centre in a chelated (C_{2v}) fashion. The basic difference between the methods of syntheses of diperoxyvanadate(V) and triperoxyvanadate(V) complexes has been discussed.

Two direct and new methods of syntheses of bis(acetylacetonato)-nickel(II) dihydrate, $Ni(C_5H_7O_2)_2\cdot 2H_2O$, as well as the isolation of $\alpha,\alpha,\beta,\beta$ -tetra-acetylethane as the oxidation product of acetylacetone ($C_5H_8O_2$, Hacac) from one of the two reactions provide the subject matter of Chapter 6. In view of the difficulties encountered in the synthesis of $Ni(C_5H_7O_2)_2\cdot 2H_2O$ using the literature reported method, two direct procedures have been developed for the synthesis of $Ni(C_5H_7O_2)_2\cdot 2H_2O$. While one of the methods involve a straight reaction between $Ni(OH)_2$ and acetylacetone, the other is based on the electron-transfer reaction between nickel(III) compound, NiO(OH), and acetylacetone conducted in the presence of an excess of acetylacetone. No buffer is required in either of the new methods, and a very high yield of the desired product is obtained in each case. The isolation of $\alpha,\alpha,\beta,\beta$ -tetra-acetylethane as the oxidation product of acetylacetone from the reaction of NiO(OH) with Hacac, which has been acheived for the first time from such a reaction, provides a very important piece of information regarding the afore-mentioned reaction. In order to generalise the contention, electron-transfer reactions between manganese(VII) and Hacac, and also between chromium(VI) and Hacac were conducted, and $\alpha, \alpha, \beta, \beta$-tetra-acetylethane was isolated, in addition to $Mn(acac)_3$ and $Cr(acac)_3$ in the respective reactions, in each case. Electron-impact induced mass spectrometric studies of bis(acetylacetonato)nickel(II) have been done, and an interpretative account of the mass spectrometric results has been presented.

A novel method of synthesis of tetrafluoronickelate(II) complexes, $A_2[NiF_4]$ (A = K, Rb or NH_4), their characterisation, and also the scope of the new method as a paradigm for other such syntheses have been reported in <u>Chapter 7</u>. The complexes $A_2[NiF_4]$ (A = K, Rb or NH_4) have been synthesised from the reaction of bis(acetylacetonato)nickel(II) dihydrate, $Ni(C_5H_7O_2)_2.2H_2O$, with 40% hydrofluoric acid and alkali fluoride, AF, in very high yields. The compounds have been characterised by elemental analyses, magnetic susceptibility measurements, and infrared spectroscopic studies. The specific advantages of the method have been discussed. To demonstrate the scope of the new synthetic procedure, similar reactions involving $[VO(C_5H_7O_2)_2]$, $[Cr(C_5H_7O_2)_3]$, or $[Mn(C_5H_7O_2)_3]$ with NH_4F and 40% hydrofluoric acid were carried out and the products obtained were identified as $(NH_4)_2[VOF_5]$, $(NH_4)_2[CrF_5(H_2O)]$, and $(NH_4)_2[MnF_5]$ respectively; this supports the contention that the method can be used as a paradigm for other such syntheses, and a host of fluorometalates can be easily accessible.

Chapter 8, indeed the last Chapter of the thesis, provides a detailed account of the first reported syntheses and characterisation of alkali trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$ (A = Na, K or NH_4). It has been shown that bis(acetylacetonato)nickel(II) dihydrate, $Ni(C_5H_7O_2)_2.2H_2O$, and alkali fluoride, AF (A = Na, K or NH_4), react with an excess of 40% hydrofluoric acid on a steam-bath, and the product upon treatment with water gives light green crystalline alkali trifluoronickelate(II) monohydrate, $ANiF_3.H_2O$, in a high yield. The compounds were characterised, and their identity was established from the results of chemical analyses, pyrolysis at 120°C, infrared spectroscopic and cryomagnetic (300 - 80K) studies. Although IR spectra suggest the occurrence of uncoordinated water, the H_2O molecule is not lost even on prolonged heating of the $ANiF_3.H_2O$ compounds at ca 120°C suggesting thereby that the water molecule is tightly held in the crystal lattice. The results of cryomagnetic studies show that $NH_4NiF_3.H_2O$ behaves as a normal octahedral nickel(II) compound, whereas $NaNiF_3.H_2O$ is ferromagnetic with its Curie point being 145K. The $KNiF_3.H_2O$ compound, however, behaves antiferromagnetically; its Neel point is 230K.

The results of studies described in Chapters 6 and 7 have been published, and those described in Chapters 3 and 8 are now in press, while the work described in Chapters 4 and 5 have been communicated for publication.

Chapter 3

J. Chem. Soc. Dalton Trans., in press (DAL-5/576).

Chapter 6

J. Chem. Soc. Dalton Trans., 2561, 1983.

Chapter 7

J. Chem. Soc. Dalton Trans., 1763, 1984.

Chapter 8

Transition Metal Chem., 0000, 10, 1985.

[illegible] Library
Acc. No. 101899
Acc. by
Class by
Sub. Heading by 7/8/87
Data. by
Transcribed by

SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF HETEROLIGAND-PEROXYVANADATE(V) AND FLUORONICKELATE(II) COMPLEXES AND DIRECT SYNTHESIS OF BIS(ACETYLACETONATO)NICKEL(II) DIHYDRATE AS WELL AS THE ISOLATION OF $\alpha,\alpha,\beta,\beta$-TETRA-ACETYLETHANE AS THE OXIDATION PRODUCT OF ACETYLACETONE

ZAVEI HIESE
DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES
NEHU

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

To

THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG
INDIA

NOVEMBER 1985

To

My Parents

Chem.

[illegible]
[illegible] No. 101892
Acc. by
Class by 19/8/87
Sub. Heading by
Cata. by
[illegible] by
26/9/89
4/10
7/10/89

D.S
547.3
HIE

For from Him and through Him and to Him
are all things.

To Him be the glory forever!

Romans 11:36

Phone : 26593
Grams : NEHU

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

Department of Chemistry

Dr. Mihir K. Chaudhuri

Reader in Chemistry

I certify that the thesis entitled "SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF HETEROLIGAND PEROXYVANADATE(V) AND FLUORONICKELATE(II) COMPLEXES AND DIRECT SYNTHESIS OF BIS(ACETYLACETONATO)-NICKEL(II) DIHYDRATE AS WELL AS THE ISOLATION OF $\alpha,\alpha,\beta,\beta$-TETRA-ACETYLETHANE AS THE OXIDATION PRODUCT OF ACETYLACETONE", submitted by Mr. Zavei Hiese for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered, and the thesis presented is worthy of being considered for the award of the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

Mihir Kanti Chaudhuri
Signature of the Supervisor

Date: 28 Nov. 1985

Place: Shillong

Phone :
Grams : NEHU

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

Department of..................

This is to certify that Mr. Zavei Hiese has satisfactorily completed the following Pre-Ph.D. courses, as prescribed by this University:

CHEM 612	Nuclear and Radiochemistry
CHEM 630	Biogenesis of Natural Products
CHEM 631	Medicinal Chemistry

HEAD
DEPARTMENT OF CHEMISTRY
NORTH-EASTERN HILL UNIVERSITY
SHILLONG 793003.

CONTENTS

ACKNOWLEDGEMENT

It is with great pleasure that I wish to express my deepest gratitude to Dr. Mihir K. Chaudhuri, Reader, Department of Chemistry, N.E.H.U., for guiding and supervising me throughout the Ph.D. programme. I thank him especially for his constant patience and encouragement, without which this work would not have been possible. I wish to acknowledge my sincere gratitude to the Vice-Chancellor, North-Eastern Hill University, the Dean of the School of Physical Sciences, the Head of the Department of Chemistry, and the Head of R.S.I.C., N.E.H.U., for allowing me to use all the research facilities available in the University.

I am very grateful to Professor Alois Haas of Rurh University, Bochum, West Germany, and Dr. A. L. Verma, Department of Physics, N.E.H.U., for their kindness in allowing me to make use of some of the facilities available in their laboratories. I also thank all the faculty members of Chemistry Department, N.E.H.U., for their help and encouragement.

I am indebted to my parents for their keen interest and encouragement in my work. I am priviledged to thank all my fellow colleagues of our laboratory and my friends for their cooperation and encouragement over all these years.

I am grateful to the Council of Scientific and Industrial Research, Govt. of India, New Delhi, for awarding me a Junior Research

Fellowship and subsequently a Senior Research Fellowship, which enabled me to carry out the research work for the Ph.D. degree.

I acknowledge my sincere thanks to Mr. Sadhu for typing the thesis.

Dated: Shillong, the 28th Nov. 1985.

(ZAVEI HIESE)

CHAPTER 1

Introduction

VANADIUM the element 23, a d-block transition metal of periodic group VB, has the configurations of its outermost electron shells : $3d^3 4s^2$. Pentavalent state is the highest oxidation state of the metal, and in this state it forms two oxo-species, viz., VO^{3+} and VO_2^{+}, neither of which disproportionates because of their being better oxidants. The VO^{3+} unit occurs in the oxyhalides VOX_3 (X = F, Cl or Br) in which the V —— O stretching frequencies occur at 1058, 1035 and 1025 cm^{-1} respectively. In addition, a number of complexes of the types $VOCl_3.L$ and $VOCl_3.2L$, in which L can be either an oxygen-donor or a nitrogen-donor ligand, have been characterized.[1,2] The complexes appear to be either five or six coordinated monomers. Vanadium oxychloride has been shown also to react[1] with ligands containing replaceable hydrogen atoms to give substitution products e.g. $VO(OMe)_3$, $VOCl_2(OMe)$, $VOCl_2(OEt)$, $VOCl(OEt)_2$, $VOCl_2(acac)$ and $VOCl(acac)_2$ (Hacac = acetylacetone). Very little structural information is available for these types of complexes except for the alkoxide $VO(OMe)_3$ which has been shown to be a linear polymer molecule, with a dimeric repeat unit and alkoxide bridging.[3] The oxo-species VO^{3+} is very commonly encountered in the peroxy-vanadium chemistry,[4] and there are some X-ray crystallographic evidences for the occurrence $V{=}O$ in the peroxyvanadate(V) compounds, viz., $(NH_4)[VO(O_2)_2(bipy)].4H_2O$[5], $[VO(O_2)_2C_2O_4]^{3-}$ (Ref. 5), $(NH_4)[VO(O_2)(C_4H_5O_4N)]$[6] . The other example of complexes containing VO^{3+} include $VOCl_4^-$ and VOF_4^- (Ref. 7-9), and $[VOF_3(H_2O)]^-$ (Ref. 10).

The second oxovanadium(V) species, the VO_2^+ ion, is not very much characterized, but it is believed to occur discretely in the complexes $VO_2(NO_3)$, VO_2F, and $VO_2(SbF_6)$, and as a cis-VO_2 unit in the complexes[11] $K_3[VO_2F_4]$ and $K_3[VO_2(C_2O_4)_2]$.

The most characteristic feature of the infrared spectra of oxovanadium complexes is the very strong and sharp band at 980 ± 50 cm^{-1}. This band is assigned to the V$=$0 stretching frequency[12,13] and as expected it lies near the upper frequency limit for those complexes which are known, from X-ray work, to have the shortest V — 0 bonds.

It has been known for over a century that characteristic colour reactions may take place when hydrogen peroxide is added to solutions of transition metal derivatives,[14,15] and some peroxy transition metal compounds have been isolated in the solid state. Peroxy compounds of metals, besides having an intrinsic interest of their own,[16-37] are of considerable and growing importance particularly in relation to the catalysis of oxidation[38] involving H_2O_2[39] itself, and the storage and transport of oxygen in biological systems.[40,41]

Although the term molecular oxygen refers to the free uncombined O_2 molecule with the ground state $^3\Sigma_g^-$, the term dioxygen has been used as a generic designation for the O_2 moiety in any of its several forms, and can refer to O_2 in either a free or a combined state.[42] For use of this term, it is essential that a covalent bond has to exist between the oxygen atoms. Thus, a metal-dioxygen complex refers to a metal containing O_2 group coordinated to the metal centre, and no distinction is made between neutral dioxygen or dioxygen in any of its reduced forms. Accordingly, a metal-peroxide complex is one in which the coordinated dioxygen resembles a peroxide (O_2^{2-}) anion.[40] The incorporation of O_2 into a metal complex to form a metal-dioxygen compound is called oxygenation, and the reverse is known as deoxygenation.

Simple peroxy compounds of transition metals are the ones which contain peroxides, hydroperoxides, and water molecules, whereas heteroligand peroxy complexes are mixed ligand complexes containing one to three coordinated peroxy groups, and one or more monodentate or polydentate ligands. Heteroligands range from monodentate halide ions to bulky porphyrin[41] (F^-, Cl^-, NH_3, $C_2O_4^{2-}$... , NTA, EDTA,... dipy, o-phen, oxine ... , porphyrin, ... , pyridine - 2, 6- dicarboxylate ... etc.). The stability of peroxy complexes is generally enhanced by specific heteroligand combinations. Thus, many simple transition metal peroxides often explode spontaneously; some are sensitive to shock or decompose above 0°C, and several do not exist at all as stoichiometric compounds.[14] Many heteroligand peroxy complexes, on the other hand, survive recrystallization from boiling aqueous solutions, heating *in vacuo*, and many remain unchanged for prolonged periods[6,37,43-48] in closed containers.

The biochemical significance of peroxy metal complexes has been emphasized in the literature.[21, 37,40,41,49-52] The reactivity of peroxides,[53-60] and the lability of metal-oxygen bonds in special heteroligand environments in solutions are of particular interest in biochemistry, but are not easy to measure directly.

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

The importance of neutral dioxygen complexes in biochemistry is well known,[61] but the biochemical connection of the metal peroxy complexes with biological processes is not very well understood. The metals, Se, Ti, V, Cr, Y, Zr, Nb, Mo, La, Hf, Ta, W,[41] and U[62] form stable heteroligand peroxy complexes, and there is increasing evidence that vanadium has a significant biological role.[63-66] It is reasonable to assume that the participation of vanadium will depend upon parameters such as pH, and the availability of inorganic or organic species that can act as heteroligands.

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

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

where KK term indicates that the K shells of two oxygen atoms are filled. The two unpaired electrons in the $^3\Sigma_g^-$ ground state are found in the two degenerate antibonding 2p π_g^* orbitals (Fig. 1), leaving

O_2 with a formal bond order of two.

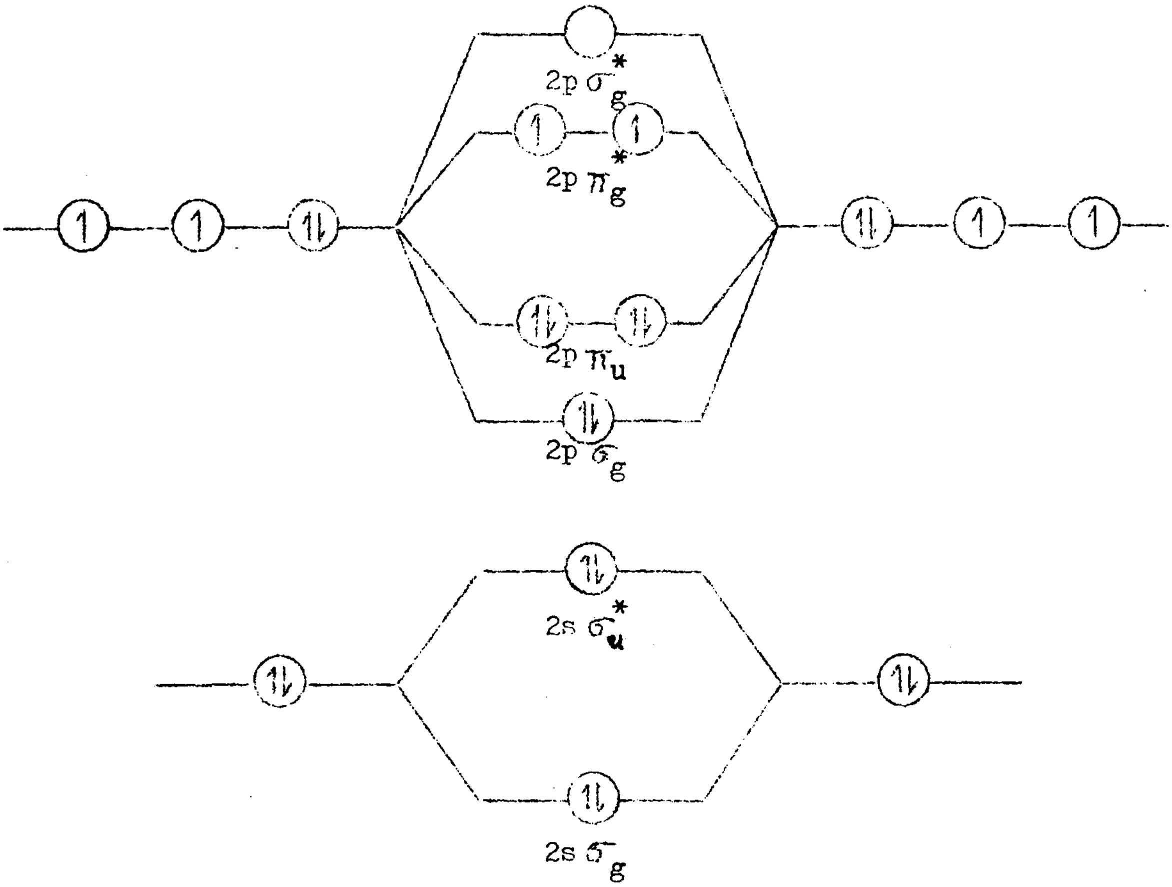


Fig. 1

The MO description of O_2 $(^3\Sigma_g^-)$ shows a vacancy for the addition of a single electron in both of $2p\ \pi_g$ orbitals. The addition of one or two electrons to a neutral O_2 results in formation of the superoxide (O_2^-) and peroxide (O_2^{2-}) species, respectively, leaving O_2^- with a bond order of 1.5, and the peroxide O-O link with a normal bond order of one. Some of the salient features for O_2, O_2^- and O_2^{2-} are summarized in Table 1.

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

	Bond Order	Compound	O — O distance (Å)	Bond Energy (Kcal/mol)	ν(O — O) cm^{-1}
O_2	2	O_2	1.207[67]	117.2	1554.7[69]
O_2^-	1.5	KO_2	1.28	-	1145[70]
O_2^{2-}	1	Na_2O_2	1.49[68]	48.8	842[71]

The way in which a peroxo group is expected to coordinate to metals[41] (Fig. 2) can range from a symmetrical bidentate to a terminal monodentate position, including all the possible angles in between.

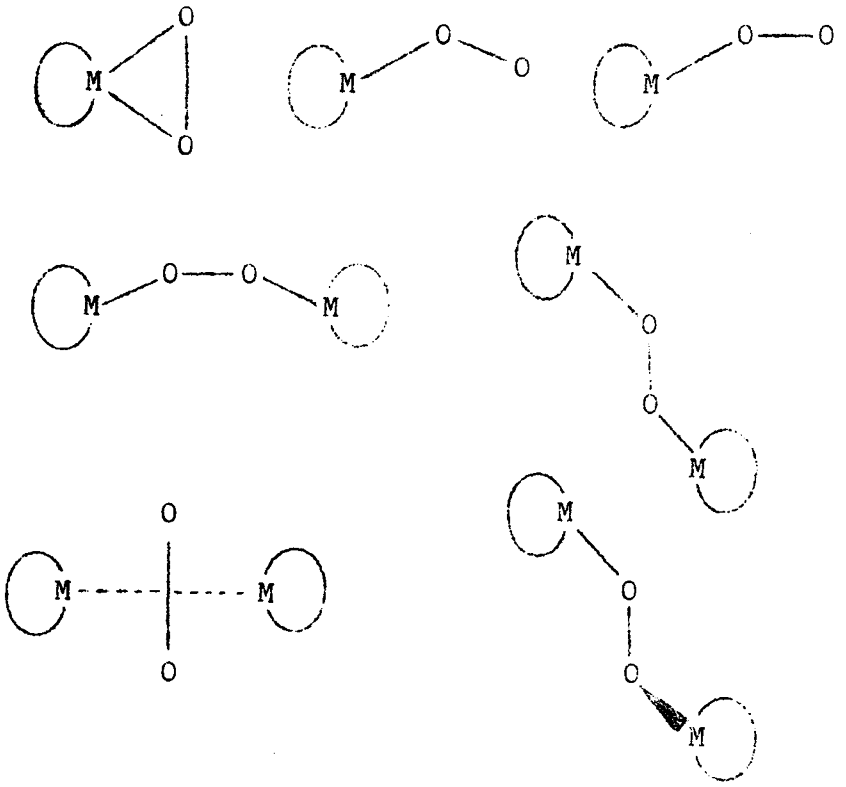


Fig. 2

The bridging μ-peroxo could vary from cis-planar and trans-planar to trans-nonplanar configurations. An unusual symmetrical double bridging was also found.[72] Deviations from the ideal symmetry are not uncommon. In the case of heteroligand fields they are due to the inherent symmetry of different donor atoms. Additional $p\pi^*$ electron delocalization to the metal ion is anticipated which would therefore favour a d^0 or a low d^n metal ion configuration.

The stereochemical polyhedra in heteroligand peroxy complexes are fairly predictable. For the second row elements Nb and Mo, coordination number 8 with a dodecahedral (D_{2d}) symmetry has invariably been observed in the absence of oxo groups. In oxoperoxy-heteroligand surroundings the pentagonal bipyramidal arrangement is the most common,[5,6] usually with two coordinated peroxy groups in the cis positions and one oxo group in an axial position. There is also an interesting non-octahedral example of coordination number 6 for a peroxy-vanadium complex.[73]

Infrared spectroscopic studies are essential, and Raman spectroscopic studies are very important for the characterisation of peroxy metal complexes.[74-81] The peroxy-metal complexes involving a metal-triangular bidentate peroxide (O_2^{2-}) would be expected[82] to give rise to three vibrations of symmetry species ($2\,A_1 + B_2$), and these may be designated as ν_1(A_1 ; O —— O stretching), ν_2(A_1 ; symmetric metal-peroxide stretch), and ν_3(B_2 ; asymmetric metal-peroxide stretch). All three modes should be active in both the infrared as well as Raman, but the A_1 modes should be polarized and the B_2 mode depolarized in Raman. The ν(O-O) band is the most sensitive and intense one, and characteristically occurs between 800 and 900 cm^{-1}. The frequency of this band remains fairly independent of the heteroligand environment, but is sometimes affected by the mass of the metal centre indicating coupling of the ν(O-O) with metal —— O_2 vibrations. This most familiar way of bonding of O_2^{2-} groups, in a triangular bidentate fashion, is similar to that proposed by Griffith[83] for the bonding of O_2 in oxyhemoglobin. The dimeric peroxy complex is sometimes more stable than the monomeric complex, and are generally formed unless its formation is inhibited (e.g., $[(NH_3)_5Co - O_2 - Co(NH_3)_5]^{4+}$). These complexes are diamagnetic with the oxygen being viewed as "peroxide-like" with a concomitant oxidation of the metal centres to low-spin d^6 (Co^{III}). The ν(O-O) for such complexes span a range of 790-844 cm^{-1} with an average value of 810 cm^{-1} (cf. μ-peroxo).[40]

Heteroligand complexes of niobium and tantalum are rather easily formed. Structural analysis of some such niobium complexes show that the coordination polyhedron is dodecahedral.[84] Vanadium, however, presents a different story. Although some peroxy- and oxoperoxy- vanadium(V) species occur,[14] only a few heteroligand complexes are known.[6,41,73,85] Unlike Nb and Ta, vanadium has a strong tendency to form oxoperoxy species.

The reaction of concentrated alkali hydroxide with a concentrated solution of vanadium pentoxide (V_2O_5) in aqueous hydrogen peroxide at low temperatures (0° or below 0°C) gives a deep blue solution owing to the formation of tetraperoxyvanadate(V) species,[14] $[V(O_2)_4]^{3-}$. The salts of the complex $[V(O_2)_4]^{3-}$ ion were obtained by the addition of ethanol to such a solution. The salts are stable only at low temperatures, and their stability decreases with increasing cation size.[14] The potassium salt, $K_3[V(O_2)_4]$, which is isomorphous with $K_3[Cr(O_2)_4]$[86], presumably having a dodecahedral structure, has a magnetic moment of 0.6 BM, consistent with the presence of vanadium(V). The IR spectra of the $(NH_4)_3[V(O_2)_4]$ and $K_3[V(O_2)_4]$ contains bands in the region 800-900 cm^{-1} that have been assigned to $\nu(O-O)$ modes of peroxy groups.[87] It was suggested that slight excess of a base causes the destruction of the tetraperoxy species leading to the formation of the anion $[VO(O_2)_3]^{3-}$,

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

which is stable at room temperature.

The yellow colour produced by the addition of aqueous hydrogen peroxide to a dilute solution of a metavanadate has been shown to be due to a diperoxy anion by cryescopy[88] as well as by thermochemical studies.[89] There is, however, some controversy as to how the anion should be formulated, although the results of cryoscopic and spectrophotometric studies have been interpretated in terms of the anion $[VO(O_2)_2]^-$.

The addition of aqueous H_2O_2 to (i) V_2O_5[90], (ii) an acid solution of a metavanadate,[91] (iii) a vanadium(V) salt in a weakly acid solution,[92] (iv) or a decavanadate[93] produces in each case a red colour believed to be due to the formation of a monomeric monoperoxyvanadate(V) cation $VO(O_2)^+$. The red colour thus obtained is stable in moderately acid media. In an excess of H_2O_2 the red cation is converted to the yellow oxodiperoxyvanadate(V) anion[92,93] $[VO(O_2)_2]^-$. It was concluded[14] from the results of various studies that,

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

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

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

Studies involving vanadium peroxo complexes are of special interest because the actual function of vanadium in living cell is unknown.[64] From biochemical point of view, the most interesting aspect of peroxy-vanadium chemistry remains the experimental approach to measuring the reactivity of the coordinated peroxo group in an environment of various heteroligand fields. The reactivity of coordinated peroxo groups means essentially the ease of electron-transfer to and from the dioxygen (O_2^{2-}) anion. Whereas most of the recent reports on peroxyvanadium chemistry deal with the studies in solutions,[50,51,94-98] the synthesis and structural assessment of such compounds have received only scant attention.

The synthesis of well defined heteroligand peroxyvanadate(V) complexes, and the study of their properties provide a heuristic approach to an understanding of the role of vanadium in the catalytic reactions. The chemistry of heteroligand peroxyvanadates(V) thus embraces a fascinating, rewarding, and worthwhile area of investigation.

Chapters 3 - 5 of the present thesis describe the syntheses, characterisation, structural assessment, and some properties of new heteroligand peroxyvanadates(V), viz., $A_3[VO(O_2)_2CO_3].3H_2O$, $A[VO(O_2)_2en]$ (en = ethylenediamine) and $A_3[V(O_2)_3CO_3].3H_2O$ (A = Na, K or NH_4).

Complexes with 1,3-diketones, particularly involving acetylacetone, have been reported for almost all of the non-radioactive metallic or metalloid elements in the periodic table.[99] Since β-ketoenol complexes have been a very commonly used commodity in chemistry laboratories, and many of such compounds can be purchased commercially, many text and reference books provide information regarding them. However, interests in their syntheses, and chemical and physico-chemical studies of these types of compounds never seem to be diminishing.[100-114] Bis(acetylacetonato) nickel(II) dihydrate, $Ni(acac)_2.2H_2O$, a typical example of metal β-diketonate, has drawn a lot attention of many workers.[107-114] This compound, in the presence of reducing agents, acts as a well recognised catalyst for very important organic reactions such as, for instance, oligomerisation, polymerisation, hydrogenation, and isomerisation of olefins, hydrosilylation of alkynes, and coupling of organic halides.[106] $Ni(acac)_2.2H_2O$ is obtained from aqueous solutions of nickel(II) salts in the presence of acetylacetone and a weak base such as sodium acetate; the compound is readily dehydrated to the green anhydrous compound at 50°C *in vacuo*.[115] In the crystalline state the molecule is trimeric with a slightly distorted octahedral coordination about the nickel atoms in the trimer.[116,117] In the vapour state, however, the molecule is most probably monomeric, and in solution (10^{-2}M) in chloroform the electronic spectrum indicates it to be planar.[99] The method, used in practice, for the synthesis of bis(acetylacetonato)nickel(II) dihydrate, $Ni(C_5H_7O_2)_2.2H_2O$ requires the addition of a large amount of sodium acetate (buffer).[115] The chances of contamination of the desired product owing to the use of such a large amount of buffer cannot be ruled out.[118] Moreover, it is evident from various reports that under the appropriate conditions acetylacetone (Hacac) is capable of acting both as a reducing agent as well as a chelating agent.[103,104,119-121] However, the nature of the oxidation product of acetylacetone when it acted as a reducing agent has not been established.

It is therefore highly necessary to develope direct method(s) for the synthesis of $Ni(acac)_2.2H_2O$, without making use of any buffer. Moreover, the question of isolation and identification of the oxidation product of acetylacetone (Hacac), formed in the reaction between higher valent metals and Hacac ($C_5H_8O_2$), calls for an immediate attention of the workers engaged in the study of metal acetylacetonates.

The details of two new methods of syntheses of bis(acetylacetonato)-nickel(II) dihydrate, $Ni(C_5H_7O_2)_2.2H_2O$, and the isolation of $\alpha,\alpha,\beta,\beta$ -tetraacetylethane as the oxidation product of acetylacetone (Hacac), as achieved from the reaction of nickel(III) with Hacac, constitute the subject matter of Chapter 6 of the thesis. The two new methods of syntheses do not require any buffer.

Interest in the field of chemistry involving fluoro-containing transition metal compounds seem to be never diminishing.[120-132] Peculiarities of such compounds in respect of their magnetic and

and structural behaviours probably make them relatively more interesting than the compounds containing other halides bonded to a metal centre. Some of the fundamental properties of fluorine, e.g., its high electronegativity and small ionic size render it suitable for stabilising higher oxidation states of metals, and knowledge of fluoro-compounds of the transition metals has been increasing considerably, mainly because fluorine itself has ceased to be a laboratory curiosity as a result of simplification of its preparation and purification. New materials and improved techniques have made newer synthetic methods[120,121, 133-137] very effective, but it is certainly true that a surprising amount of new work in this field has to be done.

Coming to the case of complexes of nickel(II), it is evident that coordination compounds of nickel(II) are exceedingly numerous.[138,139] The maximum coordination number shown is six and whilst octahedral or distorted octahedral complexes are the most usual, divalent nickel also forms many 5-coordinate (square pyramidal and trigonal bipyramidal), and 4-coordinate (tetrahedral and square planar) complexes. One of the most remarkable facts, about the stereochemistry of nickel(II) complexes is that equilibria between the different structural types often exist in solution and these equilibria are frequently temperature dependent and often concentration dependent. It must, however, be noted that there are also many nickel(II) compounds that exist practically completely in one stereochemical form.[139]

The electronic spectral and magnetic properties of nickel(II) complexes are quite characteristic and well understood.[139-141] The Ni^{2+}

ion has the $3d^8$ outer electron configuration which gives rise to the triplet and singlet terms (in order of increasing energy) ^3F, ^1D, ^3P, ^1G, ^1S. The simple crystal field diagrams for this ion in tetrahedral, octahedral and tetragonal fields are shown in Fig.3. It can be readily seen from these diagrams in octahedral and slightly tetragonally distorted octahedral fields, two unpaired electrons are present; the ground state makes no orbital contribution to the magnetic moment, so that these moments are expected to be not greatly different from the "spin-only" moment (2.83 BM). In tetrahedral fields, again, two unpaired electrons are present, but there is now orbital contribution to the magnetic moment through the equivalence and degeneracy of the incompletely filled t_2 orbitals; magnetic momemts are thus expected to be well in excess of the spin-only value, and typically lie in the range 3.2 - 4.0 BM. In strong tetragonal and square crystal fields the electrons pair and the complexes become diamagnetic. We shall not elaborate our discussion on the magnetic and spectral properties of nickel(II) complexes, as several excellent reviews on this subject are available.[140,141]

Like other transition metals, nickel(II) also forms fluoronickelate(II) complexes. Thus, yellow tetrafluoronickelates(II) are prepared by fusion of nickel(II) fluoride with stoichiometric amount of an alkali metal or alkaline earth metal fluoride in vacuo, or in an atmosphere of hydrogen fluoride.[142] The tetrafluoronickelates(II) contain octahedrally coordinated nickel(II); the potassium, rubidium, ammonium and thallium(I) salts are tetragonal,[143] $LiNiF_4$ is cubic,[144] and $BaNiF_4$ is orthorhombic.[145] While the lithium salt has a magnetic moment of 3.8 BM, the other compounds are antiferromagnetic showing room temperature moments around

101892.

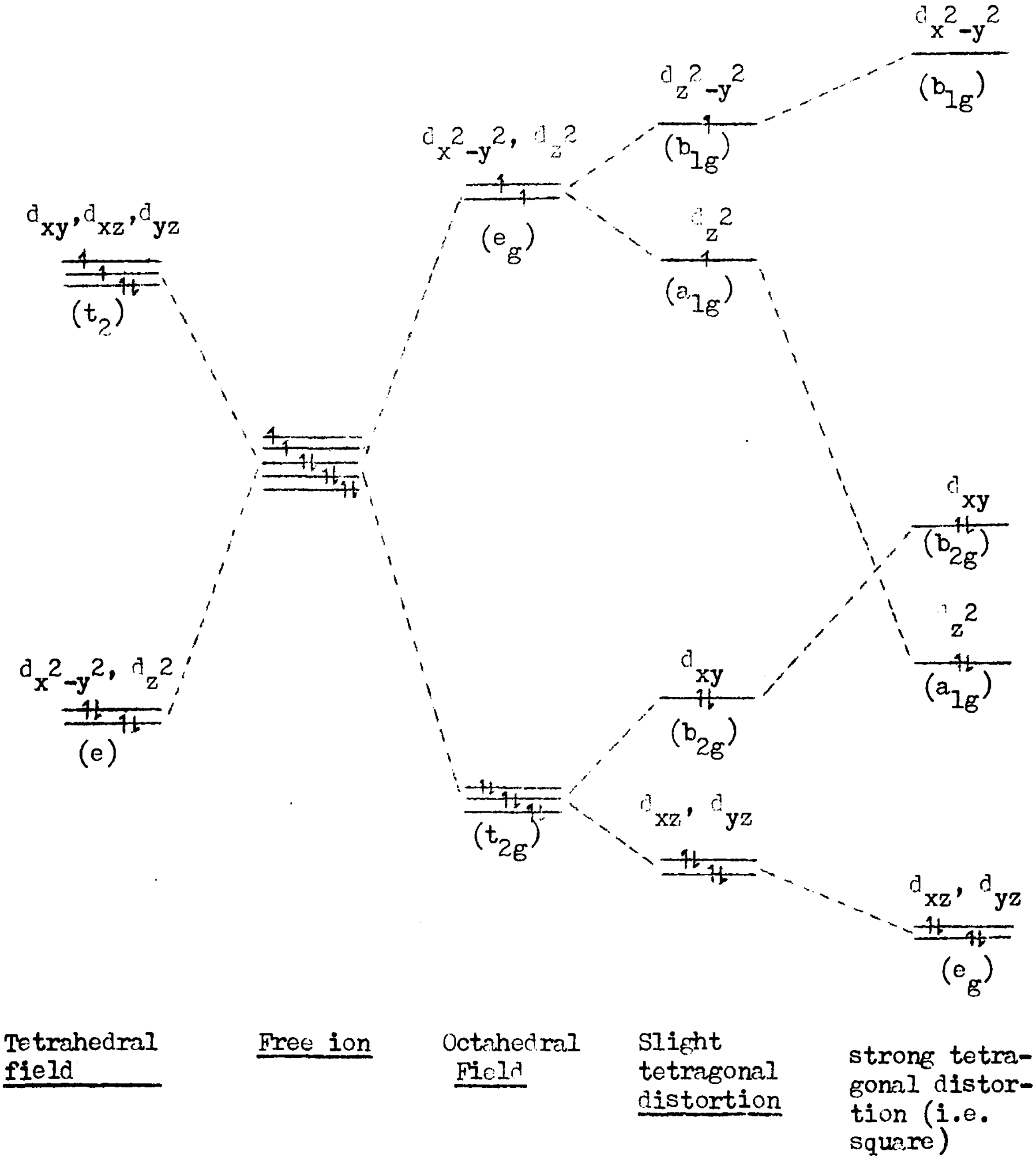


Fig. 3. Simple crystal field splitting diagrams for nickel(II) ions in various crystal fields.

2.0 BM. The reflectance spectra of Na_2NiF_4, K_2NiF_4, and Rb_2NiF_4 have been assigned on O_h symmetry.[143]

The trifluoronickelates(II) are obtained when nickel(II) fluoride and alkali metal fluoride are reacted in boiling water.[123] They all contain octahedrally coordinated nickel. The potassium salt $KNiF_3$ has the perovskite-type structure with the Ni —— F distance of 2.01A°, while the sodium and rubidium salts occur in two different modifications (Na salt, cubic and orthorhombic, and Rb salt, cubic and hexagonal).[142] The trifluoronickelates(II) are antiferromagnetic.[146,147]

It is also reported that a hexafluoronickelate(II), Ba_2NiF_6, has been obtained as a yellow solid by fusing a 2 : 1 mixture of barium fluoride and nickel(II) fluoride at 1200°.[148,149] The NiF_6^{4-} octahedra are tetragonally alongated with Ni —— F distances being 2.03 and 1.97 A°. This compound has a room temperature magnetic moment of 3.76 BM, and becomes antiferromagnetic at low temperatures.

Another series of fluoronickelates(II), namely alkali metal trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$ (A = Na, K or NH_4) has been reported in the literature.[147] The compounds are very simple, yet show very interesting properties. For example, the mere change of the counter cation in $ANiF_3.H_2O$ brings about very drastic and significant changes of magnetic properties.[147] Although Machin and Nyholm[147] reported the analytical data and magnetic properties of $ANiF_3.H_2O$ compounds about twenty years ago, there is no report until date on their syntheses.

It is evident from the above discussion on fluoronickelates(II) chemistry that while no reported method is available in the literature for the synthesis of alkali trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$ (A = alkali metal or ammonium), the recommended methods for the synthesis of tetrafluoronickelate(II), $[NiF_4]^{2-}$, employ fusion of NiF_2 with stoichiometric amount of alkali metal fluorides either in vacuo or in an atmosphere of dry HF. Such methods require not only NiF_2 but also anhydrous HF which is difficult to handle.

Thus it is imperative and necessary to improvise suitable methods for the synthesis of alkali trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$, and to develope new and much simpler routes to alkali tetrafluoronickelates(II), $A_2[NiF_4]$. Studies in the afore-mentioned directions are therefore warranted.

Chapter 7 of the present thesis describes about a novel route to alkali tetrafluoronickelate(II), $A_2[NiF_4]$ (A = K, Rb or NH_4), as well as the scope of the new method.

Chapter 8, indeed the last Chapter of the thesis, presents the details concerning the first reported synthesis and characterisation of alkali trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$ (A = Na, K or NH_4).

Chapters 3 to 8 report interpretative accounts of the results of studies on heteroligand-peroxyvanadates(V), bis(acetylacetonato)nickel(II) dihydrate, and fluoronickelates(II). Each of these Chapters has been so designed as to make it a self-contained one with a brief introduction, sections on experimental, and results and discussion, followed by relevant bibliography. Some of the new results have been published, some more are now in press, while the rest are under communication.

References

[1] H. Funk, W. Weiss, and M. Zeising, Z. Anorg. Allgem. Chem., 1958, 296, 36.

[2] H. L. Krauss and G. Gnatz, Chem. Ber., 1962, 95, 1023.

[3] R. J. H. Clark, "The Chemistry of Titanium and Vanadium," Elsevier, Amsterdam, 1968.

[4] S. K. Ghosh, Ph. D. Thesis, North-Eastern Hill University, Shillong, 1984.

[5] N. J. Campbell, M. V. Capparelli, W. P. Griffith, and A. C. Skapski, Inorg. Chim. Acta, 1983, 77, L215.

[6] C. Djordjevic, S. A. Craig, and E. Sinn, Inorg. Chem., 1985, 24, 1281. and references therein.

[7] D. Nicholls and D. N. Wilkinson, J. Chem. Soc. (A), 1970, 1103.

[8] J. A. S. Howell and K. C. Moss, J. Chem. Soc.(A), 1971, 270.

[9] M. K. Chaudhuri, S. K. Ghosh, H. S. Dasgupta and D. T. Khathing, Synth. React. Inorg. Met.-Org. Chem., 1982, 12, 63.

[10] M. C. Chakravorti and A. R. Sarkar, J. Fluorine Chem., 1976, 8, 421.

[11] W. P. Griffith and T. D. Wickins, J. Chem. Soc. (A), 1968, 400.

[12] J. Selbin, Chem. Rev., 1965, 63, 153.

[13] J. Selbin, Coord. Chem. Rev., 1966, 1, 293.

[14] J. A. Connor and E. A. V. Ebsworth, Adv. Inorg. Chem. Radiochem., 1964, 6, 279.

[15] R. J. H. Clark and D. Brown, "The Chemistry of Vanadium, Niobium and Tantalum," Pergamon Texts in Inorganic Chemistry, Vol. 20, Pergamon Press, New York, 1975, p 519.

[16] J. S. Valentine, *Chem. Rev.*, 1973, **73**, 235.

[17] D. H. Chin, J. Del Gaudio, G. N. La Mar, and A. L. Black, *J. Am. Chem. Soc.*, 1977, **99**, 5486.

[18] D. H. Chin, G. N. La Mar, and A. L. Black, *J. Am. Chem. Soc.*, 1980, **102**, 4344.

[19] D. H. Chin, G. N. La Mar, and A. L. Black, *J. Am. Chem. Soc.*, 1980, **102**, 5945.

[20] R. Guilard, M. Fontesse, P. Fournari, C. Lecompte, and J. Protas, *J. Chem. Soc. Chem. Commun.*, 1976, 161.

[21] R. Guilard, M. J. Latour, C. Lecompte, J. C. Marchon, J. Protas, and D. Ripoll, *Inorg. Chem.*, 1978, **17**, 1228.

[22] M. J. Latour, B. Galland, and J. C. Marchon, *J. Chem. Soc. Chem. Commun.*, 1979, 570.

[23] M. J. Latour, J. C. Marchon, and M. Nakajima, *J. Am. Chem. Soc.*, 1979, **101**, 3974.

[24] M. M. Rohmer, M. Barry, A. Didieu, and A. Veillard, *Int. J. Quantum Chem., Quantum Biol. Symp.*, 1977, **4**, 337.

[25] C. J. Boreham, M. J. Latour, B. Boisselier-Cocolios, and R. Guilard, *Inorg. Chim. Acta*, 1980, **45**, L 69.

[26] M. Inamo, S. Funahashi, and M. Tanaka, *Inorg. Chim. Acta*, 1983, **76**, L 93.

[27]E. McCandlish, A. R. Miksztal, M. Nappa, A. Q. Sprenger, J. S. Valentine, J. D. Stong, and T. G. Spiro, J. Am. Chem. Soc., 1980, 102, 4268.

[28]C. H. Welborn, D. Dolphin, and B. R. James, J. Am. Chem. Soc., 1981, 103, 2869.

[29]A. Shirazi and H. M. Goff, J. Am. Chem. Soc., 1982, 104, 6318.

[30]B. Chevrier, Th. Diebold, and R. Weiss, Inorg. Chim. Acta, 1976, 19, L 57.

[31]H. Ledon, M. Bonnet, and J. Y. Lallemand, J. Chem. Soc., Chem. Commun., 1979, 702.

[32]K. M. Kadish, D. Chang, T. Malinski, and H. Ledon, Inorg. Chem., 1983, 22, 3490.

[33]C. J. Weschler, B. M. Hoffman, and F. Basolo, J. Am. Chem. Soc., 1975, 97, 5278.

[34]B. M. Hoffman, C. J. Weschler, and F. Basolo, J. Am. Chem. Soc., 1976, 98, 5437.

[35]B. M. Hoffman, T. Szymanski, T. G. Brown, and F. Basolo, J. Am. Chem. Soc., 1978, 100, 7253.

[36]K. L. Hansen and B. M. Hoffman, J. Am. Chem. Soc., 1980, 102, 4602.

[37]A. R. Miksztal and J. S. Valentine, Inorg. Chem., 1984, 23, 3548.

[38]R. A. Sheldon and J. K. Kochi, "Metal-Catalyzed Oxidations of Organic Compounds", Academic Press, New York, 1981.

[39]S. Patai, "The Chemistry of Peroxides," Wiley, New York, 1983.

[40]R. D. Jones, D. A. Summerville, and F. Basolo, Chem. Rev., 1979, 79, 139.

[41]C. Djordjevic, Chem. Brit. 1982, 18, 554.

[42] L. Vaska, *Acc. Chem. Res.*, 1976, *9*, 175.

[43] C. Djordjevic and N. Vuletic, *Inorg. Chem.*, 1980, *19*, 3049 and references therein.

[44] M. K. Chaudhuri and S. K. Ghosh, *Polyhedron*, 1982, *1*, 553.

[45] M. K. Chaudhuri and S. K. Ghosh, *Inorg. Chem.*, 1982, *21*, 4020.

[46] I. B. Svensson and R. Stromberg, *Acta Chem. Scand.*, 1971, *25*, 898.

[47] D. Begin, F. W. B. Einstein, and J. Field, *Inorg. Chem.*, 1975, *14*, 1785.

[48] P. Schwendt and D. Joniakova, *Polyhedron*, 1984, *3*, 287.

[49] D. T. Sawyer and J. S. Valentine, *Acc. Chem. Res*, 1981, *14*, 393.

[50] S. Funahashi, T. Midokikawa, and M. Tanaka, *Inorg. Chem.*, 1980, *19*, 91 and references therein.

[51] S. Funahashi, K. Haraguchi, and M. Tanaka, *Inorg. Chem.*, 1977, *16*, 1349.

[52] J. Stein, J. P. Fackler, Jr., G. J. McClune, J. A. Fee, and L. T. Chan, *Inorg. Chem.*, 1979, *18*, 3511.

[53] H. Mimoun, *J. Mol. Catal.*, 1980, *7*, 1.

[54] S. Oae, and T. Takata, *Tetrahedron Lett.*, 1980, *21*, 3689.

[55] H. Mimoun, I. Seree de Roch, and L. Sajus, *Tetrahedron*, 1970, *26*, 37.

[56] S. E. Jacobson, D. A. Muccigrosso, and F. Mares, *J. Org. Chem.*, 1979, *44*, 921.

[57] H. B. Kagan, H. Mimoun, C. Mark, and V. Shurig, *Angew. Chem., Int. Ed. Engl.*, 1979, *18*, 485.

[58] T. Katsuki, and K. B. Sharpless, J. Am. Chem. Soc., 1980, 102, 5974.

[59] B. E. Rossiter, T. Katsuki, and K. B. Sharpless, J. Am. Chem. Soc., 1981, 103, 464.

[60] L. Saussine, E. Brazi, A. Robine, H. Mimoun, J. Fisher, and R. Weiss, J. Am. Chem. Soc., 1985, 107, 3534.

[61] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry, " 4th Ed., Wiley, New York, 1980.

[62] M. N. Bhattacharjee, M. K. Chaudhuri, and R. N. Dutta Purkayastha, J. Chem. Soc. Dalton Trans., 1985, 409, and references therein.

[63] I. R. Gibbons, M. P. Cosson, J. A. Evans, B. H. Gibbons, B. Houck, K. H. Martinson, W. S. Sate, and W. Y. Tang, Proc. Natl. Acad. Sci., USA, 1978, 75, 2220.

[64] W. Mertz, Science, 1981, 213, 1332.

[65] J. Granot and J. Reuben, J. Am. Chem. Soc., 1978,100, 5210.

[66] N. M. Senozan, J. Chem. Education, 1974, 51, 503.

[67] J. C. Abrahams, Quart. Rev. Chem. Soc., 1956, 10, 407.

[68] S. N. Foner and R. L. Hudson, J. Chem. Phys., 1962, 36, 2676.

[69] G. Herzberg, "Molecular Spectra and Molecular Structure," 2nd Ed., Van Nostrand, New York, 1950.

[70] J. A. Creighton and E. R. Lippencott, J. Chem. Phys., 1964, 40, 1779.

[71] J. C. Evans, J. Chem. Soc. (D), 1969, 682.

[72] D.C. Bradley, J. S. Ghotra, F. A. Hart, M. B. Hursthouse, and P. R. Raithby, J. Chem. Soc. Dalton Trans., 1977, 1166.

[73] D. Begin, F. W. B. Einstein, and J. Field, *Inorg. Chem.*, 1975, **14** 1785.

[74] W. P..Griffith and T. D. Wickins, *J. Chem. Soc. (A)*, 1967, 590.

[75] W. P. Griffith, *J. Chem. Soc.*, 1964, 5248.

[76] W. P. Griffith, *J. Chem. Soc.*, 1963, 5345.

[77] W. P. Griffith and T. D. Wickins, *J. Chem. Soc. (A)*, 1967, 675.

[78] O. Brain and P. A. Giguere, *Canad. J. Chem.*, 1955, **33**, 527.

[79] E. Wendling, *Bull. Soc. Chim. France*, 1967, 16

[80] L. Vaska, *Science*, 1963, **140**, 809.

[81] O. Knop and P. A. Giguere, *Canad. J. Chem.*, 1959, **37**, 1794.

[82] W. P. Griffith and T. D. Wickins, *J. Chem. Soc.(A)*, 1968, 397.

[83] J. S. Griffith, *Proc. Royal Soc. London, Ser(A)*, 1956, **235**, 23.

[84] G. Mathern and R. Weiss, *Acta Cryst.*, 1971, **B27**, 1598.

[85] I. B. Svensson and R. Stromberg, *Acta Chem. Scand.*, 1971, **25**, 898.

[86] J. D. Swalen and J. A. Ibers, *J. Chem. Phys*. 1962, **37**, 17.

[87] J. E. Ferguson, C. J. Wilkins, and D. F. Young, *J. Chem. Soc.*, 1962, 2136.

[88] F. Chauveau, *Bull. Soc. Chim. France*, 1960, 819.

[89] L. Pissarevski, *Z. Physik. Chem.*, 1902, **40**, 368.

[90] L. Pissarevski, *Z. Physik. Chem.*, 1903, **43**, 173.

[91] M. E. Rumpf, *Annalen Chim. (Paris),* 1937, **8**, 456.

[92] G. Kakabadse and H. J. Wilson, J. Chem. Soc., 1960, 2475.

[93] J. Magee and E. Richardson, J. Inorg. Nucl. Chem., 1960, 15, 272.

[94] S. Yamada, Y. Ukei, and H. Tanaka, Inorg. Chem., 1976, 15, 964.

[95] K. Wieghardt, Inorg. Chem., 1978, 17, 57.

[96] U. Quititzsch and K. Wieghardt, Inorg. Chem., 1979, 18, 869.

[97] S. Funahashi, K. Ishihara, and M. Tanaka, Inorg. Chem., 1981, 20, 51.

[98] R. Mitra, T. P. McAndrew, and G. Mitra, J. Inorg. Nucl. Chem., 1981, 43, 421.

[99] J. P. Fackler, Jr., Progr. Inorg. Chem., 1966, 7, 361.

[100] M. Bartlett and G. J. Palenik, J. Chem. Soc., Chem. Commun., 1970, 416.

[101] J.P. Fackler, Jr., M. J. Weeks, and T. S. Davis, Inorg. Chem., 1968, 7, 1994.

[102] J. P. Fackler, Jr. and A. Avdeef, Inorg. Chem., 1974, 13, 1864.

[103] M. N. Bhattacharjee, M. K. Chaudhuri, and D. T. Khathing, J. Chem. Soc. Dalton Trans., 1982, 669.

[104] M. K. Chaudhuri, N. Roy, and D. T. Khathing, Synth. React. Inorg. Met.-Org. Chem., 1982, 12, 715.

[105] M. K. Chaudhuri and S.K. Ghosh, J. Chem. Soc. Dalton Trans., 1983, 839.

[106] P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel," Vol. 2, Academic Press, New York, 1975.

[107] G. Bontempelli, M. Andreuzzi-Seda, and M. Fiorani, Talanta, 1982, 29, 1101.

[108] R. E. Desay, F. E. Stary, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, 1766, *88*, 471.

[109] S. Kudo, A. Iwase, and N. Tanaka, *Bull. Chem. Soc. Jpn.*, 1981, *54*, 207.

[110] O. Sock, P. Lemoine, and M. Gross, *Electrochim. Acta*, 1981, *26*, 99.

[111] R. W. Murray and L. K. Hiller, Jr., *Anal. Chem.*, 1967, *39*, 1221.

[112] G. Gritzner, H. Murauer, and P. Gutman, *J. Electroanal. Chem.*, 1979, *101*, 177.

[113] C. W. Anderson, K. R. Lung, and T. A. Nile, *Inorg. Chim. Acta*, 1984, *85*, 33.

[114] G. Bontempelli, R. Piccolo, S. Deniele, and P. Ugo, *Inorg. Chim. Acta*, 1985, *99*, 43.

[115] R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, 1958, *62*, 440.

[116] G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, 1965, *4*, 456.

[117] H. Montgomery and E. C. Lingafelter, *Acat Cryst.*, 1964, *17*, 1481.

[118] W. C. Fernelius and B. E. Bryant, *Inorg. Synth.*, 1957, *5*, 105.

[119] B. E. Bryant and W. C. Fernelius, *Inorg. Synth.*, 1957, *5*, 114.

[120] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and D. T. Khathing, *J. Chem. Soc. Dalton Trans.*, 1981, 2587.

[121] M. N. Bhattacharjee and M. K. Chaudhuri, *Inorg. Synth.*, 1985, *24*, 0000.

[122] R. D. Peacock, *Irgr. Inorg. Chem.*, 1966, *2*, 41.

[123] R. Colton and J. H. Canterford, "Halides of the First Row Transition Metal," Wiely-Interscience, 1969.

[124] W. Massa, *Inorg. Nucl. Chem. Lett.*, 1977, *13*, 253.

[125] J. W. Vaughn, *Synth. React. Inorg. Met-Org. Chem.*, 1979, *9*, 585.

[126] R. G. Limck, *Inorg. Chem.*, 1977, *16*, 3143.

[127] J. W. Vaughn, *Inorg. Chem.*, 1981, *20*, 2397.

[128] J. W. Vaughn, *Inorg. Chem.*, 1983, *22*, 844.

[129] M. N. Bhattacharjee, M. K. Chaudhuri, and R. N. Dutta Purkayastha, *Inorg. Chem.*, 1985, *24*, 447.

[130] G. S. Phull, R. G. Plevey, and J. C. Tatlow, *J. Fluorine Chem.*, 1984, *25*, 111.

[131] G. S. Phull, R. G. Plevey, and J. C. Tatlow, *J. Chem. Soc. Perkin Trans. I*, 1984, 455.

[132] A. Haas and M. Lieb, *Chimia*, 1985, *39*, 134.

[133] M. K. Chaudhuri and N. Roy, *Synth. React. Inorg. Met.-Org. Chem.*, 1981, *11*, 677.

[134] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, A. Kathipri and D. T. Khathing, *Synth. React. Inorg. Met.-Org. Chem.*, 1982, *12*, 485.

[135] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, N. Roy, and D. T. Khathing, *Synthesis*, 1982, 588.

[136] M. N. Bhattacharjee, and M. K. Chaudhuri, *Polyhedron*, 1984, *3*, 599.

[137] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and A. Kathipri, *Polyhedron*, 1985, *4*, 621.

[138] Gmelin's Handbuch der Anorganischen Chemie, *57* (C, 1), Verlag Chemie, 1968.

[139] D. Nicholls, "The Chemistry of Iron, Cobalt and Nickel," Pergamon Texts in Inorganic Chemistry, Vol. 24, Pergamon Press, 1975, p 1139.

[140] L. Sacconi, *Transition Metal Chem.*, 1968, **4**, 199.

[141] A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, 1968.

[142] Ref. 139, p 1145.

[143] W. Rudorff, J. Kandler, and D. Babel, *Z. Anorg. Allgem. Chem.*, 1962, **317**, 261.

[144] D. H. Brown, K. Forrest, R. H. Nuttall, and D. W. A. Sharp, *J. Chem. Soc. (A)*, 1968, 2146.

[145] J. C. Cousseins and M. Samouel, *Compt. Rend.*, 1967, **265C**, 1121.

[146] D. J. Machin, R. L. Martin, and R. S. Nyholm, *J. Chem. Soc.*, 1963, 1490.

[147] D. J. Machin and R. S. Nyholm, *J. Chem. Soc.*, 1963, 1500.

[148] H. G. Schrering, *Z. Anorg. Allgem. Chem.*, 1967, **353**, 1.

[149] H. G. Schrering, *Z. Anorg. Allgem. Chem.*, 1967, **353**, 13.

CHAPTER 2

Chapter 2

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

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

Elemental Analyses

Vanadium[1]

Vanadium was estimated volumetrically by titration with standard potassium permanganate solution. A near boiling solution of an accurately weighed amount of the vanadium(V) compound, after removing peroxide, was treated with a stream of sulphur dioxide for *ca* 10 min, and then with a stream of carbon dioxide to expel any excess of sulphur dioxide. The vanadium(IV) solution thus obtained was cooled to *ca* 80°C, and finally titrated with a standard potassium permanganate solution[1].

Active Oxygen (Peroxy Oxygen)[2-4]

(i) Permanganometry[2]

An accurately weighed amount of the peroxyvanadate(V) compound was dissolved in 7(N) sulphuric acid containing ca 4 g of boric acid (boric acid is used to prevent any loss of active oxygen through the formation of peroxyboric acid). The solution was then titrated with a standard potassium permanganate solution.

1 cm^3 N $KMnO_4$ solution = 0.01701 g of H_2O_2

This method is suitable for determination of peroxide contents in peroxy-vanadium(V)compounds.

(ii) Iodometry[3]

In a freshly prepared 2(N) sulphuric acid solution, containing an appropriate amount of potassium iodide, was added an accurately weighed amount of the peroxyvanadate(V) compound with stirring. The solution was kept under an atmosphere of CO_2. After about 7 min, liberated iodine was titrated with a standard sodium thiosulphate solution.

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

(iii) Determination of Peroxide (O_2^{2-}) by Titration with a Ce^{4+} Solution[4]

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

Nickel[5]

Nickel was estimated gravimetrically as nickel dimethylglyoximate.[5]

In a typical procedure, an accurately weighed amount of the nickel compound was dissolved in a hot (70-80°C) dilute solution of hydrochloric acid (1 : 40). To it was added the requisite amount of 1% solution of dimethylglyoxime reagent in ethanol followed by the dropwise addition of aqueous ammonia, until the solution was faintly alkaline whereupon nickel dimethyl glyoximate was precipitated. The whole was heated on a boiling water-bath for ca 30 min, and the precipitate was allowed to settle for ca 2h, while cooling at the same time. Quantitative precipitation of nickel dimethylglyoximate was checked by adding a few drops of the dimethylglyoxime reagent solution. The precipitate was filtered on a weighed sintered Gooch crucible (G-4), washed several times with cold water until the washing was free from chloride. The crucible along with the precipitate was dried, to constant weight, at 110-120°C. The precipitate was weighed as nickel dimethylglyoximate.

Fluoride[6]

A weighed amount of the fluoronickelate(II) compound was dissolved in water, and the solution was treated with alkali (e.g. potassium hydroxide solution) in order to decompose the compound, and to separate nickel as $Ni(OH)_2$. The solution was filtered, the residue was washed thoroughly with water, and the filtrate and washings were collected for the estimation of fluoride.

From the above solution, fluoride was precipitated quantitatively as lead chloride fluoride, PbClF. The PbClF precipitate was filtered on a weighed sintered crucible (G-4), washed 4-5 times with a saturated solution of lead chloride fluoride, and finally dried to constant weight following the recommended procedure[6]. The precipitate was weighed as PbClF from which the fluoride content was found out.

Zinc[7]

Zinc, in fluorozincate(II) complexes, was estimated gravimetrically as zincammoniumphosphate.

In a representative procedure, an accurately weighed amount of the zinc compound was dissolved in water, from which zinc was precipitated out as zinc hydroxide by the addition of dilute sodium hydroxide solution. The precipitated zinc hydroxide was separated by filtration, washed several times with water to make it free from alkali, and then dissolved in 5(N) hydrochloric acid. The clear solution thus obtained was neutralised with dilute ammonia solution (4(N)) using methyl red as the indicator. The neutralised solution was heated to boiling, and then 10 %

diammonium hydrogen phosphate reagent was added with stirring until white precipitate ceased to appear. The whole was heated on a steam-bath for ca 1 h followed by cooling at room temperature for another period of about 45 min. The precipitate was filtered on a weighed sintered glass crucible (G-4), washed first with 1% solution of diammonium hydrogen phosphate and then with ethanol, and finally dried to constant weight by heating at 100-105°C. The precipitate was weighed as $ZnNH_4PO_4$.

Sodium and Potassium

Sodium and potassium contents were determined by flame photometry. The salts were first dissolved in deionised water and then acidified with hydrochloric acid. The acidified solution thus obtained was used for flame photometry.

Rubidium and Cesium[8]

Rubidium and cesium contents in the respective salts were estimated gravimetrically as their perchlorates. The precipitate was obtained by following the standard procedure[8], and weighed as $AClO_4$ ($A = Rb$ or Cs).

Carbon, Hydrogen, and Nitrogen

Carbon, hydrogen and nitrogen were estimated by microanalytical methods. The results of analyses were obtained from Amdel Australian Microanalytical Service, Port Melbourne, Victoria 3207, Australia, and also Microanalytical Laboratories, RSIC - NEHU, Shillong 793003.

Particulars of Instruments/Equipment Used

pH Measurement

The pH of the reaction solutions, whenever required, were measured by using a Systronics Type 335 digital pH meter.

Molar Conductance

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

Magnetic Susceptibility

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

Electronic Spectra

Electronic spectral measurements of solutions were made on a Beckman model UV-26 spectrophotometer.

Reflectance spectra of solids were recorded against MgO using Carl Zeiss Jena VSU 2-P instrument.

Infrared Spectra

Infrared spectra were recorded on the following spectrophotometers.

(a) Perkin-Elmer Model 297.

(b) Perkin-Elmer Model 125

and (c) 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 Argon laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube, followed by photon-count processing system.

The sample was held either in a quartz capillary or in the form of a pressed pellet. In some cases solution spectra were also recorded. The recording was done at ambient temperatures.

Mass Spectra[9,10]

The mass spectra were recorded on a Varian MAT CH-5 spectrometer. A direct insertion probe was used to introducee the samples directly into the ion source without any prior heating. The operating conditions were : electron energy 70eV (1eV = 1.6×10^{-19}J); source temperatures 50°, 100° and 150°C; resolution 10,000; accelerating voltage 8kV. The mass spectrometric observations were made with the ionising beam current held constant to obtain reproducible ion intensities.

The mass spectra were recorded with the ion source temperature being maintained at either 50°, 100° or 150°C, and the samples were introduced in the spectrometer, using a direct insertion probe, without any prior heating to avoid any pyrolytic effects prior to the compounds coming in contact with the ionising electron beam.

References

1 M.C. Steele and F.M. Hall, Anal. Chim. Acta, 1953, 9, 384.

2 A.I. Vogel, "A Text Book of Quantitative Inorganic Analysis", Longmans, Green and Co., New York, 1962, p 295.

3 A.I. Vogel, Ref. 2, p 363.

4 A.I. Vogel, Ref. 2, p 325.

5 A.I. Vogel, Ref. 2, p 479.

6 A.I. Vogel, Ref. 2, p 569.

7 A.I. Vogel, Ref. 2, p 532.

8 A.I. Vogel, Ref. 2, p 562.

9 M.K. Chaudhuri, H.S. Dasgupta, N. Roy, and D.T. Khathing, Org. Mass Spectrom., 1981, 16, 303; 1981, 16, 534.

10 M.C. Chakravorti, D. Bondypadhay, and M.K. Chaudhuri, Int. J. Mass Spectrom. Ion Processes, 1985, 64, 0000.

CHAPTER 3

Chapter 3

First Synthesis and Structural Assessment of Alkali Oxodiperoxymonocarbonatovanadate(V) Trihydrates $A_3[VO(O_2)_2CO_3].3H_2O$ (A = Na or K)*

The importance of peroxyvanadium chemistry has been emphasised in Chapter 1. It is evident from the contemporary chemistry literature that studies of peroxyvanadium chemistry have generated considerable current interest[1-9] probably owing to the special biochemical significance[10-12] of peroxy-transition metal compounds, and their involvement in the activation and transfer of molecular oxygen to organic substrates.[8,13] Whereas most of the recent reports on peroxyvanadium chemistry deal with the studies in solutions,[2-7] the synthesis and structural assessment of such compounds have received only scant attention. Moreover, only a limited number of heteroligand peroxy complexes of vanadium are known, in contrast to many such reported examples for other transition metals.[12,14-16] The synthesis of well-defined peroxy-vanadium compounds and the study of their properties provide a heuristic approach to the understanding of peroxy-vanadium chemistry.

Although a few peroxyvanadates(V) containing coordinated N-heterocyclic ligands have been well characterised,[1,5] complex peroxyvanadates(V) with oxygen containing ligands are scanty.

---

*The work described in this Chapter has been accepted for publication. J. Chem. Soc. Dalton Trans., 1985, in press.

The $[VO(O_2)_2C_2O_4]^{3-}$ and $[VO(O_2)(C_4H_5NO_4)]^{-}$ ($C_4H_5NO_4^{2-}$ = the anion of iminodiacetic acid, $C_4H_7NO_4$) ions[1,5,17] are the only examples reported to our knowledge. Recent attempts to bring about coordination of SO_4^{2-} with vanadium(V) in the presence of peroxide ligand (O_2^{2-}) were unsuccessful,[18] however, the coordination of carbonate (CO_3^{2-}) and O_2^{2-}, in the presence of each other, with vanadium(V) appeared to be possible under an appropriate condition.

Accordingly, the above considerations prompted the synthesis, characterisation, and assessment of structure and properties of alkali oxodiperoxymonocarbonatovanadate(V) trihydrates, $A_3[VO(O_2)_2CO_3]\cdot 3H_2O$ (A = Na or K). The present Chapter reports the details of the results of studies on the title compounds.

Experimental

The chemicals used were all reagent grade products (B.D.H., E. Merck, S.D's and IDPL).

Synthesis of Alkali Oxodiperoxymonocarbonatovanadate(V) Trihydrates, $A_3[VO(O_2)_2CO_3]\cdot 3H_2O$ (A = Na or K)

Since the method of synthesis of alkali oxodiperoxymonocarbonatovanadates(V) trihydrates is a general one, only a representative procedure is described below.

In a typical synthesis a mixture of 1g (5.5 mmol) of vanadium pentoxide, V_2O_5, and alkali carbonate, A_2CO_3 (A = Na or K; 16.5 mmol), maintaining V : CO_3^{2-} ratio of 1 : 1.5, was dissolved in 15 cm^3 (132.4 mmol) of 30% hydrogen peroxide to obtain a clear yellow solution. The solution was filtered and the filtrate cooled in an ice-water bath for _ca_ 15 min. An excess of pre-cooled ethanol was added to the above solution with stirring until the yellow microcrystalline alkali oxodiperoxymonocarbonatovanadate(V) trihydrate, $A_3[VO(O_2)_2CO_3].3H_2O$ (A = Na or K) was completely precipitated. The stirring and cooling (at an ice-water bath temperature) was continued for a further period of 30 min. The compound thus obtained was separated by filtration, washed four times with ethanol, and finally dried _in vacuo_ over concentrated sulphuric acid.

The yields of

$Na_3[VO(O_2)_2CO_3].3H_2O$ was 3g (87%)

and of $K_3[VO(O_2)_2CO_3].3H_2O$ was 3.2g (80%).

Elemental Analyses

Vanadium, peroxide, carbon, sodium, and potassium contents were determined by the methods described in Chapter 2.

The results of elemental analyses are summarised in Table 1, while the molar conductance values, and structurally significant infrared and Raman band positions along with their assignments are reported in Table 2.

Table 1. Analytical Data of $A_3[VO(O_2)_2CO_3]\cdot3H_2O$ (A = Na or K)

Compound	Found % (Calcd. %)			
	A	V	O^a	C
$Na_3[VO(O_2)_2CO_3]\cdot3H_2O$	23.21 (21.97)	16.7 (16.22)	20.65 (20.38)	3.86 (3.82)
$K_3[VO(O_2)_2CO_3]\cdot3H_2O$	32.62 (32.38)	14.54 (14.06)	18.2 (17.66)	3.35 (3.32)

[a] Peroxy-oxygen

Results and Discussion

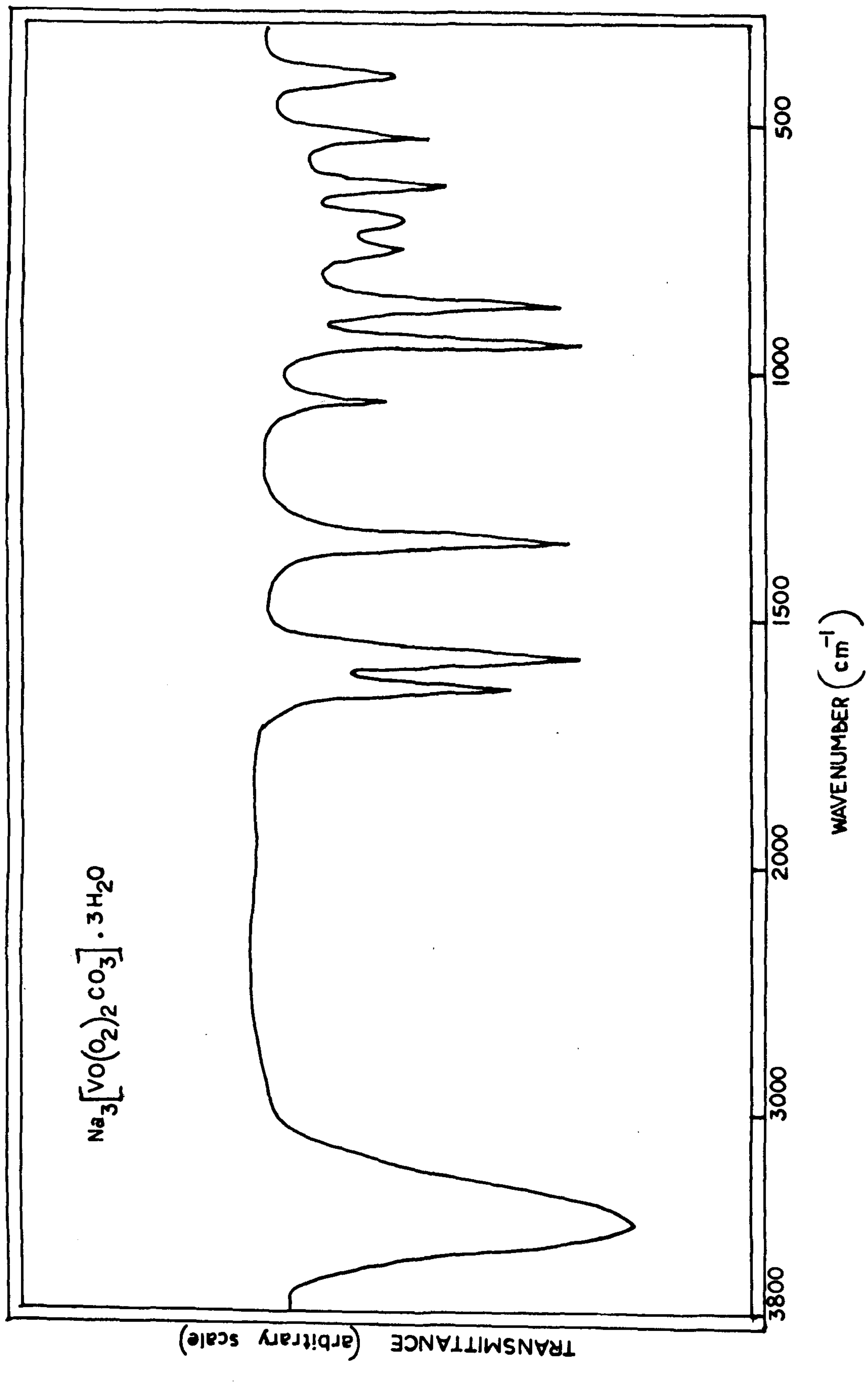
The reactions of vanadium with hydrogen peroxide are highly pH dependent, and a small variation of pH of the reaction solutions leads to the formation of peroxy-vanadium complexes of different compositions. The importance of pH, for the successful synthesis of peroxy-metal compounds, has been emphasised,[4,12,14] and it was shown very recently that a relatively higher pH was favourable for the coordination of peroxide (O_2^{2-}) with a VO^{3+} centre.[4,14] Indeed, in the present case pH $>$ 6 was considered conducive also in order to prevent carbonate (CO_3^{2-}) annihilation through $CO_3^{2-} + 2H^+ \longrightarrow CO_2 + H_2O$ reaction. Accordingly the reactions among vanadium pentoxide, alkali carbonate, A_2CO_3 (A = Na or K), and 30% hydrogen peroxide were carried out at various pH (between 2 and 8), and it was ascertained from the results that pH ca 7 was suitable for the synthesis of the title compounds. It is imperative to mention that the products isolated at pH 4 or 5 either do not show the presence of carbonate (CO_3^{2-}) at all, or do to a very small extent indicating that the CO_3^{2-} ligand might have just started coordinating with the vanadium centre. This observation therefore suggest that acidic conditions are not conducive to the desired synthesis. Thus, the reaction of V_2O_5 with H_2O_2 and A_2CO_3 at pH 7 followed by the addition of ethanol (vide Experimental) afforded alkali oxodiperoxymonocarbonatovanadate(V) trihydrates, $A_3[VO(O_2)_2CO_3].3H_2O$ (A = Na or K), in very high yields. The reaction was monitored by isolating a small amount of the product and recording its IR spectra. Appearance of a strong band at ca 860 cm^{-1} due to the ν(O-O) mode of coordinated peroxide (O_2^{2-}), and the bands due to the occurrence of coordinated carbonate[19] indicates the formation of the complex species. The role of ethanol in the present synthesis was to facilitate precipitation of the compounds. Attempts to synthesise the ammonium salt of the complex $[VO(O_2)_2CO_3]^{3-}$ ion have have not been successful. However, the corresponding Rb^+ and Cs^+ salts could be synthesised following the method analogous to that used for the synthesis of the Na^+ and K^+ salts.

Characterisation and Assessment of Structure. Alkali oxodiperoxymonocarbonatovanadate(V) trihydrates, $A_3[VO(O_2)_2CO_3].3H_2O$ (A = Na or K), are yellow microcrystalline products, and can be stored for a prolonged period in sealed containers. Their stability was ascertained from the results of chemical determinations of peroxide (O_2^{2-}), vanadium, and carbon contents periodically. The comppunds are soluble in water at ambient temperatures, but the dissolution is accompanied by simultaneous decomposition, and their molar conductance measurements at room temperature were thus precluded. While the room temperature molar conductances of A_3 $[VO(O_2)_2CO_3]\cdot 3H_2O$ were higher than the expected values, the figure obtained by recording the molar conductance at $7^{\circ}C$ was found to be ca 370 $\Omega^{-1}cm^2mol^{-1}$, in very good agreement with the formula. This leads us to believe that the complex peroxycarbonatovanadates(V) are stable in solutions only at low temperatures.

In an attempt to find out the possibility of dehydration of A_3 $[VO(O_2)_2CO_3]\cdot 3H_2O$ compounds, pyrolysis of the compounds were carried out at $100^{\circ}C$. Unfortunately the compounds started undergoing decomposition involving the simultaneous loss of both peroxide (O_2^{2-}) and H_2O, thus a genuine dehydration was not possible.

The A_3 $[VO(O_2)_2CO_3]\cdot 3H_2O$ compounds were diamagnetic in nature, as evidenced from the results of magnetic susceptibility measurements, in conformity with the occurrence of vanadium(V) in each of them. The chemical determination of peroxide contents of such compounds are to be considered very crucial in order to fix the number of peroxide (O_2^{2-}) groups bound to the metal centre. The peroxide estimations were accomplished by red-ox titrations separately involving standard potassium permanganate and Ce^{4+} solutions by following the procedures described in Chapter 2. The results obtained thereof conspicuously suggest the presence of two peroxides per vanadium(V) centre in each of the newly synthesised compounds.

The infrared and Laser Raman spectra of alkali oxodiperoxymonocarbonatovanadate(V) trihydrates, A_3 $[VO(O_2)_2CO_3]\cdot 3H_2O$ (A = Na or K), are in order and quite characteristic. The significant features of IR spectra of the compounds are the absorptions due to $\nu(V = O)$, coordinated peroxides, and coordinated carbonate (CO_3^{2-}) ligands. The strong band at ca 940 cm^{-1} has been assigned to $\nu(V = O)$ arising from the terminally bonded $V = O$ group. The bands at 865s, ca 620s and at ca 525s cm^{-1} owe their origin to the coordinated peroxides. While the band at 865s cm^{-1} is assigned to $\nu(O - O)$, ν_1, those at ca 620s and ca 525s cm^{-1} have been assigned to the ν_3 and ν_2 modes respectively of $\nu(V - O_2)$ vibrations. The frequencies observed at ca 1585s, ca 1340s, ca 1050s, ca 740m, ca 695w, and ca 395m cm^{-1} have been attributed to $\nu(C-O)$, $\nu(C-O) + \delta(O-C-O)$, $\nu(C-O)$, ring deformation + $\nu(V-O)$, $\delta(O-C-O) + \nu(V-O)$, and $\nu(V-O)$ modes[19] respectively arising from the presence of coordinated carbonate (CO_3^{2-}) ligand. The appearance of $\nu_1(A_1)$ and $\nu_5(B_2)$ modes of carbonate at ca 1585s and ca 1340s cm^{-1} respectively with an appreciable separation between the two bands provides a very good evidence for the occurence of a chelated carbonate (C_{2v}) ligand. The two additional bands at ca 1640s and ca 3455m cm^{-1} in each of the sodium and potassium salts resemble in their shapes and positions those commonly observed for the uncoordinated water,[20,21] and have been assigned to $\delta(H-O-H)$ and $\nu(O-H)$ modes. Further it was emphasised in the literature[22] that the $\nu(O-H)$ band at 3455 cm^{-1} is rather typical of lattice water. These and the loss of water at 100°C from $A_3[VO(O_2)_2CO_3]\cdot 3H_2O$ lead us to infer that the water molecules are not coordinated to the vanadium(V) centre.


$Na_3[VO(O_2)_2CO_3] \cdot 3H_2O$
TRANSMITTANCE (arbitrary scale)
WAVENUMBER (cm^{-1})
3800
3000
2000
1500
1000
500

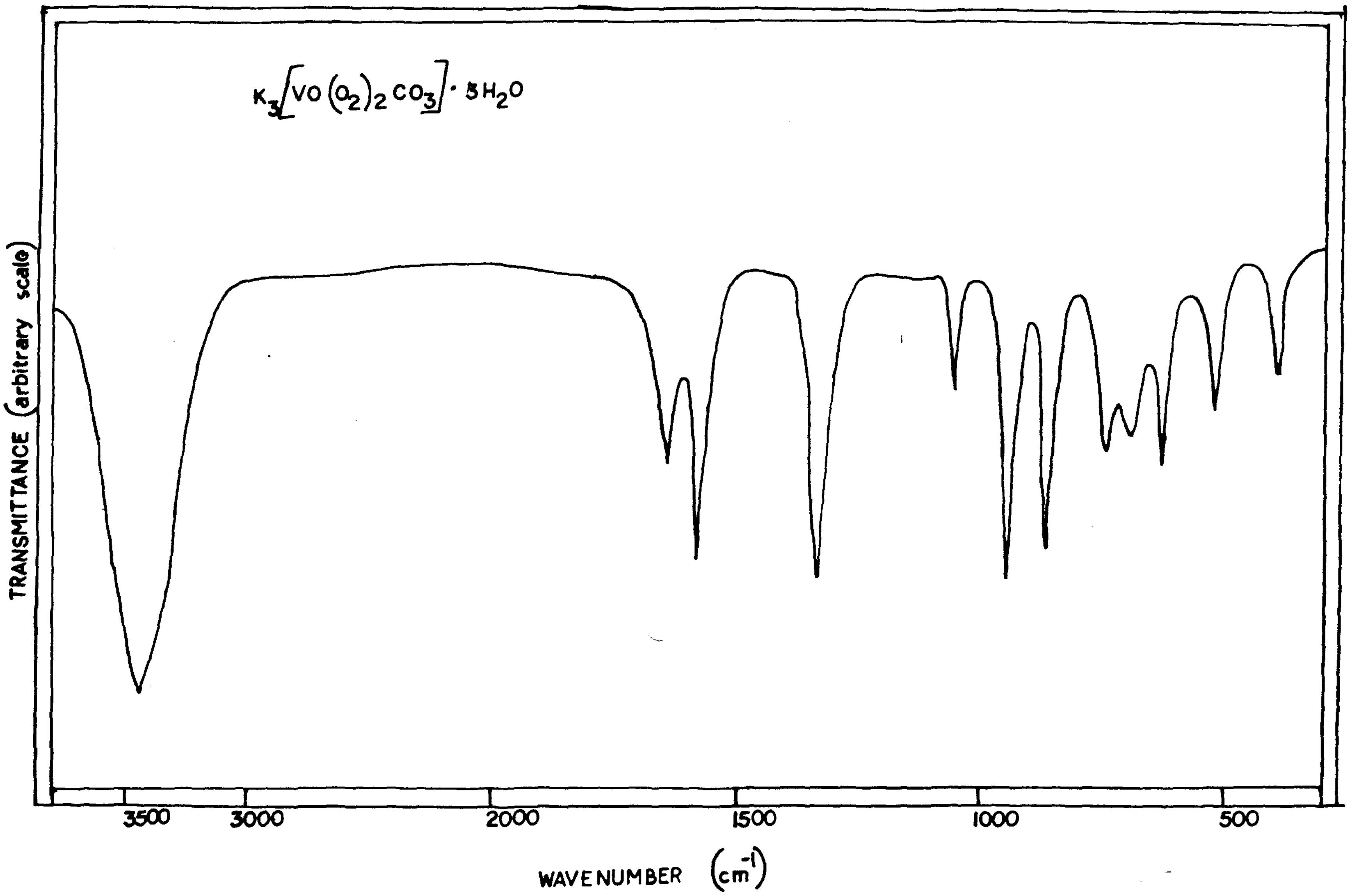

$K_3[VO(O_2)_2CO_3]\cdot 3H_2O$
TRANSMITTANCE (arbitrary scale)
3500
3000
2000
1500
1000
500
WAVENUMBER (cm^{-1})

Table 2. Molar Conductance Values, and Structurally Significant IR and Laser Raman (LR) bands of $A_3[VO(O_2)_2CO_3]\cdot 3H_2O$ (A = Na or K)

Compounds	Molar Conductance $\Omega^{-1}cm^2mol^{-1}$ (temp./°C)	IR cm^{-1}	Laser Raman cm^{-1}	Assignments
$Na_3[VO(O_2)_2CO_3]\cdot 3H_2O$	370	940s	940	$\nu(V=O)$
	(7)	865s	870	$\nu(O-O)$, ν_1
		620s	600	$\nu(V-O_2)$, ν_3
		525s	530	$\nu(V-O_2)$, ν_2
		1580s	1580	$\nu(C-O)$, ν_1, A_1
		1340s		$\nu(C-O) + \delta(O-C-O)$. ν_5, B_2
		1045s		$\nu(C-O)$
		750m		$\nu(V-O)$ + ring deformation
		690w		$\delta(O-C-O) + \nu(V-O)$
		400m		$\nu(V-O)$
		3450m		$\nu(O-H)$
		1640s		$\delta(H-O-H)$
$K_3[VO(O_2)_2CO_3]\cdot 3H_2O$	375	945s	940	$\nu(V=O)$
	(7)	865s	865	$\nu(O-O)$, ν_1
		625s	600	$\nu(V-O_2)$, ν_3
		520s	530	$\nu(V-O_2)$, ν_2
		1585s	1580	$\nu(C-O)$, ν_1, A_1
		1335s		$\nu(C-O) + \delta(O-C-O)$ ν_5, B_2
		1050s		$\nu(C-O)$
		740m		$\nu(V-O)$ + ring deformation
		695w		$\delta(O-C-O) + \nu(V-O)$
		395m		$\nu(V-O)$
		3455m		$\nu(O-H)$
		1640s		$\delta(H-O-H)$

The Laser Raman (LR) spectra of alkali oxodiperoxymonocarbonatovanadate(V) trihydrates, $A_3[VO(O_2)_2CO_3]\cdot 3H_2O$ (A = Na or K), were recorded only on solids, as the compounds decompose, at room temperature, in water. The LR spectra augment the results of IR spectral studies. The characteristic features of LR spectra are the peak at 940 cm^{-1} assigned to $\nu(V{=}O)$, and the bands at *ca* 870, *ca* 600 and *ca* 530 cm^{-1} attributed to the $\nu(O-O,\ \nu_1)$, $\nu(V-O_2,\ \nu_3)$ and $\nu(V-O_2,\ \nu_2)$ modes[23,24] respectively of co-ordinated peroxide (O_2^{2-}) ligands. The LR peaks at *ca* 1580 cm^{-1} has been assigned to the $\nu(C-O,\ \nu_1, A_1)$ mode of the coordinated CO_3^{2-} group. It may be noted that the observed positions of $\nu(O-O)$ and $\nu(V-O_2)$ modes are the ones which one would expect to observe for a triangularly bonded O_2^{2-}. Considering C_{2v} being the local symmetry of coordinated O_2^{2-} ligand, three (two A_1 and one B_2) are expected to be IR and Raman active, of which the two A_1 modes (ν_1, $\nu(O-O)$ stretching and ν_2, $\nu(V-O_2)$ symmetric stretching) are polarised, while the B_2 mode (ν_3, $\nu(V-O_2)$ assymmetric stretching) depolarised in the Raman.[23,24] The distinction between the ν_2 and ν_3 modes in the present case has been made on the basis of sharpness and intensity of the observed LR signals. Thus the peroxide ligands are bonded to the vanadium(V) centre in a triangular bidentate manner.

It may be inferred that peroxycarbonatovanadates(V) of the $A_3[VO(O_2)_2CO_3]\cdot 3H_2O$ can be synthesised directly from the reaction of V_2O_5 with A_2CO_3 and hydrogen peroxide at pH 7. The typical pattern of the IR as well as the LR spectra due to the coordinated peroxides (O_2^{2-}), and due to the coordinated CO_3^{2-} ligand especially the appreciable separation between $\nu_1(A_1)$ and $\nu_5(B_2)$ modes (Table 2) and also the appearance of Raman peak at ca 1580 cm^{-1} due to ν(C-O), ν_1, A_1 render it certain that both peroxide (O_2^{2-}) as well as carbonate (CO_3^{2-}) ligands are bonded to the vanadium(V) centre in a bidentate chelated (C_{2v}) fashion. The complex $[VO(O_2)_2CO_3]^{3-}$ ion may have a pentagonal bipyramidal structure like that of $[VO(O_2)_2C_2O_4]^{3-}$ ion (Ref. 5).

References

1 J.A. Connor and E.A.V. Ebsworth, Adv. Inorg. Chem. Radiochem., 1964, 6, 345.

2 R.J.H. Clark and D. Brown, "The Chemistry of Vanadium, Niobium and Tantalum," Pergamon Texts in Inorganic Chemistry, Vol. 20, Pergamon Press, Elmsford, NY, 1975, p 519.

3 J.A. Connor and E.A.V. Ebsworth, Ref. 1., p 352.

4 M. K. Chaudhuri and S.K. Ghosh, Inorg. Chem., 1984, 23, 534, and references therein.

5 N.J. Campbell, M.V. Capparelli, W.P. Griffith, and A.C. Skapski, Inorg. Chim. Acta, 1983, 77, L 215.

6 N. Vuletic and C. Djordjevic, J. Chem. Soc., 1973, 1137.

7 M.K. Chaudhuri, S.K. Ghosh, and N. S. Islam, Inorg. Chem., 1985, 24, 2706.

[8] H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fischer, and R. Weiss, *J. Am. Chem. Soc.*, 1983, **105**, 3101.

[9] P. Schwendt and P. Joniakova, *Polyhedron*, 1984, **3**, 287.

[10] G.V. Jere and S. M. Kausik, *Synth. React. Inorg. Met.-Org. Chem.*, 1980, **10**, 255.

[11] R.D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.

[12] J. A. Connor and E. A. V. Ebsworth, Ref. 1, p 292.

[13] H. Mimoun, M. Postel, F. Casabianca, J. Fischer, and A. Mitschler, *Inorg. Chem.*, 1982, **21**, 1301.

[14] M. K. Chaudhuri and S.K. Ghosh, *Inorg. Chem.*, 1982, **21**, 4020; *J. Chem. Soc. Dalton Trans.*, 1984, 507.

[15] K. W. Bagnall, D. Brown, and J. F. Easey, *J. Chem. Soc. A*, 1968, 2223.

[16] A. R. Miksztal and J.S. Valentine, *Inorg. Chem.*, 1984, **23**, 3548, and reference therein.

[17] C. Djordjevic, S. A. Craig and E. Sinn, *Inorg. Chem.*, 1985, **24**, 1283.

[18] M. K. Chaudhuri and N. S. Islam, *Transition Met. Chem.*, 1985, in press.

[19] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd. Ed., Wiley-Interscience, London, 1970, p 169.

[20] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, and D. T. Khathing, *J. Chem. Soc. Dalton Trans.*, 1981, 2587.

[21] A. J. Edwards, *J. Chem. Soc. A*, 1971, 2653.

[22] N. F. Curtis, J. Chem. Soc. A, 1968, 1584.

[23] W. P. Griffith, J. Chem. Soc., 1963, 5345; 1964, 5248.

[24] W. P. Griffith and T. D. Wickins, J. Chem. Soc. A, 1968, 397.

CHAPTER 4

Chapter 4

Monokis(ethylenediamine)oxodiperoxyvanadate(V) Complexes, $[VO(O_2)_2en]^-$. Synthesis and Assessment of Structure of $A[VO(O_2)_2en]$ (A = Na, K or NH_4) Compounds

Peroxy-vanadium compounds are known to act as catalysts,[1,2] and have been proposed as one of the model systems for the biochemistry of vanadium[3]. Although vanadium has been recently recognised as an essential element for mammals[4], its actual function remains unknown[5,6]. It has been reported in a very recent communication [3] that some heteroligand peroxyvanadate(V) compounds have shown "antitumor activity". Also it has been emphasised that the biological activity of such compounds strongly depends upon the heteroligand[3]. Thus a systematic study involving heteroligand peroxyvanadium(V) complexes is extremely important. Recently some heteroligand peroxyvanadate(V) complexes were synthesised[7] in the laboratory where the present work was carried out, however, their limitation was that the heteroligand was a highly electronegative one viz., F^- or Cl^-, and the resultant complexes were unstable in solutions. It was expected that a suitable chelating heteroligand should be able to impart stability to peroxyvanadate(V) systems rendering them stable not only in the solid state but also in solutions. It is pertinent to mention that a few heteroligand peroxyvanadate(V) containing bidentate heteroligand have been reported.[3,8,9]

In a continuation of the work on peroxyvanadates(V) described in Chapter 3, it was decided to investigate such complexes containing bidentate amine ligands, to find out general methods for their syntheses, mode of coordination of both peroxide as well as the heteroligand, the stability, and finally the reactivity of coordinated peroxides.

The present Chapter provides an account of the hitherto unreported compounds, alkali monokis(ethylenediamine)oxodiperoxyvanadates(V), $A[VO(O_2)_2en]$ (A = Na, K or NH_4), in terms of their method of synthesis, the mode of coordination of the ligands, and also the effect of the bidentate ligand 'en' (en = ethylenediamine) on the stabilities of the peroxyvanadate(V) complexes in going from $[VO(O_2)_2X]^{2-}$ ($X = F^-$ or Cl^-) to $[VO(O_2)_2en]^-$. Also reported in this Chapter is the importance of pH as the vital factor for the successful synthesis of heteroligand peroxyvanadate(V) complexes of the general formula $[VO(O_2)_2(L-L)]^-$ (L - L = ethylenediamine (en), 2,2 - bipyridyl (bipy), or 1,10- phenanthroline (o-phen)).

Experimental

Reagent grade chemicals were used for the syntheses.

Synthesis of Alkali Monokis(ethylenediamine)oxodiperoxyvanadates(V), $A[VO(O_2)_2en]$ (A = Na, K or NH_4)

As the methods of synthesis of the afore-mentioned compounds are similar, only a typical procedure is described below.

An amount of 0.5g (2.75 mmol) of vanadium pentoxide was dissolved in 10 cm^3 (88.2 mmol) of 30% hydrogen peroxide. The solution was filtered and cooled in an ice-water bath for ca 15 min. Pre-cooled ethylenediamine (3.0g, 49.9 mmol) was slowly added to the above solution dropwise with constant stirring followed by the slow addition of alkali hydroxide, AOH (A = Na or K), or aqueous ammonia until the pH of the solution was raised to 9. While sodium or potassium hydroxide was added in the form of a 20% aqueous solution, aqueous ammonia was added as its concentrated solution (sp.gr. 0.9). The reaction container was allowed to cool in an ice-water bath for ca 25 min, and an excess of ethanol was added with slow stirring until the lemon-yellow microcrystalline A $[VO(O_2)_2(en)]$ ceased to appear. The compound was allowed to settle, and then isolated by centrifugation. The product thus obtained was washed 3-4 times with ethanol and dried in vacuo over concentrated sulphuric acid.

The specific gram amounts of reagents used and the yields of A $[VO(O_2)_2\ en]$ compounds obtained are reported in Table 1.

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

Compound	Yield in g (%)	Amount of V_2O_5 in g (mmol)	Amount of 30% H_2O_2 in cm^3 (mmol)	Amount of ethylenediamine in g (mmol)
$NH_4[VO(O_2)_2en]$	1 (87)	0.5 (2.75)	10 (88.2)	3 (49.9)
$Na[VO(O_2)_2en]$	0.9 (76)	0.5 (2.75)	10 (88.2)	3 (49.9)
$K[VO(O_2)_2\ en]$	1.1 (87)	0.5 (2.75)	10 (88.2)	3 (49.9)

Elemental Analyses

The details of the methods of analyses were given in Chapter 2. The results of elemental analyses are given in Table 2.

Table 2. Analytical Data of $A[VO(O_2)_2en]$ ($A = Na$, K or NH_4)

	Found % (Calcd, %)			
	A or N	V	O^a	C
$NH_4[VO(O_2)_2en]$	20.2 (20.1)	24.12 (24.36)	30.9 (30.61)	11.57 (11.49)
$Na[VO(O_2)_2en]$	10.21 (10.74)	23.35 (23.8)	30.8 (29.9)	11.61 (11.22)
$K[VO(O_2)_2\ en]$	16.4 (17)	22.72 (22.13)	28.2 (27.81)	10.28 (10.44)

[a] Peroxy oxygen.

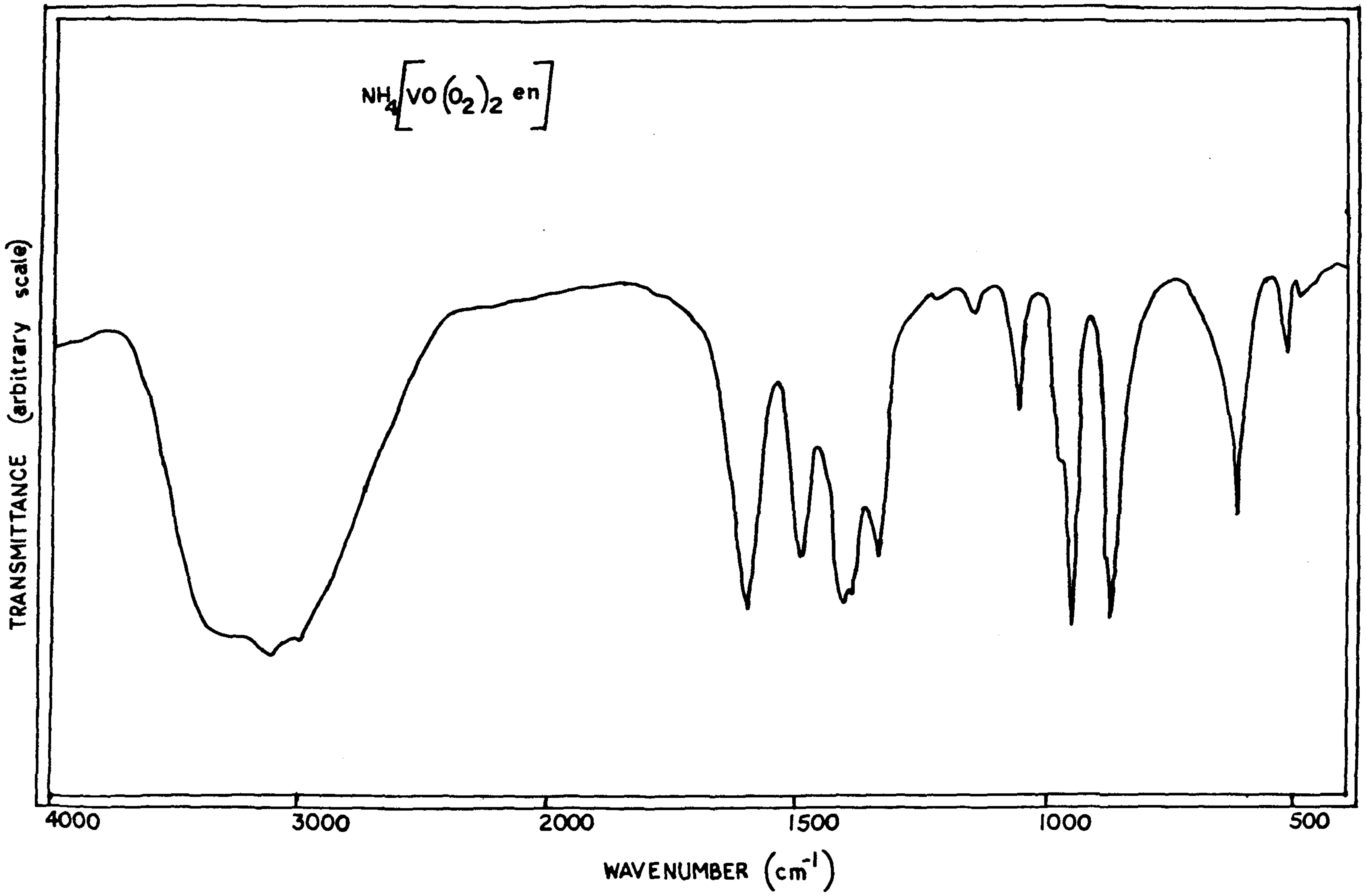
The molar conductance values and structurally important infrared and Laser Raman (LR) bands along with their assignments are summarised in Table 3.

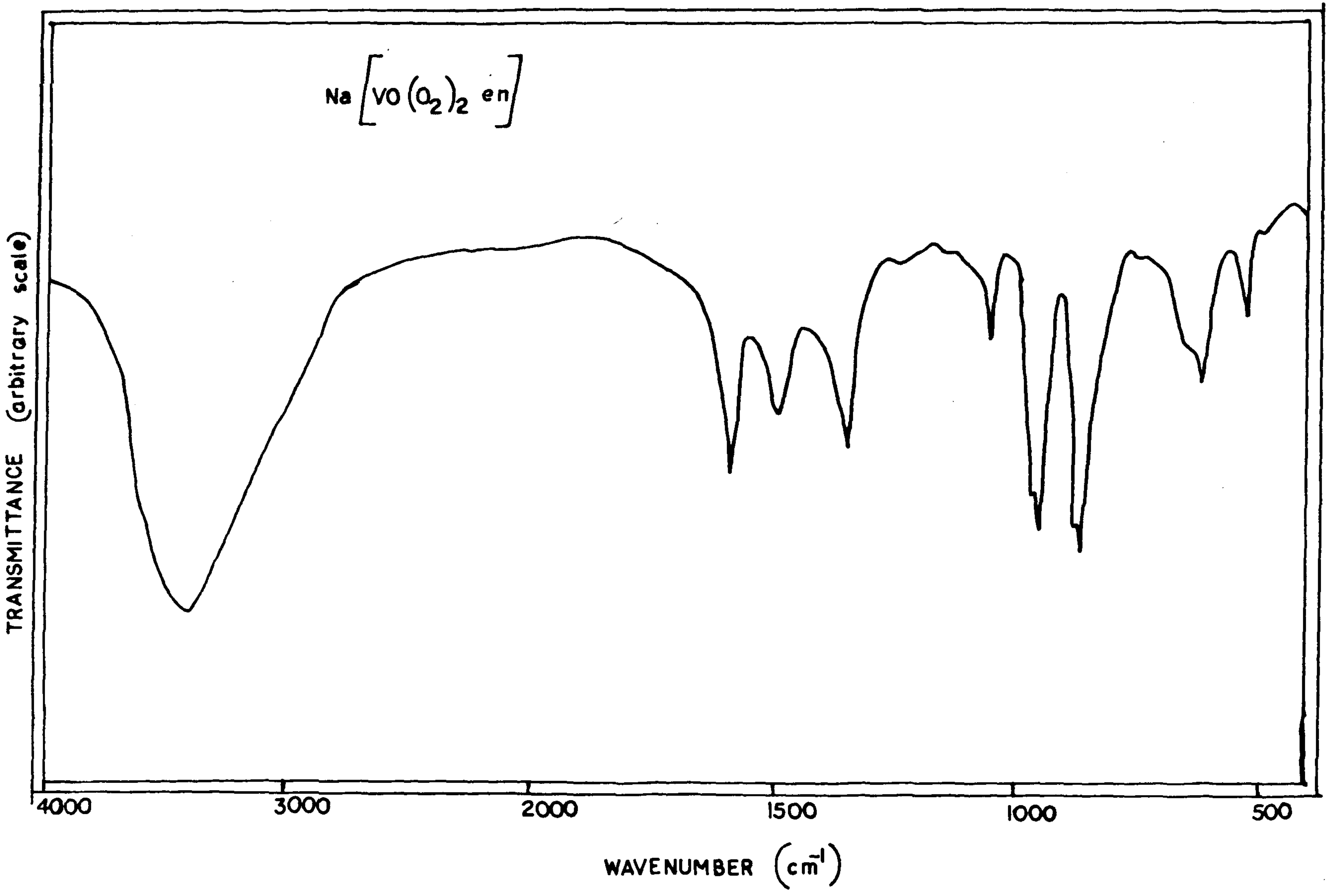
Results and Discussion

The role of pH in the syntheses of heteroligand peroxyvanadate(V) has been emphasised in the previous Chapter (Chapter 3). Albeit some peroxyvanadate(V) complexes containing chelated aromatic diamine ligands viz., 2,2 -bipyridyl (bipy) and 1,10-phenanthroline (o-phen) were reported in the literature,[8,9] no such complexes with aliphatic diamine heteroligands are known to date. A search for the suitable synthetic route for such compounds was therefore required. Attempts were made by the present worker to synthesise peroxyvanadates(V) containing coordinated aliphatic diamine heteroligand like ethylenediamine (en), under the conditions analogous to those maintained for the syntheses of the corresponding complexes containing aromatic diamines,[8,9] but the attempts were in vain. In view of this and a consideration of the fact that ethylenediamine (en) is more basic than 2,2 - bipyridyl or 1,10-phenanthroline it was expected that a comparatively higher pH of the reaction medium would be more conducive to the desired synthesis. Since no mention was made, in regard to the suitable pH for the successful syntheses of oxodiperoxyvanadate(V) complexes with coordinated aromatic diamine heteroligands, in the earlier reports[8,9], the $[VO(O_2)_2\ bipy]^-$ and $[VO(O_2)_2\ o\text{-}phen]^-$ complexes were synthesised independently and it has been ascertained that pH 4-5 is rather appropriate for the purpose. Whereas pH 4-5 is suitable for the synthesis of $[VO(O_2)_2\ bipy]^-$ or $[VO(O_2)_2\ O\text{-}phen]^-$, pH 9 has been found to be appropriate for the purpose of synthesis of the corresponding ethylenediamine (en) complex. Accordingly the reaction of vanadium pentoxide, V_2O_5, hydrogen peroxide, and ethylenediamine at pH 9, maintained by the addition of alkali hydroxide, AOH (A = Na or K), or aqueous ammonia (vide Experimental), led to the successful synthesis of the hitherto unknown alkali monokis(ethylenediamine)oxodiperoxyvanadates(V), $A[VO(O_2)_2\ en]$ (A = Na, K or NH_4), in high yields. The function of ethanol in the present synthesis was to bring about and facilitate precipitation of the desired products. Another important point that deserves a comment at this stage is the necessity of very slow addition of the requisite amount of ethylenediamine (en). A rapid addition generates heat causing a rapid decomposition of hydrogen peroxide, and this is considered detrimental to the synthesis. The progress of the reaction is monitored by infrared spectroscopy. The appearance of a strong band at ca 870 cm^{-1} due to ν (O-O), and the bands due to coordinated ethylenediamine[10,11] in the IR spectrum of the compound isolated from a small fraction of the reaction solution indicated the formation of the desired complex species. The method described (vide Experimental) can be scaled up, and higher amounts of the compounds can as well be obtained by following the present procedure.

Characterisation and Assessment of Structure. Alkali monokis(ethylenediamine)oxodiperoxyvanadates(V), $A[VO(O_2)_2en]$ (A = Na, K or NH_4), are all lemon-yellow coloured products, and stable for a prolonged period. Their stability is ascertained by chemical estimations of vanadium and peroxide contents periodically. The A $[VO(O_2)_2en]$ compounds, unlike the $A_2[VO(O_2)_2X]$ ($X = F^-$ or Cl^-)[7], are stable also in solutions from which they can be recrystallised. The observed increase of stability in going from $[VO(O_2)_2X]^{2-}$ to $[VO(O_2)_2en]^-$ is ascribed to the "chelate effect" brought about by the presence of chelating ethylenediamine ligand. The enhanced stability of the newly synthesised compounds has been ascertained from the results of molar conductance measurements. Whereas the $A_2[VO(O_2)_2X]$ ($X = F^-$ or Cl^-) compounds do not permit molar conductance measurements, the values obtained for the A $[VO(O_2)_2en]$ (A = Na, K or NH_4) complexes have been found to lie in the range 115 ——— 125 $\Omega^{-1}cm^2mol^{-1}$ (at 22°C in water) strongly supporting their 1 : 1 electrolytic nature in solutions in complete agreement with the formula.

Alkali monokis(ethylenediamine)oxodiperoxyvanadate(V) complexes are all diamagnetic in conformity with the occurrence of vanadium(V) in each of them. In order to determine the number of peroxy groups (O_2^{2-}), present in the compound, coordinated to the vanadium(V) centre, chemical determination of the peroxide content must be considered to be important. The peroxide estimation was accomplished by red-ox titrations separately involving a standard potassium permanganate solution and also a standard Ce^{4+} solution. In each case boric acid was used to avoid any loss of active oxygen. The results of replicate determinations of peroxide as well as those of vanadium contents conspicuously suggested the occurrence of V : O_2^{2-} as 1 : 2 in each of the newly synthesised compounds. This lends credence to the contention that the complex anion is a diperoxy species, $[VO(O_2)_2en]^-$.


$NH_4[VO(O_2)_2 en]$
TRANSMITTANCE (arbitrary scale)
4000
3000
2000
1500
1000
500
WAVENUMBER (cm^{-1})


Na [VO(O2)2 en]
TRANSMITTANCE (arbitrary scale)
4000
3000
2000
1500
1000
500
WAVENUMBER (cm-1)

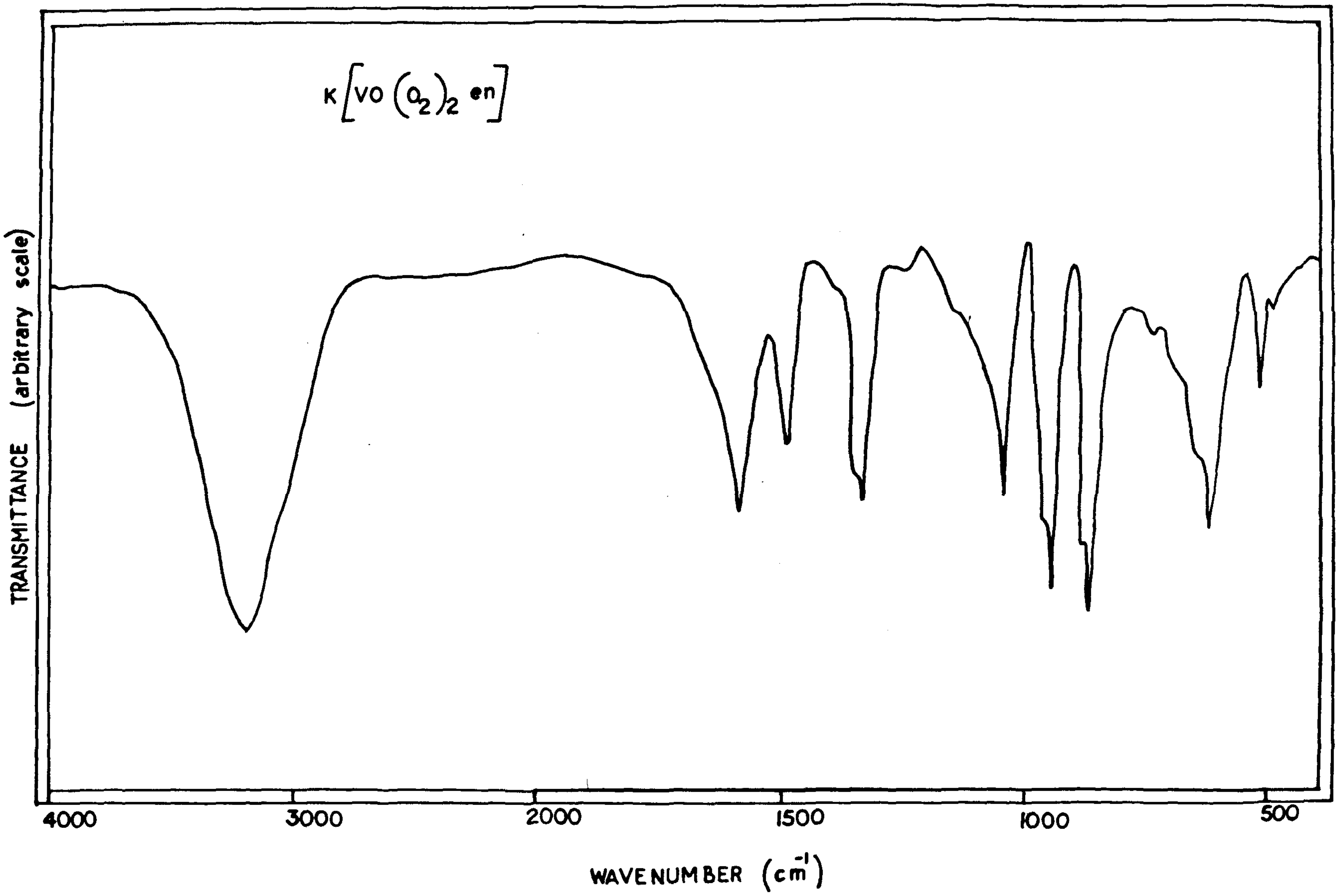

K[VO(O$_2$)$_2$ en]
TRANSMITTANCE (arbitrary scale)
4000
3000
2000
1500
1000
500
WAVENUMBER (cm^{-1})

Table 3. Molar Conductance Values, and Structurally Important Infrared and Laser Raman (LR) Bands of A $[VO(O_2)_2en]$ (A = Na, K or NH_4)

Compound	Molar conductance $\Omega^{-1}cm^2mol^{-1}$	IR cm^{-1}	LR cm^{-1}	Assignment
$NH_4[VO(O_2)_2en]$	125	950s	950	$\nu(V=O)$
		875s	880	$\nu(O-O)\ \nu_1$
		615s	600	$\nu(V-O_2)\nu_3$
		525s	530	$\nu(V-O_2)\ \nu_2$
		1595s		$\delta(NH_2)$
		1490w 1340m		$\delta(CH_2)$
		1055s		ν(skeletal)
$Na[VO(O_2)_2en]$	115	950s	945	$\nu(V=O)$
		870s	880	$\nu(O-O)\ \nu_1$
		620s	610	$\nu(V-O_2)\ \nu_3$
		525s	520	$\nu(V-O_2)\ \nu_2$
		1590s		$\delta(NH_2)$
		1490w 1345m		$\delta(CH_2)$
		1050s		ν(skeletal)
$K[VO(O_2)_2en]$	120	955s	950	$\nu(V=O)$
		870s	880	$\nu(O-O)\ \nu_1$
		620s	600	$\nu(V-O_2)\ \nu_3$
		520s	530	$\nu(V-O_2)\ \nu_2$
		1595s		$\delta(NH_2)$
		1495w 1340m		$\delta(CH_2)$
		1055s		ν(skeletal)

The infrared spectra of the $A[VO(O_2)_2en]$ compounds bear a very strong resemblance with each other (Table 3), and show absorptions at ca 950s, ca 870s, and ca 620s and ca 525s cm^{-1} representative of $\nu(V{=}O)$ owing to the presence of a terminal $V{=}O$ group, of $\nu(O\text{-}O, \nu_1)$, and $\nu(V\text{-}O_2, \nu_2$ and $\nu_3)$ modes[7,12-14] respectively. Another typical feature of the spectra is the absorptions, due to the occurrence of coordinated ethylenediamine (en). The frequencies at ca 1595s, ca 1495w and 1340m, and ca 1055s cm^{-1} are well precedented in the literature,[10,11] regarded as quite characteristic of chelated ethylenediamine, and assigned to $\delta(NH_2)$, $\delta(CH_2)$, and ν(skeletal) modes of bidentate ethylenediamine (en) ligand. The observed pattern, originating from ethylenediamine, advocates for the presence of a chelated en ligand,[10,11] and does not imply the occurrence of a trans-bridging ethylenediamine group.[15] It is pertinent to add that IR spectral pattern arising from a bridging ethylenediamine ligand should be much simpler[15] than what has been observed in the present case. Moreover, the solubility property of the compounds does not support the idea of a trans-linked ethylenediamine ligand (solubility of a compound containing a trans-bridged en group is very low). It is, therefore, very reasonable to argue that both peroxide as well as ethylenediamine ligands are bonded to the vanadium(V) centre in a chelated bidentate manner, and the coordination polyhedron of V^V centre may be pentagonal bipyramidal with a structure similar to that encountered in the case of the corresponding $[VO(O_2)_2bipy]^-$ complex as reported in 1983.[9]

The laser Raman (LR) spectra of alkali monokis(ethylenediamine)oxodiperoxyvanadates(V) show a very close similarity to each other suggesting that the compounds are structurally similar. The LR spectra of the compounds recorded both in the solid form as well as in aqueous solutions, did not exhibit any notable change in their pattern or in the positions of the signals indicating thereby that the complex $[VO(O_2)_2en]^-$ ion does not probably undergo any detectable structural change in solutions. The Laser Raman signals at ca 950, ca 880, ca 600 and ca 530 cm^{-1} have been assigned to $\nu(V{=}O)$, $\nu(O-O, \nu_1)$, $\nu(V-O_2, \nu_3)$, and $\nu(V-O_2, \nu_2)$ modes[12-14] respectively. It is owing to the large polarisability changes involved in the V — O bond that the $\nu(V{=}O)$ appears as a strong signal at ca 950 cm^{-1} supporting the view that a terminally bonded $V{=}O$ group is present in the complex. Considering sharpness and intensity of the LR signals, and the results of Raman depolarisation experiments, the LR peak at ca 600 cm^{-1} is assigned to the ν_3, while the peak at ca 530 cm^{-1} has been attributed to the ν_2 (as this is found to be polarised) mode of $\nu(V-O_2)$ vibrations. The number and positions of the peaks arising from the coordinated peroxide (O_2^{2-}) lend support to the contention that the peroxide groups, in the complex $[VO(O_2)_2en]^-$, are bonded to the metal centre in a triangular bidentate (C_{2v}) manner.

It may be concluded that the hitherto unknown alkali monokis(ethylenediamine)oxodiperoxyvanadates(V),

$$A\,[VO(O_2)_2en]\ (A = Na,\ K\ or\ NH_4)$$

can be synthesised from the reaction of V_2O_5, 30% hydrogen peroxide, and AOH at pH 9, while the suitable pH for the syntheses of the corresponding $A\,[VO(O_2)_2L\text{-}L]$ (L-L = bipy or o-phen) has been found to be 4-5. The $A\,[VO(O_2)_2en]$ compounds are comparatively more stable than the $A_2\,[VO(O_2)_2X]$ ($X = F^-$ or Cl^-) compounds, and they do not decompose in water. The complex $[VO(O_2)_2en]^-$ ion most probably has a pentagonal bipyramidal structure with the O_2^{2-} groups being bonded to the vanadium(V) centre in a triangular bidentate (C_{2v}) manner, and the en group occurring as a chelated ligand.

References

[1] H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fischer, and R. Weiss, J. Am. Chem. Soc., 1983, 105, 3101.

[2] S. Patai, "The Chemistry of Peroxides", Wiley, New York, 1983.

[3] C. Djordjevic, S. A. Craig, and E. Sinn, Inorg. Chem., 1985, 24, 1283.

[4] W. Mertz, Science, 1981, 213, 1332.

[5] N. D. Chasteen, Struct. Bonding (Berlin), 1983, 53, 105.

[6] K. Kustin and I.G. Macara, Comments Inorg. Chem., 1982, 2, 1.

[7] M. K. Chaudhuri and S. K. Ghosh, Polyhedron, 1982, 1, 553; Inorg. Chem., 1982, 21, 4020; 1984, 23, 532; J. Chem. Soc. Dalton Trans., 1984, 507.

[8] N. Vuletic and C. Djordjevic, J. Chem. Soc., 1973, 1137.

[9] N. J. Campbell, M. V. Capparelli, W.P. Griffith, and A. C. Skapski, Inorg. Chim. Acta, 1983, 77, L215.

[10] D. B. Powell and N. Sheppard, J. Chem. Soc., 1959, 791.

[11] G. Newman and D. B. Powell, J. Chem. Soc., 1961, 477.

[12] W.P. Griffith, J. Chem. Soc., 1964, 5248.

[13] W. P. Griffith and T. D. Wickins, J. Chem. Soc., 1967, 590.

[14] W. P. Griffith and T. D. Wickins, J. Chem. Soc. 1968, 397.

[15] D. B. Powell and N. Sheppard, J. Chem. Soc., 1959, 3089.

CHAPTER 5

New Heteroligand Peroxyvanadates(V). Synthesis and Physico-Chemical Studies of Alkali Triperoxymonocarbonatovanadate(V) Trihydrates, $A_3[V(O_2)_3CO_3].3H_2O$ (A = Na or K)

The importance of and the interests in peroxy transition metal compounds, which rendered them the focus of one of the active areas of oontemporary research, have been emphasised in the literature[1-7] and highlighted in Chapter 1. Many transition metals, of which vanadium is not an exception, give colour reactions with hydrogen peroxide owing to the formation of complex peroxy-metal species in solutions. Unfortunately not many of them were obtained in the solid state probably because of their instability as solids or might as well be due to the lack of suitable synthetic methods. Interestingly the introduction of specific heteroligands in the coordination sphere of metals seem to increase the stability[1,2,7] of such compounds and permit their isolation in the solid form to provide scopes for making structural assessments and studying their involvement in activation and transport of oxygen.[2,3,5,6] Synthesis of well-defined peroxy-metal compounds is thus an important prerequisite. Within the context of the chemistry of peroxyvanadates(V), it is evident that heteroligand triperoxyvanadates(V) are scanty.[8,9] The only examples of the afore said types of compounds are $A_2[V(O_2)_3X]$ (A = Na, K or NH_4 ; X = F^- or Cl^-)[14] recently synthesised in this laboratory, but there is still a lack of information regarding triperoxyvanadate(V) complexes containing bidentate heteroligands coordinated to the metal centre. It may not be out of place to mention that heteroligand triperoxyvanadates(V) have been long searched for.[11]

In view of this as well as the intrinsic importance of peroxy-metal compounds,[1-7] it was imperative to develope suitable methods for the synthesis of triperoxyvanadate(V) containing a coordinated bidentate heteroligand in the coordination polyhedron of the metal centre, to characterise the compounds, evaluate the modes of bonding of the ligands with the metal.

The present Chapter deals with the first synthesis, characterisation, and assessment of structure involving infrared and Laser Raman (LR) spectroscopy, of alkali triperoxymonocarbonatovanadate(V) trihydrates, $A_3[V(O_2)_3CO_3]\cdot 3H_2O$ (A = Na or K).

Experimental

All chemicals used were of reagent grade.

Synthesis of Alkali Triperoxymonocarbonatovanadate(V) Trihydrates, $A_3[V(O_2)_3CO_3]\cdot 3H_2O$ (A = Na or K)

A general method has been developed for the synthesis of $A_3[V(O_2)_3CO_3]\cdot 3H_2O$ compounds. A typical procedure is described below.

In a representative procedure, an intimately mixed powder of V_2O_5 (0.5g, 2.7 mmol) and alkali carbonate, A_2CO_3 (A = Na or K), was dissolved in 15 cm^3 (132.4 mmol) of 30% hydrogen peroxide with constant stirring with maintenance of molar ratio of $V_2O_5 : A_2CO_3 : H_2O_2$ as 1 : 3 : 49. The solution was filtered to remove any traces of undissolved material, and then cooled in an ice-water bath. Corresponding alkali hydroxide (15% aqueous solution) was added dropwise with stirring until a permanent deep blue colouration was developed. Addition of an excess of pre-cooled ethanol (twice that of the original volume) to the above solution with occassional stirring afforded blue microcrystalline alkali triperoxymonocarbonatovanadate(V) trihydrates in very high yeilds. The reaction container was cooled in a freezer for ca 20 min. The $A_3[V(O_2)_3CO_3].3H_2O$ compounds were separated by centrifugation and the isolated products were washed four times with ethanol, and finally dried in vacuo over concentrated sulphuric acid.

The specific amounts of reagent used for the synthesis, and the yields of $A_3[V(O_2)_3CO_3].3H_2O$ are reported in Table 1.

Table 1. Amounts of Reagents Used for the Synthesis, and the Yields of $A_3[V(O_2)_3CO_3].3H_2O$ (A = Na or K)

Compound	Yield g(%)	Amount of V_2O_5 in g (mmol)	Amount of A_2CO_3 in g (mmol)	Amount of 30% H_2O_2 in cm^3 (mmol)
$Na_3[V(O_2)_3CO_3].3H_2O$	1.6 (89)	0.5 (2.7)	0.9 (8.5)	15 (132.4)
$K_3[V(O_2)_3CO_3].3H_2O$	1.8 (85)	0.5 (2.7)	1.2 (8.7)	15 (132.4)

Elemental Analyses

The details of the methods of elemental analyses have been given in Chapter 2. The results of elemental analyses are summarised in Table 2.

Table 2. Analytical Data of $A_3[V(O_2)_3CO_3]\cdot 3H_2O$ (A = Na or K)

Compound	Found % (Calcd. %)			
	A	V	O^a	C
$Na_3[V(O_2)_3CO_3]\cdot 3H_2O$	20.7 (20.9)	15.48 (15.44)	29.7 (29.1)	3.62 (3.64)
$K_3[V(O_2)_3CO_3]\cdot 3H_2O$	31.3 (31.0)	13.51 (13.47)	25.9 (25.38)	3.12 (3.17)

[a] Peroxy oxygen

Structurally significant infrared and Laser Raman (LR) band positions along with their assignmemts are presented in Table 3.

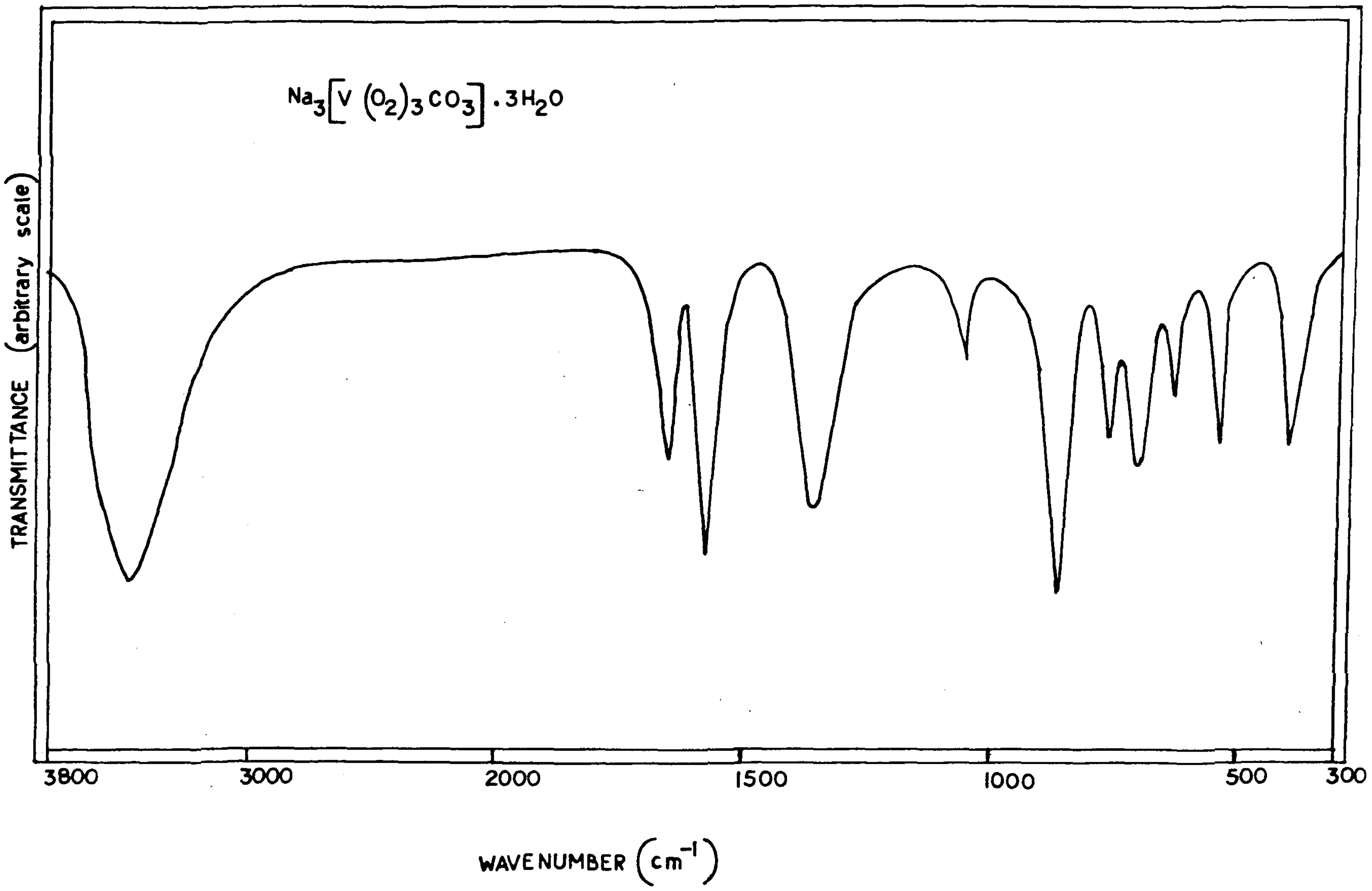
Results and Discussion

It is well known that vanadium(V) produces a characteristic colour with hydrogen peroxide solution, and it serves as a very good test reaction for the detection of the metal.[8] Reactions of vanadium(V) with H_2O_2 are, however, complicated and different types of complex peroxyvanadate species are formed with a small variation of acidity/alkalinity of the reaction media. The present interest is to synthesise well-defined heteroligand triperoxyvanadate(V) complexes. Since more than two peroxide (O_2^{2-}) groups can not be introduced into the coordination sphere of vanadium(V) till pH 7,[8] oxo-oxygen of VO^{3+} is not knocked off either in acidic or in neutral solutions, and triperoxyvanadates(V) have not been found in acidic solutions,[12] it is certain that the synthesis of heteroligand triperoxyvanadates(V) should be sought only in an alkaline medium. The results of a very recent study have shown that the parent complex triperoxyvanadate(V), $[V(O_2)_3]^-$, has to be synthesised only from a very highly alkaline solution.[13] With a very high alkaline condition being conducive to the synthesis of triperoxyvanadate(V) complex $[V(O_2)_3]^-$, it was apprehended that the heteroligand complexes of vanadium (V) containing three peroxide groups (O_2^{2-}) and a bidentate amine (e.g., 1,10-phenanthroline or 2,2-bipyridyl), as looked for,[11] might not be feasible because a diamine ligand would be unstable under such a condition. Therefore a bidentate ligand like sulphate (SO_4^{2-}) or carbonate (CO_3^{2-}) was considered to be suitable. However, the ligand selection here did not go in favour of SO_4^{2-}, as a preformed sulphate generally does not coordinate with vanadium(V) in the presence of peroxide (O_2^{2-}) ligands.[14] Thus, the reaction of vanadium(V) with alkali carbonate, A_2CO_3 (A = Na or K), and hydrogen peroxide was carried out in a highly alkaline medium (vide Experimental), and blue alkali triperoxymonocarbonatovanadate(V) trihydrates, $A_3[V(O_2)_3CO_3]\cdot 3H_2O$, were successfully synthesised. The compounds were isolated from the reaction solutions by the addition of ethanol which facilitated precipitation. The appearance of a steady blue colour of the reaction solution, and complete absence of the $\nu(V=O)$ band at ca 950 cm^{-1} and appearance of a strong band at ca 860 cm^{-1} due to $\nu(O-O)$ plus the frequencies owing to the coordinated carbonate (CO_3^{2-})[15] in the infrared spectrum of the product isolated from the solution indicate completion of the reaction. The fact that a very high concentration of the alkaline medium leads to the formation of the complex species $[V(O_2)_3CO_3]^{3-}$ while the relatively lower concentration of the alkaline medium produces $[VO(O_2)_2CO_3]^{3-}$ (as described in Chapter 3) suggests that a very high alkaline medium probably helps replacement of the last oxo-oxygen from the $[VO(O_2)_2CO_3]^{3-}$ species by a O_2^{2-} group, thereby favouring the formation of $[V(O_2)_3CO_3]^{3-}$, or that the oxo-oxygen of the $[VO(O_2)_2CO_3]^{3-}$ species is converted to the third peroxy ligand by abstracting an oxygen of hydrogen peroxide. It is difficult to say, in the absence of any direct evidence, which of the two mechanisms is more probable. However, the fact that oxygen exchange on vanadium(V) is very slow[16] and the strength of the V — O multiple bond is high, as evident from the IR spectroscopic studies on oxovanadium(V) complexes,[17,18] indicates that the latter mechanism may be more likely. It is evident, therefore, that under the appropriate conditions, the heteroligand-triperoxyvanadate(V) compounds of the type $A_3[V(O_2)_3CO_3].3H_2O$ can be synthesised and that a much higher alkaline medium is required for the successful synthesis of the complex $[V(O_2)_3CO_3]^{3-}$ ion as opposed to a lower pH ($\sim$ 7) necessary for the synthesis of the diperoxycarbonato species $[VO(O_2)_2CO_3]^{3-}$ (vide Chapter 3).

Characterisation and Assessment of Structure. The blue alkali triperoxymonocarbonatovanadate(V) trihydrates, $A_3[V(O_2)_3CO_3]\cdot 3H_2O$ (A = Na or K), are diamagnetic in conformity with the occurrence of vanadium(V) in each of them. The $A_3[V(O_2)_3CO_3]\cdot 3H_2O$ can be stored for a prolonged period in sealed containers, however, they decompose in water thus precluding molar conductance measurements. The freshly synthesised compounds start losing water on heating at *ca* 120°C, but the dehydration process is accompanied by the simultaneous loss of peroxide thereby precluding a genuine dehydration.

The results of chemical determination of peroxide contents, as accomplished by red-ox titrations separately involving a standard potassium permanganate solution and a standard Ce^{4+} solution, conspicuously suggested the occurrence of three peroxide (O_2^{2-}) groups per vanadium(V) in each of the newly synthesised compounds in agreement with their formula .

The infrared and Laser Raman (LR) spectra of the compounds are very informative and characteristic. The significant features in the spectra of $A_3[V(O_2)_3CO_3]\cdot 3H_2O$ involve the bands of coordinated peroxide ligand, carbonate (CO_3^{2-}) frequencies, O-H stretchings and H-O-H bendings. The infrared spectra of the compounds exhibited the ν(O-O) and ν(V - O_2) stretchings of the coordinated peroxide (O_2^{2-})[10,19,20] occurring at *ca* 860s (ν_1), and at *ca* 620s (ν_3) and *ca* 530s (ν_2) cm^{-1}. The other structurally significant bands are those which owe their origin to the presence of coordinated carbonate ligand (CO_3^{2-}).[15] The positions of the bands and the pattern of the spectra which originate from coordinated carbonate ligand are essentially similar to those observed previously for the diperoxycarbonatovanadates(V), $A_3[VO(O_2)_2CO_3]$, described in


$Na_3[V(O_2)_3CO_3] \cdot 3H_2O$
TRANSMITTANCE (arbitrary scale)
3800
3000
2000
1500
1000
500
300
WAVENUMBER (cm^{-1})

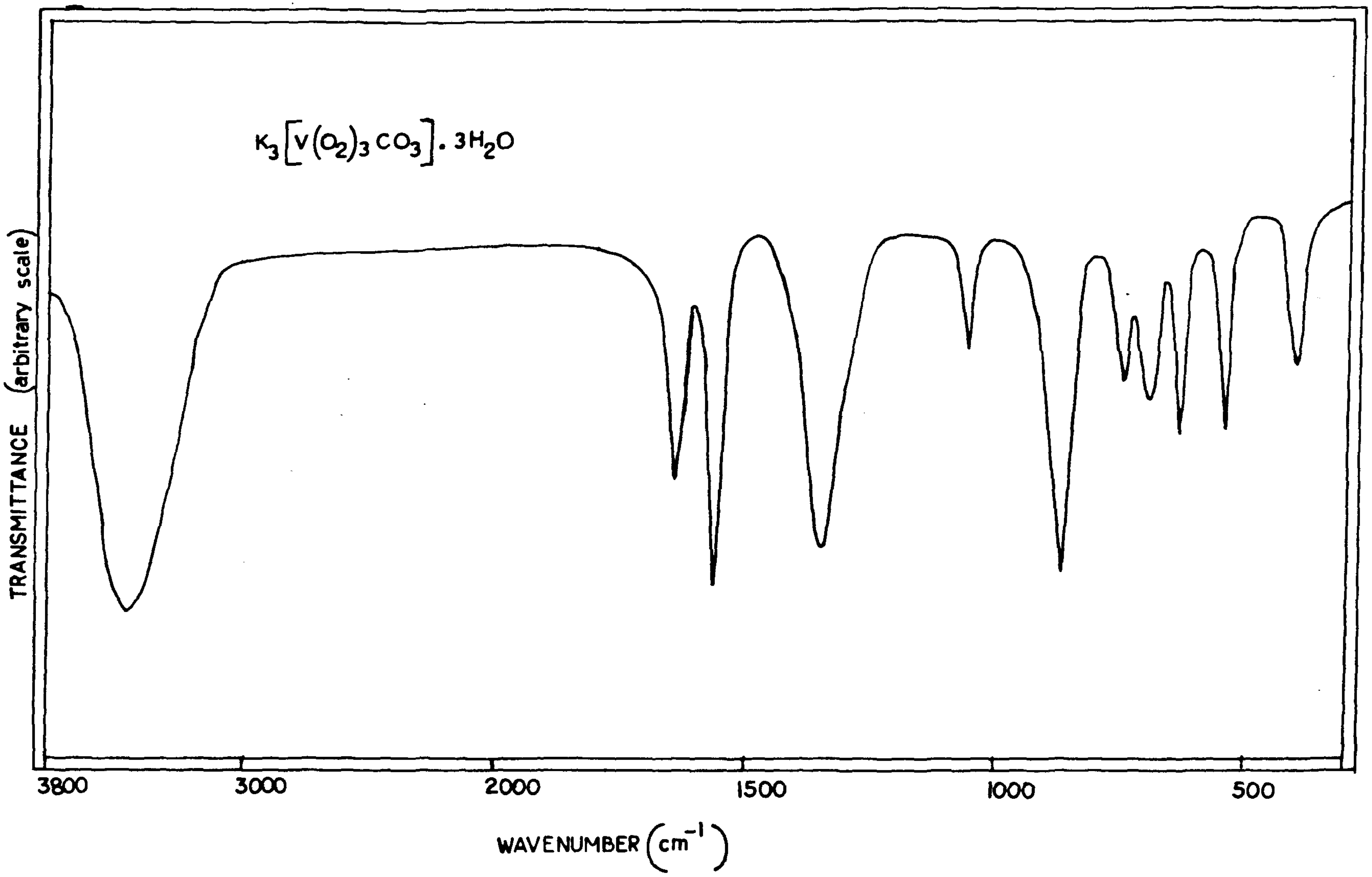

$K_3[V(O_2)_3CO_3]\cdot 3H_2O$
TRANSMITTANCE (arbitrary scale)
3800
3000
2000
1500
1000
500
WAVENUMBER (cm^{-1})

Table 3. Structurally Significant Infrared and Laser Raman Bands of $A_3[V(O_2)_3CO_3]\cdot 3H_2O$ (A = Na or K)

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment	
$Na_3[V(O_2)_3CO_3]\cdot 3H_2O$	857s	855	ν(O-O), ν_1	
	619s	615	$\nu(V\text{-}O_2)$, ν_3	
	530s	530	$\nu(V\text{-}O_2)$, ν_2	
	1566s	1570	ν(C-O), ν_1, A_1	CO_3^{2-} modes
	1350m		ν(C-O) + δ(O-C-O), ν_5, B_2	
	1040s		ν(C-O)	
	750m		ring deformation + ν(V-O)	
	690w		δ(O-C-O) + ν(V-O)	
	390m		ν(V-O)	
	3450m		ν(O-H)	
	1640s		δ(H-O-H)	
$K_3[V(O_2)_3CO_3]\cdot 3H_2O$	864s	850	ν(O-O), ν_1	
	625s	610	$\nu(V\text{-}O_2)$, ν_3	
	535s	530	$\nu(V\text{-}O_2)$, ν_2	
	1565s	1570	ν(C-O), ν_1, A_1	CO_3^{2-} modes
	1350m		ν(C-O) + δ(O-C-O), ν_5, B_2	
	1050s		ν(C-O)	
	740m		ring deformation + ν(V-O)	
	692w		δ(O-C-O) + ν(V-O)	
	390m		ν(V-O)	
	3455m		ν(O-H)	
	1640s		δ(H-O-H)	

Chapter 3 making a further detailed discussion, for the present cases, redundant. The only point to be emphasised here is the appearance of the $\nu_1(A_1)$ and $\nu_5(B_2)$ modes at *ca* 1565 and 1350 cm^{-1} respectively. An appreciable separation between the two afore said bands provides a very strong evidence in favour of a chelated carbonate ligand. It is owing to their instability in water, that their Laser Raman spectra had to be recorded only in the solid state. The Laser Raman (LR) spectra strongly augment the IR spectral observations. The salient features of the LR spectra are the signals at *ca* 855 cm^{-1} due to ν(O-O), ν_1, and *ca* 610 and *ca* 530 cm^{-1} attributed to the ν_3 and ν_2 modes respectively of the $\nu(V\text{-}O_2)$ vibrations. The distinction between the ν_2 and ν_3 modes of $\nu(V\text{-}O_2)$ was made on the basis of sharpness and intensity of the two bands. Since the ν_2 mode is polarised, the comparatively more sharp and intense signal at *ca* 530 cm^{-1} has been assigned to ν_2. The peak at 1570 cm^{-1} has been attributed to the ν(C-O), $\nu_1(A_1)$, mode of coordinated carbonate. It is important to note that no signal was observed at *ca* 950 cm^{-1}, in the IR as well as in the Laser Raman spectra, a position typical for the $V{=}O$ group. This renders it certain that the complex ion does not have any $V{=}O$ group. Thus, it is very clear that both peroxide[10,20] and carbonate[15] ligands are coordinated to the vanadium(V) center in a triangular bidentate fashion.

A common feature of the IR spectra of $A_3[V(O_2)_3CO_3]\cdot 3H_2O$ (A = Na or K) compounds is the occurrence of two additional bands at *ca* 1640s and *ca* 3455m cm^{-1}, which resemble in their shape and position those typically observed for the presence of uncoordinated water.[21,22]

This as well as the loss of water at ca 120°C suggest that the water molecules in the title compounds are present only as lattice water.

Studies of reactivity of coordinated peroxide constitute a part of a general program involving the chemistry of peroxy-metal compounds. The results of preliminary experiments on oxidations, of some inorganic species (e.g., SO_2) and organic substrates (e.g., alcohols, polycyclic hydrocarbons etc.) using $A_3[V(O_2)_3CO_3].3H_2O$, are promising. Studies on reactivities of these compounds as well as of the other peroxy-metal compounds synthesised in our laboratory are in progress. The comprehensive results of such studies will constitute the subject matter of future reports.

Thus it is evident from the results of studies described in the present Chapter that the hitherto unknown heteroligand triperoxymonocarbonatovanadates(V)

$$A_3[V(O_2)_3CO_3].3H_2O \text{ (A = Na or K)}$$

can be synthesised from the reaction of V_2O_5 with aqueous H_2O_2 and A_2CO_3 (A = Na or K) in the presence of a highly alkaline medium (AOH). The compounds can be stored in sealed containers, however, they start losing water and peroxide on heating at ca 120°C. The $A_3[V(O_2)_3CO_3].3H_2O$ compounds show very characteristic infrared and Raman spectra. The salient features of the spectra are the bands/peaks due to coordinated peroxide (O_2^{2-}) and coordinated carbonate (CO_3^{2-}) ligands, and the frequencies due to uncoordinated H_2O molecules. Prelimary results of oxidation reactions (reactivity of coordinated peroxide) involving $A_3[V(O_2)_3CO_3].3H_2O$ are very promising, and further work on the studies of reactivities of coordinated peroxide is now underway.

References

1 C. Djordjevic, *Chem. Br.*, 1982, **18**, 554.

2 H. Mimoun, M. Postel, F. Casabianca, and A. Milshler, *Inorg. Chem.*, 1982, **21**, 1303.

3 H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fischer, and R. Weiss, *J. Am. Chem. Soc.*, 1983, **103**, 3101.

4 N. J. Campbell, M.V. Capparelli, W.P Griffith, and A. C. Skapski, *Inorg. Chim. Acta*, 1983, **77**, L215.

5 A. R. Miksztal and J.S. Valentine, *Inorg. Chem.*, 1984, **23**, 3548.

6 L. Saussine, E. Brazi, A. Robine, H. Mimoun, J. Fischer and R. Weiss, *J. Am. Chem. Soc.*, 1985, **107**, 3534.

7 C. Djordjevic, S. A. Craig, and E. Sinn, *Inorg. Chem.*, 1985, **24**, 1283.

8 J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 279.

9 R. J. H. Clark and D. Brown, " The Chemistry of Vanadium, Niobium and Tantalum", Pergamon Texts in Inorganic Chemistry, Vol. 20, Pergamon Press, Elmsford, New York, 1975, p 519.

10 M. K. Chaudhuri and S. K. Ghosh, *Inorg. Chem.*, 1982, **21**, 4020; 1984, **23**, 534.

11 N. Vuletic and C. Djordjevic, *J. Chem. Soc.*, 1973, 1137.

12 M. Orhanovic and R.G. Wilkins, *J. Am. Chem. Soc.*, 1967, **89**, 278.

13 M. K. Chaudhuri, S. K. Ghosh, and N. S. Islam, *Inorg. Chem.*, 1985, **25**, 2706.

[14] M. K. Chaudhuri and N. S. Islam, *Transition Metal Chem.*, 1985 *in press*.

[15] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd. ed., Wiley-Interscience, London, 1970, p 196.

[16] S. Funahashi, K. Ishihara, and M. Tanaka, *Inorg. Chem.*, 1981, *20*, 51.

[17] M. K. Chaudhuri, H. S. Dasgupta, S. K. Ghosh, and D. T. Khathing, *Synth. React. Inorg. Met-Org. Chem.*, 1982, *12*, 63.

[18] J. Selvin, *Chem. Rev.*, 1965, *65*, 153.

[19] M. K. Chaudhuri and B. Das, *Inorg. Chem.*, *in press*.

[20] W.P. Griffith, *J. Chem. Soc.*, 1964, 5248; W. P. Griffith and T. D. Wickins, *J. Chem. Soc.*, 1968, 397.

[21] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta and D. T. Khathing, *J. Chem. Soc. Dalton Trans.*, 1981, 2587; M. N. Bhattacharjee and M. K. Chaudhuri, *Inorg. Syntheses*, 1985, *24*, 0000.

[22] N. F. Curtis, *J. Chem. Soc. A*, 1968, 1584.

CHAPTER 6

Chapter 6

Direct Syntheses of Bis(acetylacetonato)nickel(II) Dihydrate, $Ni(C_5H_7O_2)_2.2H_2O$, and Isolation of $\alpha, \alpha, \beta, \beta$ -Tetra-acetylethane as the Oxidation Product of Acetylacetone*

The general interest in the studies involving acetylacetonato complexes of metals has been highlighted in Chapter 1. Bis(acetylacetonato)nickel(II) dihydrate, $Ni(acac)_2.2H_2O$, a representative example of such types of compounds, has engaged the attention of many research groups.[1-8] Particularly notable is its catalytic activity in very important organic reactions such as, for instance, oligomerisation, polymerisation, hydrogenation, and isomerisation of olefins, hydrosilylation of alkynes, and coupling organic halides.[9] $Ni(acac)_2.2H_2O$ is synthesised from aqueous solutions of nickel(II) salts in the presence of acetylacetone and an excess of a weak base such as sodium acetate (buffer).[10] The compound is readily dehydrated to green anhydrous compound at 50°C in vacuo. The method currently used in practice for the synthesis of bis(acetylacetonato) nickel(II) dihydrate requires the addition of a large amount of sodium acetate as a buffer.[10] The chances of contamination of the desired product, $Ni(acac)_2.2H_2O$, owing to the use of such a large amount of buffer cannot be ruled out.[11] Thus, it is required that direct methods of synthesis of $Ni(acac)_2.2H_2O$, without making use of any buffer, are developed.

---

*The results described in this Chapter have been published.

J. Chem. Soc. Dalton Trans. 1983, 2561.

Further, it has been shown that acetylacetone (Hacac) can be used as a reducing agent as well.[12] And based on this concept the compounds like $VO(acac)_2$ [13], $Mn(acac)_3$ [14] and $Cr(acac)_3$ [15] have been synthesised from vanadium(V), manganese(VII), and chromium(VI) respectively. It is important to note that no evidence in regard to the oxidation product of acetylacetone, when it acted as a reducing agent in such reactions, has any reported existence in the literature. It was therefore necessary to isolate, and to identify and characterise the oxidation product of acetylacetone from such reactions.

It is Chapter 6 of the present thesis which reports two direct methods for the synthesis of bis(acetylacetonato)nickel(II) dihydrate, $Ni(acac)_2.2H_2O$. Also reported in this Chapter is the isolation of $\alpha, \alpha, \beta, \beta$ -tetra-acetylethane as the oxidation product of acetylacetone ($C_5H_8O_2$, Hacac), for the first time, from a reaction between acetylacetone and a higher valent metal species.

Experimental

The chemicals used for the reactions were all reagent grade products.

Method I

Synthesis of Bis(acetylacetonato)nickel(II) Dihydrate, $Ni(acac)_2.2H_2O$ from $Ni(OH)_2$.

An amount of 20.0 mmol of freshly prepared alkali free $Ni(OH)_2$ was taken in the form of an aqueous suspension (in 25 cm^3 water). To this was added an amount of 80 mmol of distilled acetylacetone ($C_5H_8O_2$) with stirring. Vigorous stirring was continued for a further period of ca 30 min whereupon the green $Ni(OH)_2$ was converted into a blue-green shiny product. The reaction container was set aside for about 20 min in order to allow the product to settle. The compound was separated by filtration, washed first with 1 : 1 acetylacetone-water mixture (3-4 times) and then with ethanol (2 times), and finally dried in vacuo over concentrated sulphuric acid.

The direct product was recrystallised from boiling acetone by the addition of light petroleum (b.p. 40-60°C) and subsequent cooling at ca 0°C to obtain blue-green shiny platelet compound. The yield of $Ni(acac)_2.2H_2O$ was 88%.

Method II

Synthesis of Bis(acetylacetonato)nickel(II) Dihydrate from the Reaction of NiO(OH) and Acetylacetone, and Isolation of $\alpha, \alpha, \beta, \beta$ - tetra-acetylethane as the Oxidation Product of Acetylacetone

The Method II requires NiO(OH) as one of the starting materials which needs an extra preparation step.

Preparation of NiO(OH)

An aqueous solution of nickel(II) chloride hexahydrate, $NiCl_2.6H_2O$, was treated with an excess of sodium hydroxide solution and a precipitate of $Ni(OH)_2$ was obtained. The $Ni(OH)_2$ was separated by filtration and purified by repeated washing with water until the washing was found free from chloride. Nickel(II) hydroxide was then oxidised to NiO(OH), a nickel(III) species , by treating an alkaline suspension of it with bromine. The black NiO(OH) thus obtained was separated by centrifugation, washed with water until free from alkali, and finally dried *in vacuo* over phosphorus pentoxide.

The NiO(OH) thus obtained was used for the preparation of $Ni(acac)_2.2H_2O$.

Reaction of NiO(OH) with Acetylacetone ($C_5H_8O_2$, Hacac)

Acetylacetone (11.0g, 110.0 mmol) was added to a suspension of NiO(OH), (2.0g, 21.8 mmol) in water (*ca* 6 cm^3) with constant stirring. An exothermic reaction occurred almost immediately. The reaction mixture was stirred mechanically until the black NiO(OH) was converted completely to a blue-green product (*ca* 15 min). The mixture was filtered, and the product washed with acetone until a blue-green filtrate had just begun to appear. The combined filtrate and washing(*A*) was retained for the isolation of the oxidation product of acetylacetone .

The compound on the filter was then recrystallised from boiling acetone by the addition of light pertoleum (b.p. 40-60°C) and subsequent cooling at *ca* 0°C to obtain the blue-green shiny platelet compound. The yield of $Ni(acac)_2.2H_2O$ was 5.3g (82.3%).

Isolation of the Oxidation Product, α, α, β, β -Tetra-acetylethane from the Combined Filtrate and Washing (A)

The combined filtrate and washing (*A*) was concentrated by removing the solvent on a rotary evaporator, and colourless cubic crystals were obtained. The crystals were removed and washed three times with benzene and finally dried on a filter paper.

The product $\alpha, \alpha, \beta, \beta$ -tetraacetylethane, $(CH_3CO)_2CH$ —— CH $(COCH_3)_2$, melts at 190°C (lit.[16], 191°C). The yield was 1.85g (85.6%, on the basis of an electron-transfer reaction between Ni^{III} and Hacac).

Elemental Analyses

The details of the methods of analyses have been given in Chapter 2.

Analytical Data of $Ni(C_5H_7O_2)_2.2H_2O$

Found :(%) C, 40.8; H, 6.3; Ni, 20.2.

Calcd (%) for $C_{10}H_{18}NiO_6$: C, 41.0; H, 6.15; Ni, 20.05.

Analytical Data of $(CH_3CO)_2CH$ —— CH $(COCH_3)_2$

Found : M (mass sprometrically), 198; C, 60.49%; H, 7.19%

Calcd. for $C_{10}H_{14}O_4$: M, 198; C, 60.58%; H, 7.13%.

The infrared spectral data of $Ni(acac)_2.2H_2O$ have been reported in Table 1, while its mass spectral data have been presented in Table 2.

Results and Discussion

The problems encountered in the synthesis of bis(acetylacetonato)-nickel(II) dihydrate, $Ni(acac)_2.2H_2O$, have been already mentioned in the opening section of the present Chapter. In order to circumvent the existing difficulties two new and direct methods of syntheses of

$Ni(acac)_2.2H_2O$ have now been developed.

The two new methods are based on two different philosophies. While the Method I is based on a simple acid-base reaction, the Method II relies on an electron-transfer reaction between a nickel(III) species and acetylacetone. A common but significant feature of the two methods is that neither of them requires any buffer. According to the Method I $Ni(OH)_2$ is allowed to directly react with Hacac ($C_5H_8O_2$) to produce bis(acetylacetonato)nickel(II) dihydrate, $Ni(acac)_2.2H_2O$, in a very high yield. The pH of the reaction, recorded immediately after the reaction took place, was fount to be ca 5, a pH suitable for the purpose of successful synthesis of $Ni(acac)_2.2H_2O$. Thus, unlike the literature method[10], no buffer is required in the present synthesis. The method is fast and can be scaled up, if desired.

Our specific interest in the Method II was two folds: First, to develop another direct method for the synthesis of $Ni(acac)_2.2H_2O$, again without making use of any buffer, from the electron-transfer reaction of nickel(III) with acetylacetone (Hacac). Second, to isolate, characterise and identify the oxidation product of acetylacetone from a reaction in which it acted as a reducing agent as well. The potential of Hacac as a reducing agent has been emphasised in some recent reports.[12-15] Accordingly, a nickel(III) species, NiO(OH), was reacted with Hacac ($C_5H_8O_2$). The reaction was very facile and gave bis(acetylacetonato)nickel(II) dihydrate, $Ni(acac)_2.2H_2O$, in a very high yield. One of our main concern was to identify the oxidation product of Hacac. Work up of the mother liquor, after separating $Ni(acac)_2.2H_2O$, afford a highly crystalline organic compound. The compound was found to be very sparingly soluble in water, benzene, and ether, and its various physical and chemical properties viz., colour, m.p., solubility, reaction with $FeCl_3$, and the mass spectrum compare very well with those of a specimen prepared by the action of iodine upon sodium acetylacetonate.[16] The organic compound thus obtained has been identified as $\alpha, \alpha, \beta, \beta$ -tetra-acetylethane, $(CH_3CO)_2CH — CH(COCH_3)_2$.

In an attempt to generalise the contention that electron-transfer reactions between higher-valent transition metal ions and acetylacetone leading to the corresponding acetylacetonates give $(CH_3CO)_2CH -- CH(COCH_3)_2$ as the oxidation product, the reactions of Hacac with manganese(VII) and chromium(VI) were performed following the procedures developed in this laboratory.[14,15] Isolation of $\alpha, \alpha, \beta, \beta$ -tetra-acetylethane, $(CH_3CO)_2CH — CH(COCH_3)_2$, as the oxidation product from each of the reactions, after separation of the corresponding $M(acac)_3$ complex, was successful again owing to the oxidation of acetylacetone. It is therefore concluded that in the electron-transfer reactions of the types discussed above, acetylacetone is oxidised to $\alpha, \alpha, \beta, \beta$ -tetra-acetylethane, $(CH_3CO)_2CH — CH(COCH_3)_2$.

The pH of the reaction solution, recorded immediately after the formation of $Ni(acac)_2.2H_2O$ was found to be ca 5, a situation conducive to the formation of metal - acac complexes, and concurs with that maintained by Charles and Powlikowski[10] by the addition of a large amount of sodium acetate (buffer). In view of the products isolated from the reaction of Ni^{III}, Mn^{VII} or Cr^{VI} with acetylacetone (e.g. see below), and observed pH of the reaction medium, it is believed that acetylacetone first undergoes ionisation giving $(CH_3CO)_2CH^-$ (acac$^-$) and H^+ (cf. the observed pH) followed by the oxidation of $(CH_3CO)_2CH^-$ ion to

$$Ni^{III}O(OH) + 3(C_5H_8O_2) \longrightarrow Ni(C_5H_7O_2)_2 + \tfrac{1}{2}\,(CH_3CO)_2CH - CH(COCH_3)_2 + 2H_2O$$

the $(CH_3CO)_2CH^{\cdot}$ radical (with corresponding reduction of the metal), which dimerises to yield $(CH_3CO)_2CH - CH(COCH_3)_2$. It appears that this route to $\alpha, \alpha, \beta, \beta$ - tetra-acetylethane is relatively simpler than methods described in the literature[16] for the purpose.

Because of the higher yield of product, considerably shorter reaction time, and redundancy of any buffer, the presently described methods of synthesis of $Ni(acac)_2.2H_2O$ offers advantages over the procedure described in the literature.[16]

The blue-green crystalline $Ni(acac)_2.2H_2O$ is soluble in many organic solvents, and also to some extent in water. It is capable of being stored for a long period. The molar conductance of the compound was found to be 10 $\Omega^{-1}cm^2mol^{-1}$ at 21°C supporting its formulation, purity and stability. The infrared spectra of $Ni(acac)_2.2H_2O$ is similar to that reported, for the compound, in the literature[17] and conforms to the occurrence of chelated acetylacetonate ligands. Moreover, the room temperature magnetic moment value of 3.17 BM (1 BM $\approx 0.927 \times 10^{-23} Am^2$) as observed in the present case is in complete accord with the value reported by Cotton and Fackler.[18]

Mass Spectrometric Studies

The importance of direct insertion technique, for the mass spectrometry of metal-acetylacetonates, has been emphasised in some recent reports on mass spectrometric studies.[1,2,19] A similar technique was adopted in the present studies in order to introduce the samples straight into the ion-source without any prior heating. This technique was also necessary for $(CH_3CO)_2CH$ — $CH(COCH_3)_2$ to overcome the difficulty apprehended due to the possible formation of 2,5-dimethyl-3, 4-diacetylfuran through elimination of one molecule of water prior to electron-impact.

The mass spectra of $Ni(acac)_2.2H_2O$ was recorded with the ion-source temperature being maintained at 50^o, 160^o and 150^oC. However, the ion-source temperature of 160^oC was found to be suitable for the purpose, since the spectra recorded at 50^oC were rather weak while those run at 150^oC exhibited some pyrolysis effect. The mass spectra of $Ni(acac)_2.2H_2O$ (Table 2) showed the molecular ion signal at m/z 256 suggesting that the molecule exists as a monomer in the vapour state and does not undergo any association. The molecular ion peak was followed by a strong signal (96% intensity) at m/z 241 owing to the loss of an odd electron fragment $CH_3^{\bullet}$ with the major fragmentation pathway being:

$$Ni(C_5H_7O_2)_2^{+\bullet} \longrightarrow Ni(C_5H_7O_2)(C_4H_4O_2)^{+\bullet} \longrightarrow Ni(C_5H_7O_2)H^{+} \longrightarrow$$

$$Ni(C_4H_4O_2)^{+\bullet} \longrightarrow Ni(C_3H_4O)^{+} \longrightarrow Ni(C_2H_4)^{+} \text{ or } Ni(CO)^{+} \longrightarrow Ni^{+}$$

The above pattern is strongly supported by the appearance of metastable ion peaks and the results agree with those reported independently by other workers.[20,21]

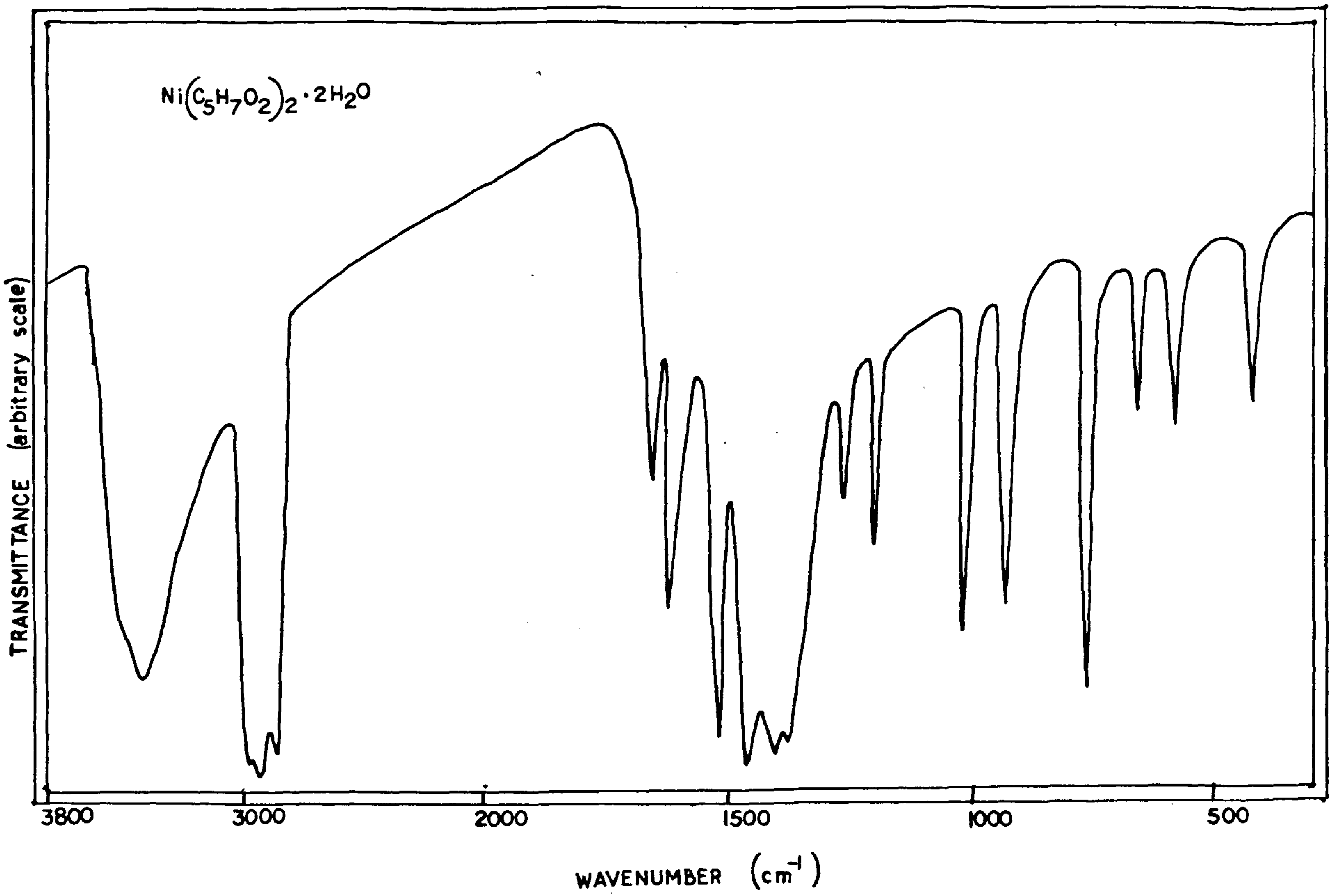

$Ni(C_5H_7O_2)_2 \cdot 2H_2O$
TRANSMITTANCE (arbitrary scale)
3800
3000
2000
1500
1000
500
WAVENUMBER (cm^{-1})

Table 1. Infrared Band Positions (and Their Assignments) of $Ni(C_5H_7O_2)_2 \cdot 2H_2O$

IR cm^{-1}	Assignment (Modes)[17]
1595	C$=$C str. (ν_8) + C$=$O str. (ν_1)
1515 1450	C$=$O str. + CH bend (ν_9)
1395	CH_3 def.
1370	CH_3 sym. def.
1260	C - C str + C - CH_3 str. (ν_2)
1210	C - H in - plane bend (ν_{10})
1020	CH_3 rock
935	C - CH_3 str. + CO str. (ν_3) + C - CH_3 str. (ν_{11})
760	CH out-of-plane bend
665	Ring def + Ni - O str. (ν_4)
450	Ni - O str. (ν_5)

Table 2. Mass Spectral Data for Ni(acac)$_2$

(a) Major Peaks

Assignment	m/Z	Intensity (%)
$Ni(C_5H_7O_2)_2^+$	256	100
$Ni(C_5H_7O_2)(C_4H_4O_2)^+$	241	96
$Ni(C_5H_7O_2)(OCCH_2)^+$	199	3
$Ni(C_5H_7O_2)H^+$	158	40
$Ni(C_5H_7O_2)^+$	157	91
$Ni(C_4H_4O_2)^+$	142	30
$Ni(C_4H_3O_2)^+$	141	23
$Ni(C_3H_4O)^+$	114	5
$Ni(OCCH_2)^+$	100	56
$Ni(CO)^+$ or $Ni(C_2H_4)^+$	86	70
Ni^+	58	16

(b) Metastable transitions

m/Z*			
observed	calculated	Process	Fragment lost
226.8	226.88	265 ⟶ 241	CH_3
102.2	102.28	241 ⟶ 157	$C_4H_4O_2$
128.4	128.43	157 ⟶ 142	CH_3
91.5	91.52	142 ⟶ 114	CO
70.3	70.42	142 ⟶ 100	C_2H_2O
64.8	64.88	114 ⟶ 86	CO or C_2H_4
39.1	39.12	86 ⟶ 58	C_2H_4 or CO

A significant feature of the spectra of $Ni(acac)_2.2H_2O$ is the presence of a metastable transition supported signal at m/z 158 which has been assigned to $Ni(C_5H_7O_2)H^+$. This owes its origin to the hydrogen(H) transfer reaction, taking place under the mass spectrometric conditions, from a methyl group to nickel. Although it was previously proposed[22] that H from the methyl carbon of one $acac^-$ ligand to an oxygen atom of the other took place, to us, however, it appears as a more likely alternative that H shift from carbon to nickel has taken place, because (i) H transfer reactions appear to be rather common for nickel complexes which may also be related to the catalytic activity of nickel in hydrogen transfer reactions, moreover, (ii) if H transfer to oxygen of the other acetylacetonate ligand were involved it would have been a common feature of most of the metal-acetylacetonates, if not of all.

The mass spectra, of $\alpha, \alpha, \beta, \beta$ - tetra-acetylethane was recorded at 20°C, showed the molecular ion signal at m/z 198 (96% intensity) due to $C_{10}H_{14}O_4^+$, in conformity with the calculated molecular weight of the compound, followed by strong signals at m/z 180 and 165 assigned to $C_{10}H_{12}O_3^+$ and $C_9H_9O_3^+$ ions respectively. The most dominant signal in the spectrum was the one appeared at m/z 165 (due to $C_9H_9O_3^+$), however, the signal at m/z 43 owing to the fragment ion $COCH_3^+$ also appeared as a very strong signal (intensity 97%).

To conclude the discussion, it may be stated that the compound $Ni(acac)_2.2H_2O$ can be directly synthesised, without involving any buffer, either from the reaction of $Ni(OH)_2$ with Hacac or from the reaction of NiO(OH) with Hacac. Both the methods give very high yields. Further, it may be stated that in the electron-transfer reactions between higher-valent metal ions and Hacac, acetylacetone is oxidised to $(CH_3CO)_2CH$ —— $CH(COCH_3)_2$.

References

1 G. Bontempelli, M. Andreuzzi-Seda, and M. Fiorani, *Talanta*, 1982, 29, 1101.

2 R. E. Desay, F.E. Stary, R.B. King, and M. Waldrop, *J. Am. Chem. Soc.*, 1966, 88, 471.

3 S. Kudo, A. Iwase, and N. Tanaka, *Bull. Chem. Soc., Jpn.*, 1981, 54, 207.

4 O. Sock, P. Lemoine, and M. Gross, *Electrochim Acta*, 1981, 26, 99.

5 R. W. Murray and L. K. Hiller, Jr., *Anal. Chem.*, 1967, 39, 1221.

6 G. Gritzner, H. Murauer, and P. Gutman, *J. Electroanal. Chem.*, 1979, 101, 177.

7 C. W. Anderson, K.R. Lung, and T.A. Nile, *Inorg. Chim. Acta.*, 1984, 85, 33.

8 G. Bontempelli, R. Piccolo, S. Deniele, and P. Ugo, *Inorg. Chim. Acta*, 1985, 99, 43.

9 P.W. Jolly, and G. Wilke, "The Chemistry of Nickel," Vol. 2, Academic Press, New York, 1975.

10 R. G. Charles and M.A. Powlikowski, *J. Phys. Chem.*, 1958, 62, 440.

11 W.C. Fernelius and B.E. Bryant, *Inorg. Syntheses*, 1957, 5, 105.

[12] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, and D. T. Khathing, J. Chem. Soc. Dalton Trans., 1981, 2587; M.N. Bhattacharjee and M.K. Chaudhuri, Inorg. Syntheses, 1985, 24, 0000 .

[13] B. E. Bryant and W. C. Fernelius, Inorg. Syntheses, 1957, 5, 114.

[14] M. N. Bhattacharjee, M. K. Chaudhuri, and D. T. Khathing, J. Chem. Soc. Dalton Trans., 1982, 669.

[15] M. K. Chaudhuri, N. Roy and D. T. Khathing, Synth. React. Inorg. Met.-Org. Chem., 1982, 12, 715.

[16] "Beilsteins Handbuch der Organishen Chemie," Springer, Berlin, Vol. 1, 1918, p 812.

[17] K. Nakamoto, P. J. McCarthy, and A. E. Martell, J. Am. Chem. Soc., 1961, 83, 1272.

[18] F. A. Cotton and J. P. Fackler, Jr., J. Am. Chem. Soc, 1961, 83, 2818.

[19] M. C. Chakravorti, D. Bondyopadhay, and M. K. Chaudhuri, Int. J. Mass Spectrom. Ion Processes, 1985 in press.

[20] C. G. McDonald and J. S. Shannon, Aust. J. Chem., 1966, 19, 1545.

[21] G. M. Bancroft, C. Reichert and J. B. Westmore, Inorg. Chem., 1968, 7, 870.

[22] M. J. Lacey, C. G. McDonald and J. S. Shannon, Aust. J. Chem., 1972, 25, 2559.

CHAPTER 7

Chapter 7

Synthesis of Tetrafluoronickelate(II) Complexes $[NiF_4]^{2-}$: A Novel Route to Fluorometalates and the Scope of the New Method*

One of the main reasons for a limited access to fluorometalates, of which tetrafluoronickelate(II), $[NiF_4]^{2-}$, is no exception, is the lack of suitable easy methods for their synthesis. As the case in point, for example, the synthesis of tetrafluoronickelate(II), $[NiF_4]^{2-}$, involves[1,2] fusion of anhydrous nickel(II) fluoride, NiF_2, with a stoichiometric amount of alkali fluorides or alkaline-earth metal fluorides either _in vacuo_ or in an atmosphere of dry hydrogen fluoride. Such methods therefore require not only anhydrous NiF_2 which itself is difficult to obtain, but also dry hydrogen fluoride that is difficult to handle thereby restricting the study of their chemistry. More direct and simpler routes to such compounds are thus looked for. Recently some success has been made in this direction, in the laboratory where the present doctoral research was carried out, and comparatively easier methods have been developed, for instance, for the syntheses of $[MnF_5]^{2-}$, $[MnF_4]^-$, $[MnF_3(C_2O_4)]^{2-}$, $[CrF_5(H_2O)]^{2-}$, $[CrO_3F]^-$, $[VOF_4]^-$, $[VOF_3]^-$, and $[VF(C_5H_7O_2)_2]$ complexes.[3-10] However, the search for a new and more general method has been continued. Simple

---

*The work described in this Chapter has been published.

J. Chem. Soc. Dalton Trans., 1984, 1763.

methods of syntheses of acetylacetonates of chromium[11], manganese[12], iron[13], and nickel (vide Chapter 6) have also been developed in this laboratory, and as a part of a programme aimed at utilising such compounds as precursors, it was envisaged that they would react with aqueous hydrofluoric acid and alkali metal fluorides to provide an easy access to alkali metal salts of fluorometalate complexes.

The main theme of the present Chapter is the synthesis of tetrafluoronickelate(II), $[NiF_4]^{2-}$, complexes directly from bis(acetylacetano)nickel(II) dihydrate, $Ni(C_5H_7O_2)_2.2H_2O$, and also the scope of the new method as a paradigm for other such syntheses. In order to demonstrate the scope of the method, tetrafluorozincate(II) complexes $[ZnF_4]^{2-}$, and also a few more fluorometalates of some other metals have been synthesised from their respective acetylacetonates.

Experimental

Reagent grade chemicals were used throughout $Ni(acac)_2.2H_2O$ (acac = acetylacetonate) was prepared by the methods described in the previous Chapter (Chapter 6). $Zn(acac)_2.H_2O$[14] and $VO(acac)_2$[15] were prepared by the literature methods. $Cr(acac)_3$[11] and $Mn(acac)_3$[12] were prepared by methods developed in this laboratory.

Synthesis of Tetrafluoronickelates(II), $A_2[NiF_4]$ (A = K, Rb or NH_4). A Typical Procedure

Freshly prepared bis(acetylacetonato)nickel(II) dihydrate, $Ni(acac)_2.2H_2O$ was added to an excess of 40% hydrofluoric acid (15 cm^3 g^{-1})

followed by the addition of alkali metal fluoride, AF (A = K, Rb or NH_4), with the molar ratio of nickel acetylacetonate and AF being maintained at 1 : 4. The mixture was then heated over a steam-bath with stirring until the metal acetylacetonate dissolved completely (*ca* 40 min). The reaction solution was filtered, and the filtrate concentrated over a steam-bath until microcrystalline yellow alkali tetrafluoronickelate(II), $A_2[NiF_4]$, started to appear. The reaction container was cooled to room temperature for *ca* 2 h, and $A_2[NiF_4]$ was separated by centrifugation, dried on filter paper and finally dried *in vacuo* over phosphorous pentoxide.

The gram amounts of reagents used and the yields of alkali tetrafluoronickelates(II) are reported in Table 1.

Table 1. Amounts of Reagents Used and Yields of $A_2[NiF_4]$ (A = K, Rb or NH_4)

Compound	Yield in g (%)	Amount of $Ni(acac)_2 \cdot 2H_2O$ in g (mmol)	Amount of alkali fluoride, AF in g (mmol)	Amount of 40% HF in cm^3 (mmol)
$(NH_4)_2[NiF_4]$	0.5 (86)	1.0 (3.41)	0.51 (13.77)	15 (300)
$K_2[NiF_4]$	0.6 (82)	1.0 (3.41)	0.8 (13.77)	15 (300)
$Rb_2[NiF_4]$	0.9 (87)	1.0 (3.41)	1.43 (13.69)	15 (300)

Synthesis of Alkali Tetrafluorozincates(II), $A_2[ZnF_4]$ (A = K, Rb, Cs, or NH_4). A Representative Procedure

Freshly prepared $Zn(acac)_2.H_2O$ was added to an excess of 40% hydrofluoric acid. To it was added alkali metal fluoride, AF (A = K, Rb, Cs or NH_4), with maintenance of molar ratio of $Zn(acac)_2.H_2O$ and AF as 1 : 4. The mixture was then heated on a steam-bath with stirring until the metal acetylacetonate dissolved completely (*ca* 35 min). The solution was filtered and the filtrate concentrated over a steam-bath until white microcrystalline alkali tetrafluorozincate(II) began to appear. Heating was discontinued and the reaction container was allowed to cool to room temperature for *ca* 2h. The $A_2[ZnF_4]$ thus formed was separated by centrifugation, dried on a filter paper, and finally dried *in vacuo* over P_4O_{10}.

The amounts of reagents used and the yields of alkali tetrafluorozincates(II) are summarised in Table 2.

Table 2. Amounts of Reagents Used and Yields of $A_2[ZnF_4]$ (A = K, Rb, Cs or NH_4)

Compound	Yield in g (%)	Amount of $Zn(acac)_2.H_2O$ in g (mmol)	Amount of AF in g (mmol)	Amount of 40% HF in cm^3 (mmol)
$(NH_4)_2[ZnF_4]$	0.5 (79)	1.0 (3.6)	0.53 (14.40)	12 (240)
$K_2[ZnF_4]$	0.7 (89)	1.0 (3.6)	0.84 (14.40)	12 (240)
$Rb_2[ZnF_4]$	0.96 (81)	1.0 (3.6)	1.5 (14.40)	12 (240)
$Cs_2[ZnF_4]$	1.2 (83)	1.0 (3.6)	2.2 (14.40)	12 (240)

Reaction of $[M(acac)_n]$ (M = Cr or Mn, n = 3; M = VO, n = 2) with NH_4F and 40% HF

The reaction of $M(acac)_3$ (M = Cr or Mn) or $VO(acac)_2$ was performed in a manner analogous to those described for the synthesis of $A_2[NiF_4]$ or $A_2[ZnF_4]$. The products obtained were blue $(NH_4)_2[VOF_5]$, green $(NH_4)_2[CrF_5(H_2O)]$, and pink $(NH_4)_2[MnF_5]$ from $VO(acac)_2$, $[Cr(acac)_3]$, and $[Mn(acac)_3]$ respectively, with yields lying between 85 and 90%.

Elemental Analyses

The methods of elemental analyses have been described in Chapter 2. The results of elemental analyses are given in Table 3.

Table 3 Analytical Data of $A_2[NiF_4]$ ($A = K$, Rb or NH_4), and $A_2[ZnF_4]$ ($A = K$, Rb, Cs or NH_4)

Compound	Found % (Calcd. %)		
	A or N	Ni[a] or Zn[b]	F
$(NH_4)_2[NiF_4]$	16.7 (16.4)	33.91[a] (33.37)[a]	44.81 (44.49)
$K_2[NiF_4]$	36.12 (36.73)	27.87[a] (27.58)[a]	35.2 (35.7)
$Rb_2[NiF_4]$	-	19.57[a] (19.21)[a]	25.17 (24.87)
$(NH_4)_2[ZnF_4]$	15.23 (15.79)	37.21[b] (36.86)[b]	42.34 (42.82)
$K_2[ZnF_4]$	35.11 (35.61)	30.15[b] (29.78)[b]	34.21 (34.61)
$Rb_2[ZnF_4]$	-	20.23[b] (20.93)[b]	24.85 (24.33)
$Cs_2[ZnF_4]$	-	16.76[b] (16.06)[b]	18.22 (18.66)

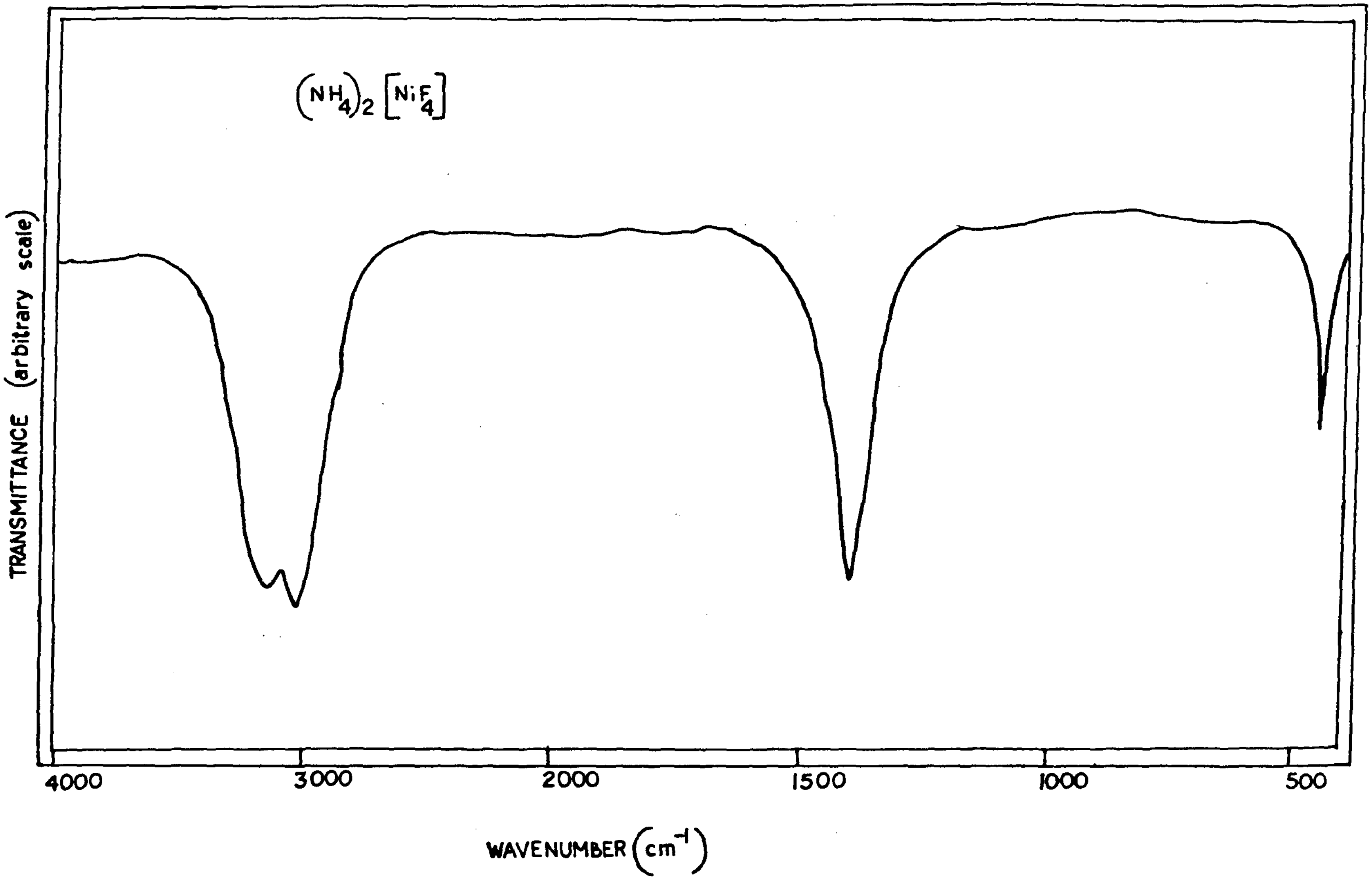
Magnetic moment values and infrared spectral band positions along with their assignments are presented in Table 4.

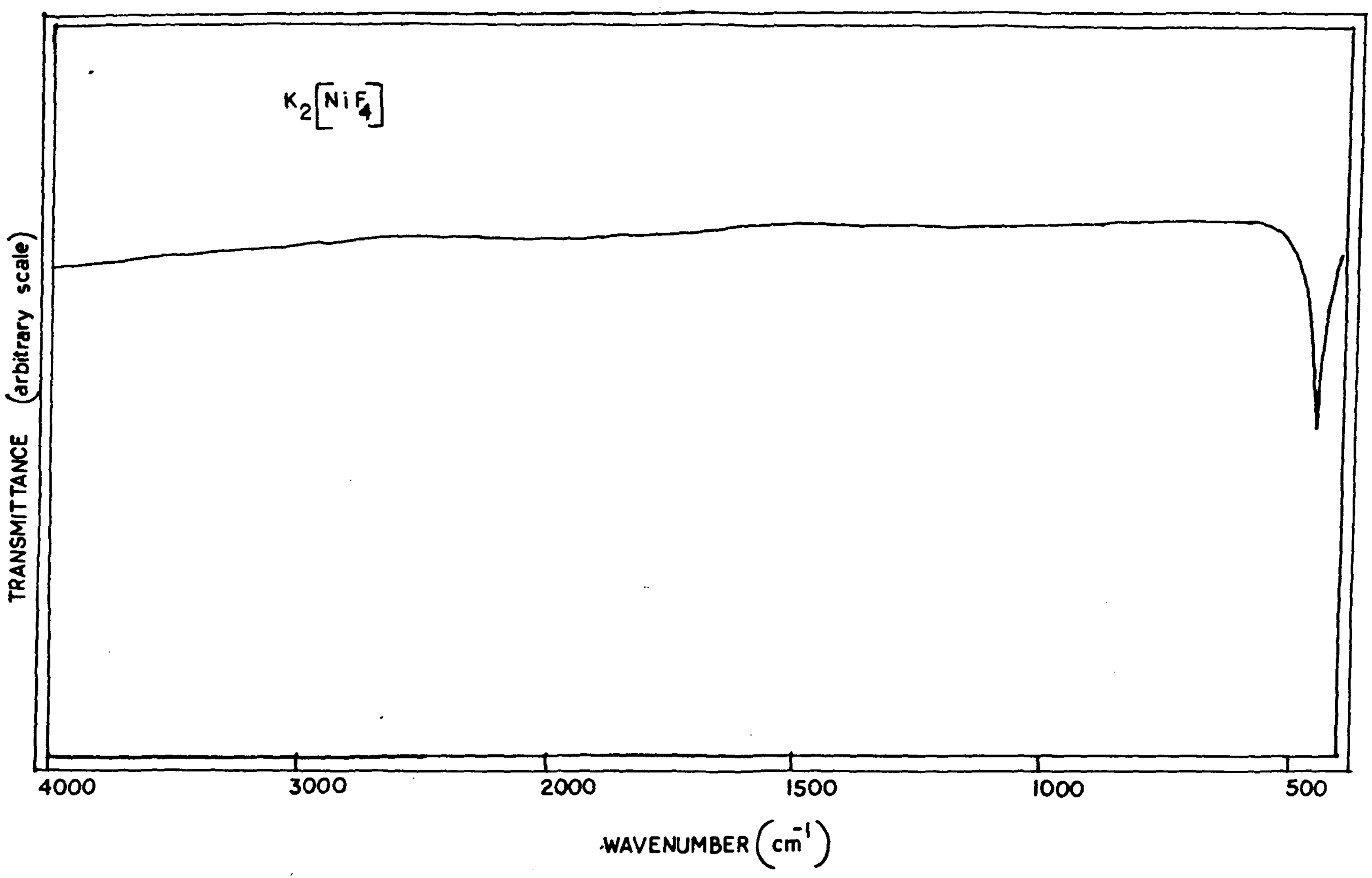
Results and Discussion

It is owing to the lack of a suitable and easier method of synthesis of tetrafluoronickelate(II) complexes that we thought it worthwhile to improvise a simple and direct method for the synthesis of the title complexes. As a part of our programme of studies of reactivities of metal acetylacetonates, the reaction of bis(acetylacetonato)nickel(II) dihydrate, $Ni(acac)_2.2H_2O$, with hot aqueous hydrofluoric acid and alkali metal fluoride, AF, was carried out. It has been observed that $Ni(acac)_2.2H_2O$ undergoes a rather facile reaction with hot 40% HF and alkali fluoride to afford yellow coloured microcrystalline alkali tetrafluoronickelates(II), $A_2[NiF_4]$, in very high yields. Subsequently, on achieving success in the afore-said reaction, a similar reaction was carried out with bis(acetylacetonato)zincate(II) monohydrate, $Zn(acac)_2.H_2O$, instead of $Ni(acac)_2.2H_2O$, and alkali tetrafluorozincate(II), $A_2[ZnF_4]$, was obtained in a very high yield with an equal ease. It may be mentioned that the recommended methods[16] involve similar difficulties as encountered in the case of corresponding nickel(II) complexes. The methods (vide Experimental) do not require dry hydrogen fluoride or elemental fluorine (F_2); they do not make use of any such starting materials as are difficult to prepare and handle. The strategy for the novel method was that aqueous hydrofluoric acid would react with metal acetylacetonates to rupture the metal-oxygen bonds in them with the simultaneous coordination of F^- ligands arising, in the reaction medium, from aqueous HF and alkali fluoride, AF, giving rise to the formation of the corresponding fluorometalates. The role of alkali fluoride is not only to enhance F^- ion concentration but also to provide counter cations A^+ to enable isolation of the complex fluorometalate anions as their alkali metal salts. The strategy seems to have worked accordingly. The method is simple, and has been used to synthesise a series of salts of $[NiF_4]^{2-}$ and $[ZnF_4]^{2-}$ complexes leaving little doubt that the synthetic procedure can be used as a paradigm for other such syntheses.

In an attempt to explore the scope of the synthetic procedure, similar reactions involving $[VO(acac)_2]$, $[Cr(acac)_3]$, or $[Mn(acac)_3]$ with NH_4F and 40% hydrofluoric acid were carried out, and the products obtained were identified as $(NH_4)_2 [VOF_5]$[17], $(NH_4)_2 [CrF_5(H_2O)]$[6], and $(NH_4)_2 [MnF_5]$[3] respectively, thereby supporting the contention that the method can be used as a paradigm for other such syntheses. It is hoped that the method will find a wide application in the syntheses of fluorometalate complexes.

The alkali tetrafluoronickelates(II), $A_2 [NiF_4]$, and the alkali tetrafluorozincates(II), $A_2 [ZnF_4]$, compounds are very sensitive to moisture, and in the presence of water they attack glass rather readily. However, the compounds can be stored undecomposed for a prolonged period in sealed polyethylene envelopes, and their stability can be ascertained from the results of metal and fluoride estimations periodically. The results of room temperature magnetic susceptibility measurements showed that while the magnetic moments of $A_2 [NiF_4]$ lie in the range 1.9 - 2.2 BM in conformity with the values reported in the literature,[18] the corresponding zinc compounds, $A_2 [ZnF_4]$, were

$(NH_4)_2[NiF_4]$
TRANSMITTANCE (arbitrary scale)
4000
3000
2000
1500
1000
500
WAVENUMBER (cm^{-1})


$K_2[NiF_4]$
TRANSMITTANCE (arbitrary scale)
4000
3000
2000
1500
1000
500
WAVENUMBER (cm^{-1})

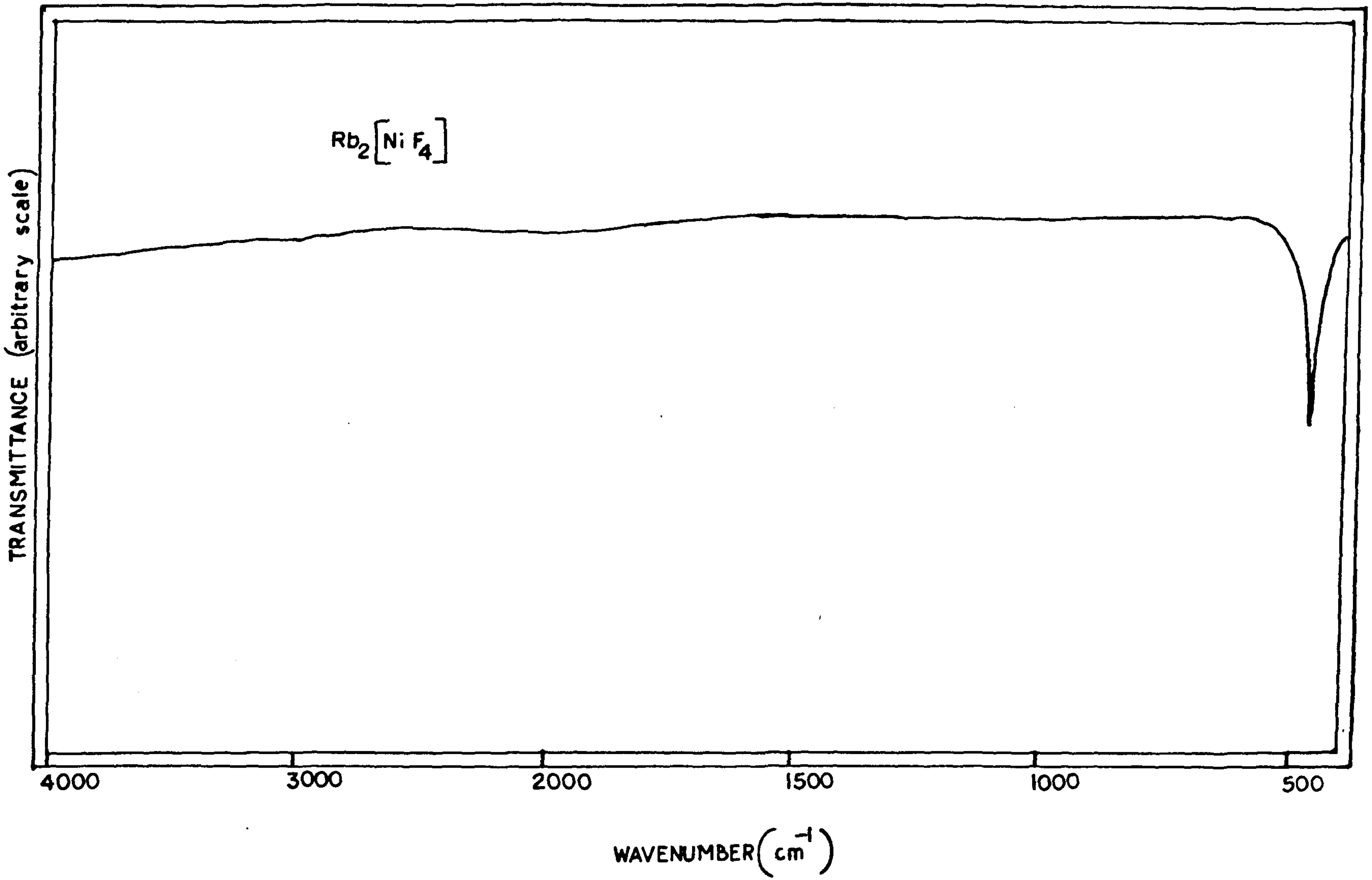

Rb$_2$[NiF$_4$]
TRANSMITTANCE (arbitrary scale)
4000
3000
2000
1500
1000
500
WAVENUMBER (cm^{-1})

Table 4 Magnetic Moments and Infrared Bands for $A_2[NiF_4]$ ($A = K$, Rb or NH_4) and $A_2[ZnF_4]$ ($A = K$, Rb, Cs or NH_4)

Compound	Magnetic Moment μ_{eff}/BM (295K)	IR cm^{-1}	Assignment
$(NH_4)_2[NiF_4]$	2.0	455	$\nu(Ni{-}F)$
$K_2[NiF_4]$	1.9	455	$\nu(Ni{-}F)$
$Rb_2[NiF_4]$	2.2	460	$\nu(Ni{-}F)$
$(NH_4)_2[ZnF_4]$	Diamagnetic	440	$\nu(Zn{-}F)$
$K_2[ZnF_4]$	Diamagnetic	445	$\nu(Zn{-}F)$
$Rb_2[ZnF_4]$	Diamagnetic	445	$\nu(Zn{-}F)$
$Cs_2[ZnF_4]$	Diamagnetic	440	$\nu(Zn{-}F)$

$1\ BM = 9.27 \times 10^{-23}\ Am^2$

diamagnetic, as expected. The analytical data and magnetic moment values suggest that the compounds are the same which have been prepared by other methods characterised structurally.[18,19] The infrared spectra of the newly synthesised $A_2[NiF_4]$ and $A_2[ZnF_4]$ (Table 4) also support this view. The IR spectral pattern is very simple. The ν(Ni-F) mode appears at ca 455 cm^{-1} while the ν(Zn-F) band has been observed to fall at ca 445 cm^{-1}. The spectra do not show any evidence for the presence of alkali metal difluorides, $A[HF_2]$,[20-22] thus ruling out the possibility of contimination of the end products by $A[HF_2]$.

It is thus evident from the results of studies described in the present Chapter that tetrafluoronickelate(II) complexes can be synthesised rather easily, directly from bis(acetylacetonato)nickel(II) dihydrate, $Ni(acac)_2.2H_2O$. A similar procedure can also be used for the direct synthesis of tetrafluorozincate(II) complexes. Further, it is evident that metal acetylacetonates can serve as useful precusors for the straight synthesis of fluorometalate complexes, and the method developed can serve as a paradigm for other such syntheses.

References

[1] D. Nicholls, "The Chemistry of Iron, Cobalt and Nickel," Pergamon Texts in Inorganic Chemistry, Vol. 24, Pergamon Press, New York, 1975, p 1145.

[2] W. Ruedorff and J. Kaendler, Naturwissenschaften, 1957, 44, 418.

[3] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, and D. T. Khathing, *J. Chem. Soc. Dalton Trans.*, 1981, 2587; M. N. Bhattacharjee and M. K. Chaudhuri, *Inorg. Syntheses*, 1985, **24**, 0000.

[4] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, and A. Kathipri, *Polyhedron*, 1985, **4**, 621.

[5] M. N. Bhattacharjee, M. K. Chaudhuri, and R. N. Dutta Purkayastha, *Inorg. Chem.*, 1985, **24**, 447.

[6] M. K. Chaudhuri and N. Roy, *Synth. React. Inorg. Met.-Org. Chem.*, 1982, **12**, 879.

[7] M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, N. Roy, and D. T. Khathing, *Synthesis*(Stuttgart), 1982, 588; M. K. Chaudhuri, H. S. Dasgupta and N. Roy, *Ind. J. Chem. (A)*, 1981, **20**, 1227.

[8] M. K. Chaudhuri, H. S. Dasgupta, S. K. Ghosh, and D. T. Khathing, *Synth. React. Inorg. Met-Org. Chem.*, 1982, **12**, 63.

[9] M. K. Chaudhuri, S. K. Ghosh, and J. Subramanian, *Inorg. Chem.*, 1984, **23**, 4439.

[10] M. K. Chaudhuri and S. K. Ghosh, *Inorg. Chem.*, 1984, **23**, 2367.

[11] M. K. Chaudhuri, N. Roy, and D. T. Khathing, *Synth. React. Inorg. Met.-Org. Chem.*, 1982, **12**, 715.

[12] M. N. Bhattacharjee, M. K. Chaudhuri, and D. T. Khathing, *J. Chem. Soc. Dalton Trans.*, 1982, 669.

[13] M. K. Chaudhuri and S.K. Ghosh, *J. Chem. Soc. Dalton Trans.*, 1983, 839.

[14] E. L. Lippert and M. R. Truter, *J. Chem. Soc.*, 1960, 4996.

[15] B. E. Bryant and W.C. Fernelius, *Inorg. Syntheses*, 1957, **5**, 114.

[16] B. J. Aylett, " The Chemistry of Zinc, Cadmium and Mercury", Pergamon Texts in Inorganic Chemistry , Vol. 18, Pergamon Press, New York, 1975, p 211.

[17] R. D. Peacock, *Progr. Inorg. Chem.*, 1960, **2**, 233.

[18] W. Ruedorff, J. Kaendler, and D. Babel, *Z. Anorg. Allgem. Chem.*, 1962, **317**, 261.

[19] H. G. Schnering and P. Bleckman, *Naturwissenschaften*, 1965, **52**, 538.

[20] J. A. A. Katelaar and W. Vedder, *J. Chem. Phys.*, 1951, **19**, 654.

[21] R. Newman and R. M. Badger, *J. Chem. Phys.*, 1951, **19**, 1207.

[22] M. K. Chaudhuri and P. K. Chaudhury, *Chem. Ind. (London)*, 1979, 88.

CHAPTER 8

Chapter 8

The First Reported Synthesis and Characterisation of Alkali Trifluoronickelate(II) Monohydrates, $ANiF_3.H_2O$ (A = Na, K or NH_4)*

The alkali trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$ (A = Na, K or NH_4), a series of very simple compounds of nickel, exhibit very interesting properties. For example, the mere change of the counter cation in $ANiF_3.H_2O$ brings about very drastic and significant changes of their magnetic properties.[1] Thus[1], while the sodium trifluoronickelate(II) monohydrate, $NaNiF_3.H_2O$, behaves ferromagnetically, the corresponding potassium salt $KNiF_3.H_2O$ shows antiferromagnetic behaviour, and the ammonium salt $NH_4NiF_3.H_2O$ behaves like a normal paramagnetic nickel(II) compound without showing any strong magnetic interaction. It is quite unfortunate that although Machin and Nyholm reported[1] the analytical data and magnetic properties of $ANiF_3.H_2O$ compounds about twenty years ago, there is no report to date on their synthesis. The synthesis of alkali trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$, should therefore be especially important, but seldom has this been realised.

Our interest in the field of fluoronickelates(II) has been emphasised in Chapter 7 (and also in Chapter 1). In a continuation to our

---

*This work has been accepted for publication.

Transition Metal Chem., 1985 in press.

effort in the field of fluoronickelate chemistry we thought it is imperative to develope a general method of synthesis of alkali trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$ (A = Na, K or NH_4).

The present Chapter, indeed the concluding Chapter of the thesis reports the details of the method of synthesis of the title compounds, and their characterisation by spectroscopic and cryomagnetic studies.

Experimental

The chemicals used were all reagent grade products. Bis(acetylacetonato)nickel(II) dihydrate, $Ni(acac)_2.2H_2O$, was prepared by the methods described in Chapter 6.

Synthesis of Alkali Trifluoronickelate(II) Monohydrates, $ANiF_3.H_2O$ (A = Na, K or NH_4)

Since the methods of syntheses of alkali trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$ (A = Na, K or NH_4), only a representative procedure is described. Polyethylene apparatus was used for the reactions.

In a typical procedure a suspension of bis(acetylacetonato)-nickel(II) dihydrate, $Ni(acac)_2.2H_2O$, in 40% hydrofluoric acid was heated on a steam-bath. Alkali metal fluoride, AF (A = Na, K or NH_4), was added to the hot stirred solution whereupon $Ni(acac)_2.2H_2O$ dissolved completely in ca 30 min. The solution was then filtered quickly, and concentrated over a steam-bath almost to dryness whereupon a yellow microcrystalline deposit formed. This was treated directly with a small amount of water, and then concentrated as above to give the light green alkali trifluoronickelate(II) monohydrate, $ANiF_3.H_2O$. The product thus obtained was separated by filtration, washed thrice with water, and finally dried in vacuo over P_4O_{10}.

The amounts of reagents used and yields of alkali trifluoronickelate(II) monohydrates prepared in this way are given in Table 1.

Table 1. Amounts of Reagents Used for the Synthesis, and Yields of $ANiF_3.H_2O$ (A = Na, K or NH_4)

	Yield in g (%)	Amount of $Ni(acac)_2.2H_2O$ in g (mmol)	Amount of AF in g (mmol)	Amount of 40% HF in cm^3 (mmol)
$NH_4NiF_3.H_2O$	0.4 (77)	1.0 (3.41)	0.51 (13.77)	15 (300)
$NaNiF_3. H_2O$	0.5 (92)	1.0 (3.41)	0.58 (13.81)	15 (300)
$KNiF_3.H_2O$	0.5 (85)	1.0 (3.41)	0.8 (13.77)	15 (300)

Elemental Analyses

The details of elemental analyses have been described in Chapter 2. The results of elemental analyses are reported in Table 2.

101892.

Table 2 Analytical Data of $ANiF_3.H_2O$ (A [illegible] K or NH_4)

Compound	Found (%) Calcd (%)		
	A or N	Ni	F
$NH_4\ NiF_3.\ H_2O$	9.4 (9.2)	38.9 (38.7)	12.7 (12.5)
$Na\ NiF_3.\ H_2O$	14.4 (14.7)	37.9 (37.5)	12.4 (12.1)
$KNiF_3.H_2O$	22.3 (22.6)	33.6 (34.0)	11.25 (11.0)

Magnetic moment values, Curie or Neel temperatures, and the infrared band positions are summarised in Table 3.

Results and Discussion

Very recently direct methods of syntheses of metal acetylacetonates have been developed.[2-5] In the course of our studies involving the reactions of such compounds, it was observed that metal-acac bonds may be easily cleaved by the interaction of metal acetylacetonates with aqueous hydrofluoric aicd. Consequent upon this, reactions of a number of metal acetylacetonates with aqueous hydrofluoric acid in the presence of alkali metal fluorides were carried out and the corresponding fluorometalate complexes were easily obtained in very high yields (as described in Chapter 7). A general method for the synthesis of fluorometalate complexes was thus improvised.

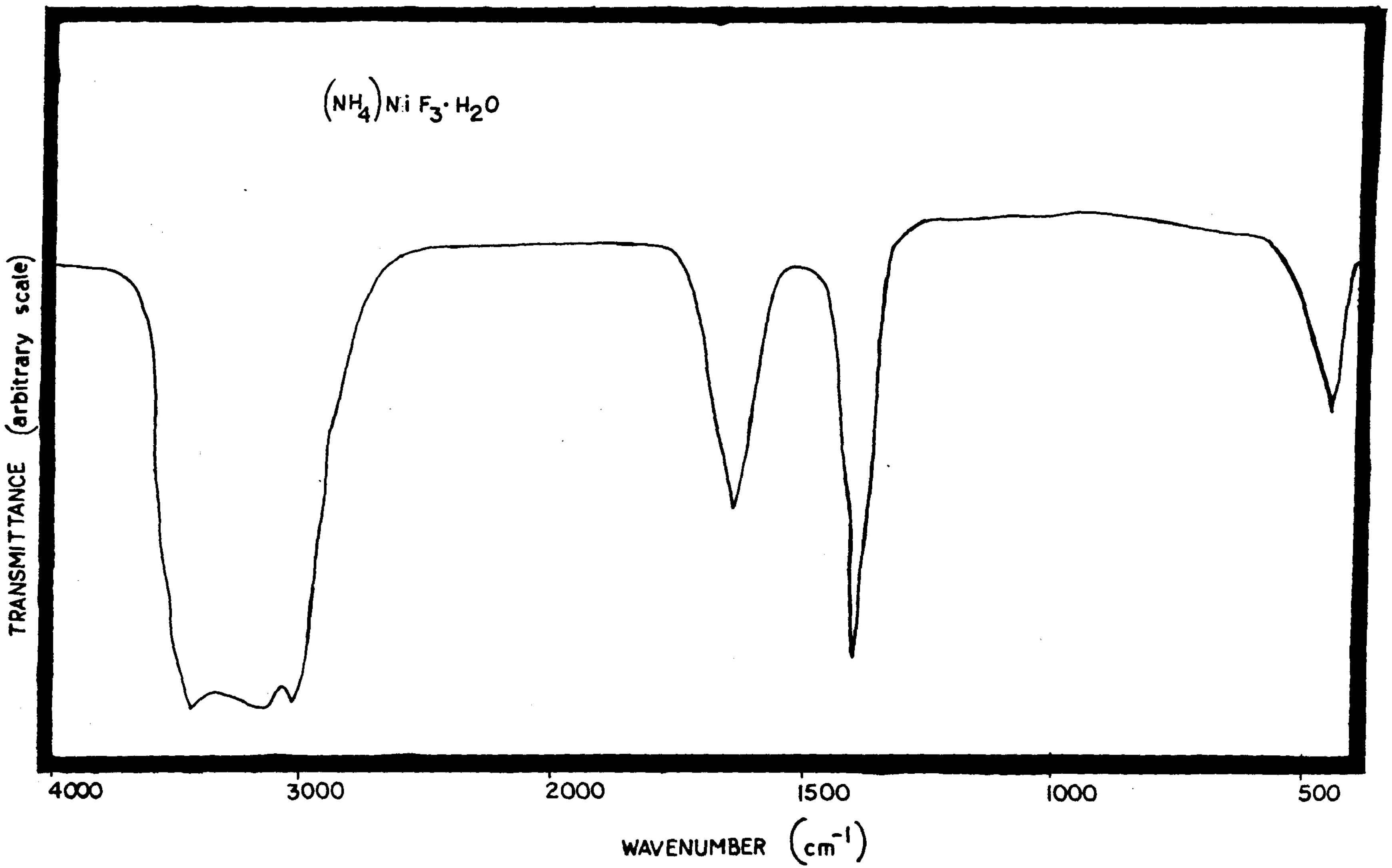
It may be recalled that emphasis was put on the synthesis of alkali tetrafluoronickelates(II), $A_2 [NiF_4]$, in Chapter 7. It was observed, while working up the reaction, carried out for the purpose of obtaining tetrafluoronickelates(II), that the yellow alkali tetrafluoronickelates(II), $A_2 [NiF_4]$, were very sensitive to moisture, and they readily reacted with water to produce light green coloured microcrystalline products. It was believed that the products must be different from $A_2 [NiF_4]$, and expected that they might as well be alkali trifluoronickelate(II) monohydrates, $A\ NiF_3.H_2O$, a class of compounds for which the method of synthesis does not seem to have any reported existence. Accordingly, bis(acetylacetonato)nickel(II) dihydrate, $Ni(acac)_2.2H_2O$, was allowed to react with aqueous hydrofluoric acid and alkali metal fluoride, AF (A = Na, K or NH_4), first to obtain an yellow product (c.f. A_2NiF_4, described in Chapter 7) which, without isolation, on being treated with water led to the successful synthesis of light green alkali trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$, in very high yields. The methods has been used for the synthesis of a series of compounds of the type $ANiF_3.H_2O$ suggesting that similar methods can be used for the syntheses of analogous compounds of other transition metals. Indeed further investigation in this direction showed that alkali trifluoromanganate(II) monohydrates, $AMnF_3.H_2O$, could be synthesised from $Mn(acac)_2.2H_2O$ by adaptation of the method similar to that used for the synthesis of $ANiF_3.H_2O$. This, therefore, provides enough hints regarding the scope of the method.

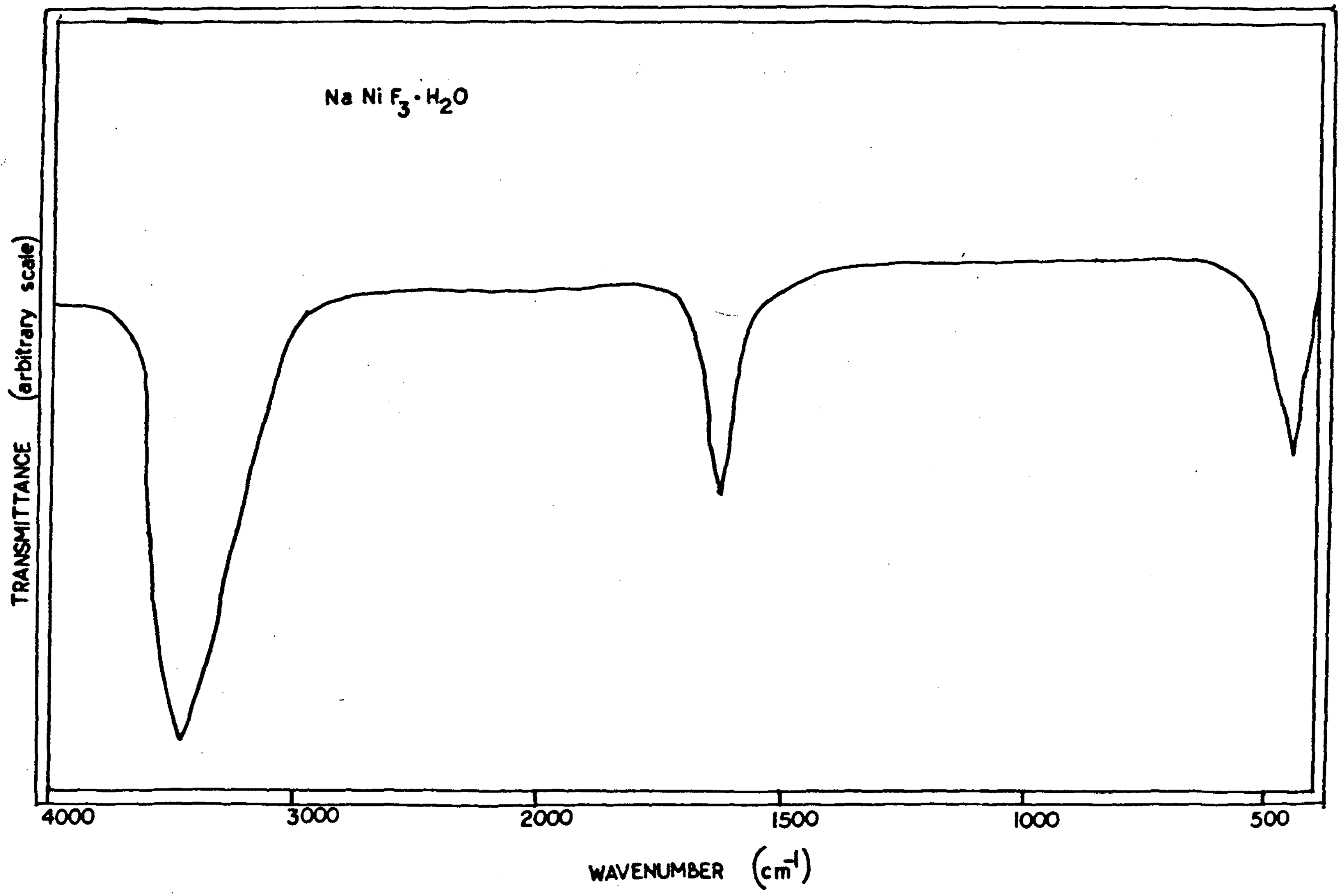
NEHU Library
Acc. No. 101892
Acc. by
Class by
Sub. Heading by 9/8/87
Cata. by
Transcribed by

Characterisation of the Compounds

The alkali trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$, are all light green stable products, and are capable of being stored for a prolonged period. The compounds, however, attack glass slowly. Quantitative estimations of alkali metal or nitrogen content, and nickel and fluoride contents gave consistent results in excellent agreement with the formulae containing one molecule of water per formula weight of each compound. Moreover, prolonged heating of the compounds at 120°C did not remove the water, as evidenced by their unaltered weight and infrared spectra recorded before and after pyrolysis, suggesting thereby that the water molecule is rather strongly held in the crystal lattice.

The infrared spectra of $ANiF_3.H_2O$ (A = Na, K or NH_4) resemble each other very closely, showing absorptions in the three characteristic regions, viz., at ca 3455, ca 1640, and at ca 450 cm^{-1} (Table 3) which have been assigned to ν(O-H), δ(H-O-H), and ν(Ni-F) vibrations respectively. Although the water could not be removed by heating at 120°C, the IR suggest, in line with the earlier observations,[1] that the water molecule in $ANiF_3.H_2O$ is most probably not coordinated to the nickel centre. This argument is supported further by the occurrence of ν(O-H) at ca 3455 cm^{-1} characteristic of the presence of lattice water.[6] The three extra vibrations at 3160m, 3040s, and 1400s cm^{-1}, in the spectrum of $NH_4NiF_3.H_2O$ are assigned to ν_3, ν_1 and ν_4 modes of NH_4^+ ion. The occurrence of ν(Ni — F) modes at ca 450 cm^{-1} is in order and compares very well with those observed elsewhere[7] for similar systems.


$(NH_4)NiF_3 \cdot H_2O$
TRANSMITTANCE (arbitrary scale)
4000
3000
2000
1500
1000
500
WAVENUMBER (cm^{-1})


Na Ni $F_3 \cdot H_2O$
TRANSMITTANCE (arbitrary scale)
4000
3000
2000
1500
1000
500
WAVENUMBER (cm^{-1})

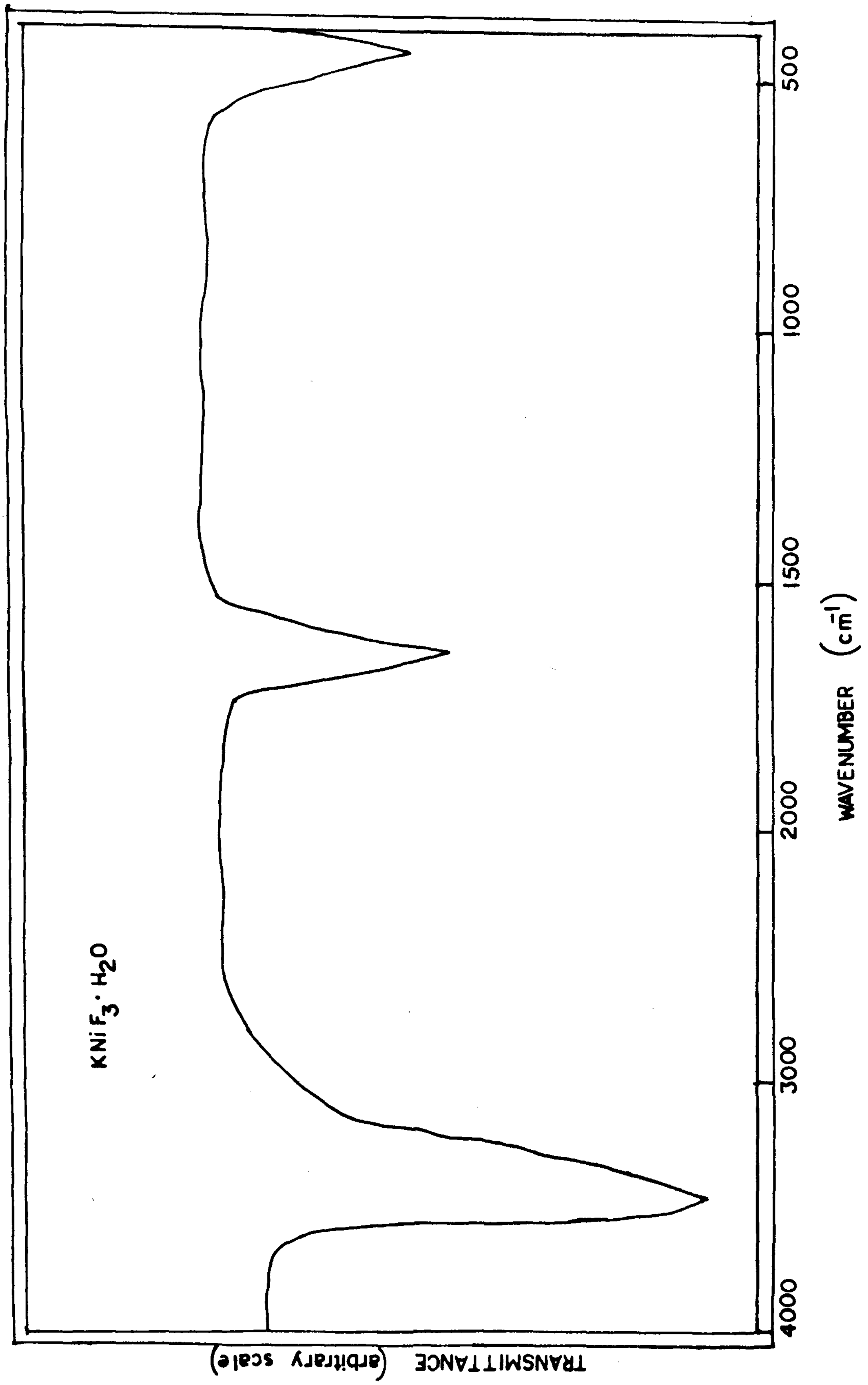
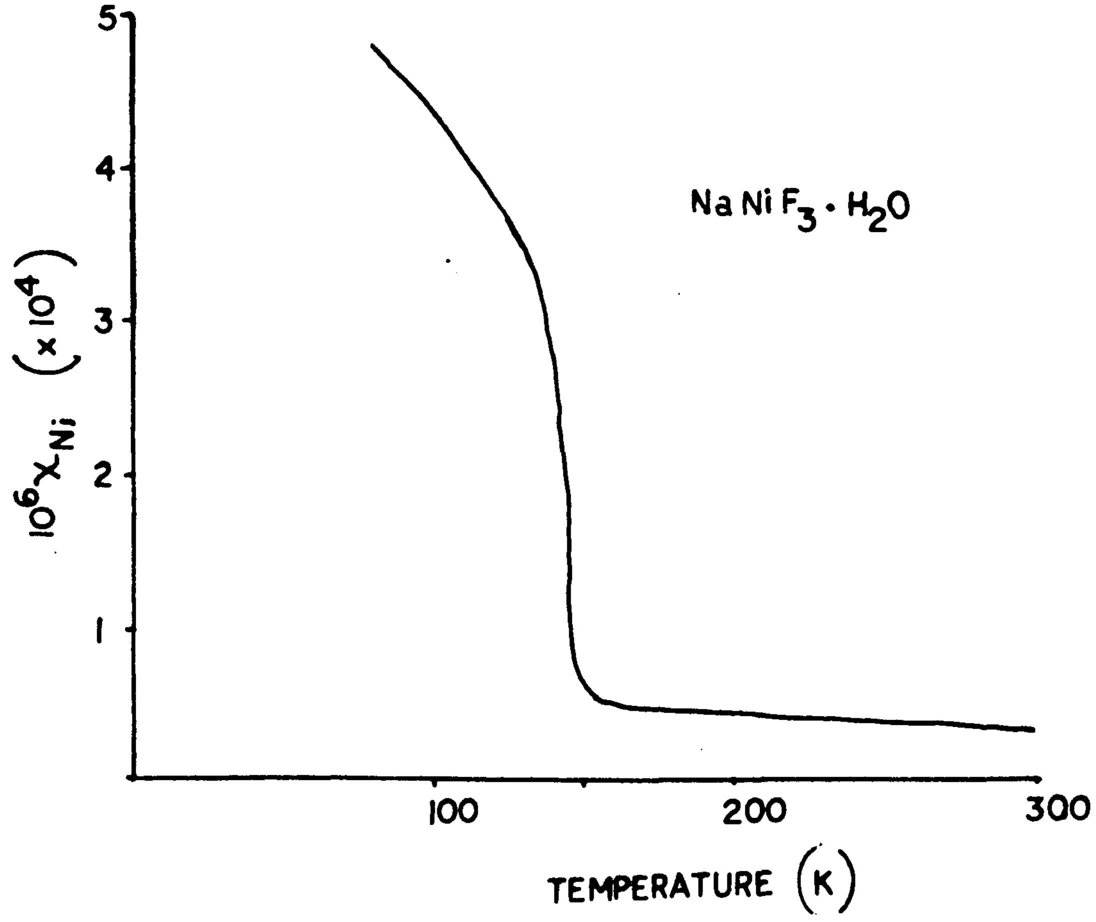

KNiF$_3$·H$_2$O
TRANSMITTANCE (arbitrary scale)
WAVENUMBER (cm^{-1})
500
1000
1500
2000
3000
4000

Table 3. Magnetic Moments, Curie or Neel Temperature and Structurally Significant IR Bands of $ANiF_3.H_2O$ (A = Na, K or NH_4)

Compound	μ_{eff}/BM (300K)	Curie[a] or Neel[b] temperature (K)	IR (cm^{-1})	Assignment
$NH_4NiF_3.H_2O$	3.2	-	450m	ν(Ni-F)
			1630m	δ (H-O-H)
			3460s	ν(O-H)
$NaNiF_3.H_2O$	2.9	145[a]	450m	ν(Ni-F)
			1640m	δ (H-O-H)
			3450s	ν(O-H)
$KNiF_3.H_2O$	2.4	230[b]	445m	ν(Ni-F)
			1640m	δ (H-O-H)
			3455s	ν(O-H)

The newly synthesised alkali trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$, display interesting magnetic properties with their relative behaviour being very important. The room temperature magnetic moments of $NH_4NiF_3.H_2O$, $NaNiF_3.H_2O$, and $KNiF_3.H_2O$ were found to be 3.2, 2.9, and 2.4 BM respectively (Table 3) in agreement with the values observed previously by Machin and Nyholm.[1] In an attempt to assess the identity of the compounds, magnetic susceptibilities of $NaNiF_3.H_2O$ and $KNiF_3.H_2O$ were measured in the 300 - 80 K range (Tables 4 and 5). The results are consistent with those observed previously[1] lending strong credence to the contention that the newly synthesised compounds are the same as those described by Machin and Nyholm.[1] Thus, while the $NaNiF_3.H_2O$ behaves ferromagnetically with the Curie temperatures of 145K, the $KNiF_3.H_2O$ is antiferromagnetic with the Neel temperature being 230K. The antiferromagnetism in $KNiF_3.H_2O$ most probably owes its origin to super-exchange interaction through a —— Ni — F ----· Ni — F — chain in the crystal lattice operative in a manner analogous to that in $KNiF_3$ (perovskite).

It may be concluded from the results of studies described in the present Chapter, that alkali trifluoronickelate(II) monohydrates, $ANiF_3.H_2O$ (A = Na, K or NH_4), can be synthesised in very high yields from the reaction of $Ni(acac)_2.2H_2O$ with 40% HF and AF at a steam-bath temperature followed by treating the product obtained thereof with water. The results of elemental analyses, infrared spectral, and cryomagnetic studies confirm that the compounds are same as those described by Machin and Nyholm.[1]


5
4
3
2
1
$10^6\chi_{Ni}$ $(\times 10^4)$
$NaNiF_3 \cdot H_2O$
100
200
300
TEMPERATURE (K)

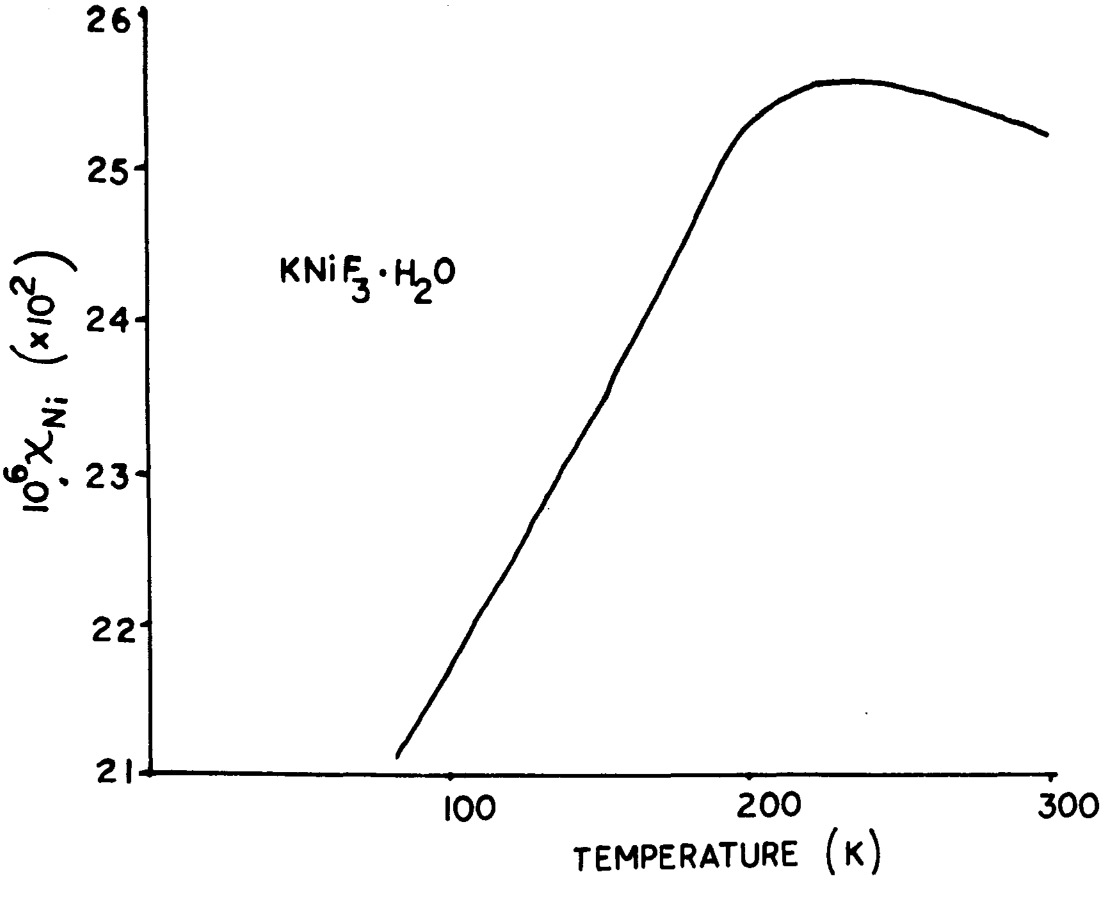

26
25
24
23
22
21
$10^6\chi_{Ni}$ $(\times 10^2)$
$KNiF_3 \cdot H_2O$
100
200
300
TEMPERATURE (K)

Table 4. Cryomagnetic Data (at 6300 oersted) of $NaNiF_3.H_2O$

Temp.(K)	$10^6\chi_{Ni}$
300	3,500
280	3,600
270	3,690
250	3,800
230	3,910
220	4,000
200	4,450
180	4,890
160	5,000
150	6,000
144	14,000
142	19,000
140	21,000
135	35,000
130	35,500
110	40,500
80	48,000

Table 5. Cryomagnetic Data (at 6300 oersted) of $KNiF_3.H_2O$

Temp.(K)	$10^6\chi_{Ni}$
300	2,520
290	2,530
275	2,545
265	2,550
250	2,555
240	2,560
225	2,550
215	2,545
200	2,530
190	2,500
175	2,440
155	2,360
130	2,275
85	2,125

References

---

[1] D. J. Machin and R. S. Nyholm, J. Chem. Soc., 1963, 1500.

[2] M. M. Bhattacharjee, M. K. Chaudhuri and D. T. Khathing, J. Chem. Soc. Dalton Trans., 1982, 669.

[3] M. K. Chaudhuri, N. Roy, and D. T. Khathing, Synth. React. Inorg. Met.-Org. Chem., 1982, 12, 715.

[4] M. K. Chaudhuri and S. K. Ghosh, J. Chem. Soc. Dalton Trans., 1983, 839.

[5] M. C. Chakravorti, D. Bandyopadhay, and M. K. Chaudhuri, Int. J. Mass Spectrom. Ion Processes, 1985, in press.

[6] N. F. Curtis, J. Chem. Soc. A, 1968, 1584.

[7] R. D. Peacock and D. W. A. Sharp, J. Chem. Soc., 1959, 2762.

APPENDIX

NEHU Library
Acc. No.------
Acc. by------
Class by------
Sub. Heading by--
Cata. by------
Transcribed by--

Appendix

LIST OF PUBLICATIONS

1. Direct Synthesis of Bis(acetylacetonato)nickel(II) Dihydrate and Isolation of $\alpha,\alpha,\beta,\beta$-Tetra-acetylethane as the Oxidation Product of Acetylacetone.
Manabendra N. Bhattacharjee, Mihir K. Chaudhuri, Soumitra K. Ghosh, Zavei Hiese, and Nirmalendu Roy.
J. Chem. Soc. Dalton Trans., 1983, 2561.

2. Synthesis of Tetrafluoronickelate(II), NiF_4^{2-}, and Tetrafluorozincate(II), ZnF_4^{2-}, Complexes from Aqueous Media. A Novel Route to Fluorometalates.
Mihir K. Chaudhuri, Soumitra K. Ghosh, and Zavei Hiese.
J. Chem. Soc. Dalton Trans., 1984, 1763.

3. The First Reported Synthesis and Identity of Magnetically Anomalous Alkali-Metal Trifluoronickelate(II) Monohydrates, $ANiF_3.H_2O$ ($A = NH_4$, Na or K).
Mihir K. Chaudhuri, Soumitra K. Ghosh, and Zavei Hiese.
Transition Met. Chem., 1985, 10, 0000.

4. Complex Peroxo(carbonato)metalates. First Synthesis and Structural Assessment of Alkali Dioxoperoxomonocarbonatouranate(VI) Monohydrates, $A_2[UO_2(O_2)CO_3].H_2O$, and Alkali Oxodiperoxymonocarbonatovanadate(V) Trihydrates, $A_3[VO(O_2)_2CO_3].3H_2O$.
Jayanta K. Basumatary, Mihir K. Chaudhuri, Ranendra N. Dutta Purkayastha, and Zavei Hiese.
J. Chem. Soc. Dalton Trans., 1985, in press (DAL - 5/576).

Direct Synthesis of Bis(acetylacetonato)nickel(II) Dihydrate and Isolation of α,α,β,β-Tetra-acetylethane as the Oxidation Product of Acetylacetone

Manabendra N. Bhattacharjee, Mihir K. Chaudhuri,* Soumitra K. Ghosh, Zavei Hiese, and Nirmalendu Roy
Department of Chemistry, North-Eastern Hill University, Shillong 793 003, India

NiO(OH) undergoes a facile reaction with acetylacetone affording a very high yield of bis(acetylacetonato)nickel(II) dihydrate, $[Ni(acac)_2]\cdot 2H_2O$, and giving α,α,β,β-tetra-acetylethane as the oxidation product of acetylacetone.

Our interest in the area of acetylacetonates of transition metals extended to the development of new synthetic routes to such compounds [1-3] has led to an investigation of the reaction of NiO(OH) with acetylacetone (Hacac). In our previous papers [1,2] we emphasised the role of Hacac as a reducing agent in the direct synthesis of $[Mn(acac)_3]$ and $[Cr(acac)_3]$. We now wish to report the reaction between NiO(OH) and Hacac leading to the direct synthesis of bis(acetylacetonato)nickel(II) dihydrate in a very high yield, in the absence of any buffer {unlike the synthesis of $[Ni(acac)_2]\cdot 2H_2O$ by Charles and Powlikowski [4]}, and also enabling the isolation of α,α,β,β-tetra-acetylethane as the oxidation product of Hacac, for the first time, from such a reaction.

Experimental

The chemicals used for the reactions were all reagent grade products. Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. The mass spectra were recorded on a Varian MAT CH-5 mass spectrometer using a direct insertion probe (Table).

Preparation of NiO(OH).—An aqueous solution of nickel(II) chloride hexahydrate was treated with an excess of sodium hydroxide and a precipitate of $Ni(OH)_2$ was obtained. The $Ni(OH)_2$ was separated by filtration and purified by repeated washing with water until free from chloride. Nickel(II) hydroxide was then oxidised to NiO(OH) by treating an alkaline suspension of it with bromine. The black NiO(OH) thus obtained was separated by centrifugation, washed with water until free from alkali, and finally dried *in vacuo* over phosphorus pentoxide.

Reaction of NiO(OH) *with Acetylacetone.*—Acetylacetone (11.0 g, 110.0 mmol) was added to a suspension of NiO(OH), (2.0 g, 21.8 mmol) in water (*ca.* 6 cm^3) with constant stirring. An exothermic reaction occurred almost immediately. The reaction mixture was stirred mechanically until the black NiO(OH) was converted completely to a blue-green product (*ca.* 15 min). The mixture was filtered and the product washed with acetone until a green-blue filtrate had just begun to appear. The combined filtrate and washing (A) was retained for the isolation of the oxidation product of Hacac.

The compound on the filter was then recrystallised from boiling acetone by the addition of light petroleum (b.p. 40—60 °C) and subsequent cooling at *ca.* 0 °C to obtain the blue-green shiny platelet compound. The yield of $[Ni(acac)_2]\cdot 2H_2O$ was 5.3 g (82.3%) (Found: C, 40.8; H, 6.3; Ni, 20.2. Calc. for $C_{10}H_{18}NiO_6$: C, 41.0; H, 6.15; Ni, 20.05%). The compound was characterized by its i.r. spectrum, magnetic susceptibility,[5] and molar conductance.

Table. Mass spectral data for $[Ni(acac)_2]$

(*a*) Major peaks

Assignment	*m/z*	Intensity (%)
$[Ni(C_5H_7O_2)_2]^+$	256	100
$[Ni(C_5H_7O_2)(C_4H_4O_2)]^+$	241	96
$[Ni(C_5H_7O_2)(OCCH_2)]^+$	199	3
$[Ni(C_5H_7O_2)H]^+$	158	40
$[Ni(C_5H_7O_2)]^+$	157	91
$[Ni(C_4H_4O_2)]^+$	142	30
$[Ni(C_4H_3O_2)]^+$	141	23
$[Ni(C_3H_4O)]^+$	114	5
$[Ni(OCCH_2)]^+$	100	56
$[Ni(CO)]^+$ or $[Ni(C_2H_4)]^+$	86	70
Ni^+	58	16

(*b*) Metastable transitions

m/z *			
Observed	Calculated	Process	Fragment lost
226.8	226.88	$256 \longrightarrow 241$	CH_3
102.2	102.28	$241 \longrightarrow 157$	$C_4H_4O_2$
128.4	128.43	$157 \longrightarrow 142$	CH_3
91.5	91.52	$142 \longrightarrow 114$	CO
70.3	70.42	$142 \longrightarrow 100$	C_2H_2O
64.8	64.88	$114 \longrightarrow 86$	CO or C_2H_4
39.1	39.12	$86 \longrightarrow 58$	C_2H_4 or CO

Isolation of the Oxidation Product, α,α,β,β-*Tetra-acetylethane from the Combined Filtrate and Washing* (A).—The combined filtrate and washing (A) was concentrated by removing the solvent on a rotary vacuum evaporator, and colourless cubic crystals were obtained. The crystals were removed and washed three times with benzene and finally dried on a filter paper.

The $(CH_3CO)_2CH\text{-}CH(COCH_3)_2$ melts at 190 °C (lit.,[6] 191 °C) and the yield was 1.85 g (85.6%, on the basis of an electron-transfer reaction between Ni^{III} and Hacac). The compound is very sparingly soluble in water, benzene, and ether, and its various physical and chemical properties (colour, m.p., solubility, reaction with $FeCl_3$, and mass and n.m.r. spectra) compare very well with those of a specimen prepared by the action of iodine upon sodium acetylacetonate.[6]

Results and Discussion

It is evident from various reports that under the appropriate conditions Hacac is capable of acting both as a reducing agent and a chelating agent.[1,2,7,8] However, the nature of the oxidation product of acetylacetone when it acts as a reducing agent has not been established until now. We have carried out the reaction of NiO(OH) with acetylacetone leading to the direct synthesis of $[Ni(acac)_2]\cdot 2H_2O$ with oxidation of acetylacetone. One of our main concerns was to identify the oxidation product. Work up of the mother-liquor obtained after separating $[Ni(acac)_2]\cdot 2H_2O$ afforded a crystalline organic compound which has been identified as $(CH_3CO)_2CH-CH(COCH_3)_2$.

In an attempt to generalise the contention that electron-transfer reactions between higher-valent transition metal ions and acetylacetone leading to the corresponding acetylacetonates give $(CH_3CO)_2CH-CH(COCH_3)_2$ as the oxidation product, we performed the reactions of Hacac with Mn^{7+} and Cr^{6+} following the procedures described in our previous papers.[1,2] Isolation of $(CH_3CO)_2CH-CH(COCH_3)_2$ from each of the reactions, after separation of the corresponding $[M(acac)_3]$ complex, was successful again owing to the oxidation of acetylacetone; we therefore conclude that in the electron-transfer reactions of the types discussed above, acetylacetone is oxidised to $(CH_3CO)_2CH-CH(COCH_3)_2$.

The pH of the solution, recorded immediately after the formation of $[Ni(acac)_2]\cdot 2H_2O$ was found to be *ca.* 5, a situation conducive to the formation of metal–acac complexes, and concurs with that maintained by Charles and Powlikowski [4] by the addition of a large amount of sodium acetate. The chances of contamination of the product owing to the use of such a large amount of buffer can not be ruled out.[9] In view of the products isolated from the reaction of Ni^{3+}, Mn^{7+}, or Cr^{6+} with acetylacetone (*e.g.* see below), and the pH of the reaction medium, we feel that acetylacetone first undergoes

$$[Ni^{III}O(OH)] + 3\ Hacac \longrightarrow [Ni(acac)_2] + \tfrac{1}{2}(\text{'acac-acac'}) + 2\ H_2O$$

ionization giving $(CH_3CO)_2CH^-$ ($acac^-$) and H^+ (*cf.* the observed pH) followed by the oxidation of $(CH_3CO)_2CH^-$ ion to the $(CH_3CO)_2CH^\bullet$ radical (with corresponding reduction of the metal), which dimerises to yield $(CH_3CO)_2CH-CH(COCH_3)_2$. It appears that this route to α,α,β,β-tetraacetylethane is relatively simpler than methods described in the literature.[6] Because of the higher yield of product, considerably shorter reaction time, and redundancy of any buffer, this method of synthesis of $[Ni(acac)_2]\cdot 2H_2O$ offers advantages over the procedure described in the literature.[4]

Acknowledgements

We thank the C.S.I.R. (New Delhi) for the award of two fellowships (to S. K. G. and Z. H.) and the University for the award of a U.G.C. fellowship (to M. N. B.).

References

1 M. N. Bhattacharjee, M. K. Chaudhuri, and D. T. Khathing, *J. Chem. Soc., Dalton Trans.*, 1982, 669.

2 M. K. Chaudhuri, N. Roy, and D. T. Khathing, *Synth. React. Inorg. Met.-Org. Chem.*, 1982, **12**, 715.

3 M. K. Chaudhuri and S. K. Ghosh, *J. Chem. Soc., Dalton Trans.*, 1983, 839.

4 R. G. Charles and M. A. Powlikowski, *J. Phys. Chem.*, 1958, **62**, 440.

5 F. A. Cotton and J. P. Fackler, jun., *J. Am. Chem. Soc.*, 1961, **83**, 2818.

6 'Beilsteins Handbuch der Organishen Chemie,' Springer, Berlin, 1918, vol. 1, p. 812.

7 B. E. Bryant and W. C. Fernelius, *Inorg. Synth.*, 1957, **5**, 114.

8 M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, and D. T. Khathing, *J. Chem. Soc., Dalton Trans.*, 1981, 2587.

9 W. C. Fernelius and B. E. Bryant, *Inorg. Synth.*, 1957, **5**, 105.

Received 7th February 1983; *Paper* 3/183

Synthesis of Tetrafluoronickelate(II) and Tetrafluorozincate(II) Complexes from Aqueous Media: A Novel Route to Fluorometalates

Mihir K. Chaudhuri,* Soumitra K. Ghosh, and Zavei Hiese
Department of Chemistry, North-Eastern Hill University, Shillong 793003, India

The complexes $A_2[NiF_4]$ (A = NH_4^+, K^+, or Rb^+) and $A_2[ZnF_4]$ (A = NH_4^+, K^+, Rb^+, or Cs^+) have been synthesised, from the corresponding metal acetylacetonates (acac) with 40% HF and AF, in very high yields. The new method also allows the preparation of $[VOF_5]^{2-}$, $[MnF_5]^{2-}$, and $[CrF_5(H_2O)]^{2-}$ from $[VO(acac)_2]$, $[Mn(acac)_3]$, and $[Cr(acac)_3]$ respectively.

Recommended methods [1-3] for the synthesis of $[NiF_4]^{2-}$ or $[ZnF_4]^{2-}$ complexes employ fusion of NiF_2 or ZnF_2 with stoicheiometric amounts of alkali-metal or alkaline-earth-metal fluorides *in vacuo* or in an atmosphere of dry HF. Such methods require not only MF_2 (M = Ni or Zn) but also anhydrous HF which is difficult to handle. Very recently, we described simple syntheses of acetylacetonates of nickel,[4] manganese,[5] chromium,[6] and iron,[7] and as part of a programme aimed at utilising such compounds as precursors, it was envisaged that they would react with aqueous HF and alkali-metal fluorides to provide an easy access to alkali-metal salts of fluorometalates. In this paper we report the synthesis of $[NiF_4]^{2-}$ and $[ZnF_4]^{2-}$ complexes directly from their respective acetylacetonates, and also the scope of the method as a paradigm for other such syntheses.

Experimental

Reagent-grade chemicals were used throughout. $[Zn(acac)_2]\cdot H_2O$ [8] (acac = acetylacetonate) and $[VO(acac)_2]$ [9] were prepared by the literature methods. $[Ni(acac)_2(H_2O)_2]$,[4] $[Mn(acac)_3]$,[5] and $[Cr(acac)_3]$ [6] were prepared by methods developed in these laboratories. Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. Magnetic susceptibility measurements were made by the Guoy method using $Hg[Co(NCS)_4]$ as calibrant.

Synthesis of $A_2[NiF_4]$ (A = NH_4^+, K^+, *or* Rb^+) *and* $A_2[ZnF_4]$ (A = NH_4^+, K^+, Rb^+, *or* Cs^+).—*A typical procedure.* Freshly prepared $[Ni(acac)_2(H_2O)_2]$ or $[Zn(acac)_2]\cdot H_2O$ was added to an excess of 40% HF (15 $cm^3\ g^{-1}$) followed by the addition of AF, with the molar ratio of metal acetylacetonate and AF being maintained at 1 : 4. The mixture was then heated over a steam-bath with stirring until the metal acetylacetonate dissolved completely (*ca.* 40 min). The solution was filtered, and the filtrate concentrated over a steam-bath until microcrystalline yellow $A_2[NiF_4]$ or white $A_2[ZnF_4]$ started to appear. The reaction container was cooled to room temperature for *ca.* 2 h, and $A_2[NiF_4]$ or $A_2[ZnF_4]$ was separated by centrifugation, dried on a filter paper, and finally dried *in vacuo* over phosphorus pentoxide. Yields varied between 80 and 90%. Analytical data, magnetic moments, and structurally significant i.r. band positions are summarised in the Table.

Reaction of $[M(acac)_n]$ (M = Cr *or* Mn, $n = 3$; M = VO, $n = 2$) *with* NH_4F *and* 40% HF.—The reaction was performed in a manner analogous to that described above. The products obtained were blue $[NH_4]_2[VOF_5]$, green $[NH_4]_2[CrF_5(H_2O)]$, and pink $[NH_4]_2[MnF_5]$ from $[VO(acac)_2]$, $[Cr(acac)_3]$, and $[Mn(acac)_3]$ respectively, with yields lying between 85 and 90%.

Table. Analytical data, magnetic moments, and i.r. bands for $A_2[NiF_4]$ (A = NH_4^+, K^+, or Rb^+) and $A_2[ZnF_4]$ (A = NH_4^+, K^+, Rb^+, or Cs^+)

		Analysis [b]/%				
Compound	$\mu_{eff.}$ [a]/B.M.	A	Ni or Zn	F	I.r./cm^{-1}	Assignment
$[NH_4]_2[NiF_4]$	2.0	16.7 [c] (16.4) [c]	33.90 (34.35)	44.80 (44.50)	455	ν_{Ni-F}
$K_2[NiF_4]$	1.9	36.10 (36.75)	27.85 (27.60)	35.2 (35.7)	455	ν_{Ni-F}
$Rb_2[NiF_4]$	2.2		19.55 (19.20)	25.15 (24.85)	460	ν_{Ni-F}
$[NH_4]_2[ZnF_4]$	Diamagnetic	15.25 [c] (15.80) [c]	37.20 (36.85)	42.35 (42.80)	440	ν_{Zn-F}
$K_2[ZnF_4]$	Diamagnetic	35.10 (35.60)	30.15 (29.80)	34.20 (34.60)	445	ν_{Zn-F}
$Rb_2[ZnF_4]$	Diamagnetic		20.25 (20.95)	24.85 (24.35)	445	ν_{Zn-F}
$Cs_2[ZnF_4]$	Diamagnetic		16.75 (16.05)	18.20 (18.65)	440	ν_{Zn-F}

[a] T = 295 K; 1 B.M. = 9.27×10^{-23} A m^2. [b] Calculated values in parentheses. [c] Analysis for N.

Results and Discussion

$[Ni(acac)_2(H_2O)_2]$ or $[Zn(acac)_2]\cdot H_2O$ undergo a rather facile reaction with hot aqueous HF and alkali-metal fluorides (AF) to afford yellow $A_2[NiF_4]$ ($A = NH_4^+$, K^+, or Rb^+) or white $A_2[ZnF_4]$ ($A = NH_4^+$, K^+, Rb^+, or Cs^+) in a very high yield. The method does not require anhydrous HF or any starting material which is difficult to prepare. The role of AF was not only to increase the F^- ion concentration in the medium but also to provide counter cations, A^+, to enable isolation of the fluorometalates as their alkali-metal salts. In an attempt to explore the scope of the synthetic procedure, similar reactions involving $[VO(acac)_2]$, $[Cr(acac)_3]$, or $[Mn(acac)_3]$ with NH_4F and 40% HF were carried out and the products obtained were identified as $[NH_4]_2[VOF_5]$,[9] $[NH_4]_2[CrF_5(H_2O)]$,[10] and $[NH_4]_2[MnF_5]$[11] respectively, thereby supporting our contention that the method can be used as a paradigm for other such syntheses.

The room-temperature magnetic susceptibility measurements show that while the $A_2[ZnF_4]$ compounds are all diamagnetic, as expected, the magnetic moments of the $A_2[NiF_4]$ compounds lie between 1.9 and 2.2 B.M. in conformity with those reported in the literature.[12] The analytical data and magnetic moments suggest that the compounds are the same as those which have been prepared by other methods and characterized structurally.[13,14] The i.r. spectra of $A_2[NiF_4]$ and $A_2[ZnF_4]$ (Table) also support this view. The spectra do not show any evidence for the presence of alkali-metal difluorides, $A[HF_2]$,[15-17] thus ruling out the possibility of contamination of the end products by $A[HF_2]$.

Acknowledgements

We thank the Department of Atomic Energy for financial support and CSIR (New Delhi) for awarding fellowships (to S. K. G. and Z. H.).

References

1 D. Nicholls, 'The Chemistry of Iron, Cobalt and Nickel,' in Pergamon Texts in Inorganic Chemistry, Pergamon Press, Oxford, 1975, vol. 24, p. 1145.
2 W. Ruedorff and J. Kaendler, *Naturwissenschaften*, 1957, **44**, 418.
3 B. J. Aylett, 'The Chemistry of Zinc, Cadmium and Mercury,' in Pergamon Texts in Inorganic Chemistry, Pergamon Press, Oxford, 1975, vol. 18, p. 211.
4 M. N. Bhattacharjee, M. K. Chaudhuri, S. K. Ghosh, Z. Hiese, and N. Roy, *J. Chem. Soc., Dalton Trans.*, 1983, 2561.
5 M. N. Bhattacharjee, M. K. Chaudhuri, and D. T. Khathing, *J. Chem. Soc., Dalton Trans.*, 1982, 669.
6 M. K. Chaudhuri, N. Roy, and D. T. Khathing, *Synth. React. Inorg. Metal-Org. Chem.*, 1982, **12**, 715.
7 M. K. Chaudhuri and S. K. Ghosh, *J. Chem. Soc., Dalton Trans.*, 1983, 839.
8 E. L. Lippert and M. R. Truter, *J. Chem. Soc.*, 1960, 4996.
9 B. E. Bryant and W. C. Fernelius, *Inorg. Synth.*, 1957, **5**, 114.
10 M. K. Chaudhuri and N. Roy, *Synth. React. Inorg. Metal-Org. Chem.*, 1982, **12**, 879.
11 M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, and D. T. Khathing, *J. Chem. Soc., Dalton Trans.*, 1981, 2587.
12 Ref. 1, p. 1146.
13 W. Ruedorff, J. Kaendler, and D. Babel, *Z. Anorg. Allg. Chem.*, 1962, **317**, 261.
14 H. G. Schnering and P. Bleckmann, *Naturwissenschaften*, 1965, **52**, 538.
15 J. A. A. Katelaar and W. Vedder, *J. Chem. Phys.*, 1951, **19**, 654.
16 R. Newman and R. M. Badger, *J. Chem. Phys.*, 1951, **19**, 1207.
17 M. K. Chaudhuri and P. K. Chaudhury, *Chem. Ind.* (*London*), 1979, 88.

Received 31*st August* 1983; *Paper* 3/1519 n1260tm

TMC — 1260 VERLAG CHEMIE
D-6940 Weinheim

1

Short title: $MNiF_3 \cdot H_2O$ (M = NH_4, Na or K)

---

* Author to whom all correspondence should be directed.

The First Reported Syntheses and Characterisation of Alkali Metal Trifluoronickelate(II) Monohydrates, $MNiF_3 \cdot H_2O$ (M = NH_4, Na or K)

Mihir K Chaudhuri*, Soumitra K. Ghosh and Zavei Hiese

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

Summary

$Ni(acac)_2 \cdot (H_2O)_2$ (1 mol) and alkali metal fluorides (4 mols), MF (M = NH_4, Na or K), react with an excess of 40% HF on a steam-bath. The product upon treatment with water gives light green crystalline alkali metal trifluoronickelate(II) monohydrate, $MNiF_3 \cdot H_2O$ in a high yield. Chemical analyses, pyrolysis at 120°C, i.r. spectroscopic, and cryomagnetic (300–80 K) data have been used to characterise, and establish the identity of the compounds. While $NH_4NiF_3 \cdot H_2O$ behaves as a normal octahedral nickel(II) compound, $NaNiF_3 \cdot H_2O$ is ferromagnetic with Curie point 145 K, $KNiF_3 \cdot H_2O$ behaves antiferromagnetically; its Neel point is 230 K.

/ H_2O

Introduction

The alkali metal trifluoronickelate(II) monohydrates, $MNiF_3 \cdot H_2O$ (M = NH_4, Na or K), are simple, yet show interestng properties. The mere change of the counter cation in $MNiF_3 \cdot H_2O$ brings about very drastic and significant changes of magnetic properties(1). Although Machin and Nyholm reported(1) the analytical data and magnetic properties of $MNiF_3 \cdot H_2O$ about twenty years ago, there is no report to date on their syntheses. As part of a programme involving studies on fluorometallates(2, 3), we have developed a general syntheses of $MNiF_3 \cdot H_2O$, described here.

/ N

(2, 3)

Experimental

Reagent grade chemicals were used. $Ni(acac)_2 \cdot (H_2O)_2$ was prepared by the method developed in this laboratory(4). I.r. spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. Magnetic susceptibility measurements were made by the Gouy method in the 300–80 K range using $Hg[Co(NCS)_4]$ as calibrant.

Alkali Trifluoronickelate(II) Monohydrates, $MNiF_3 \cdot H_2O$ (M = NH_4, Na or K).

A respresentative procedure is described. Polyethylene apparatus was used for the reactions.

1. 2. 3. Korrektur
6. MRZ. 1985
von Verlag

A suspension of $Ni(acac)_2 \cdot (H_2O)_2$ in 40% HF was heated on a steam-bath. Alkali metal fluoride, MF (M = NH_4, Na or K), was added to the hot stirred solution whereupon $Ni(acac)_2 \cdot (H_2O)_2$ dissolved completely in *ca.* 30 min. The solution was then filtered quickly, and concentrated over a steam-bath almost to dryness whereupon a yellow microcrystalline deposit formed. This was treated directly with a small amount of H_2O and then concentrated as above to give the light green alkali trifluoronickelate(II) monohydrate, $MNiF_3 \cdot H_2O$. This product was separated by filtration, washed thrice with H_2O, and finally dried *in vacuo* over P_4O_{10}.

The amounts of reagents used and yields of alkali trifluoronickelate(II) monohydrates prepared in this way are given in Table 1.

Table 1

Elemental analysis

Nickel and fluorine were estimated gravimetrically as nickel dimethylglyoximate(5) and lead chlorofluoride(6), respectively. Sosium, potassium and nitrogen were estimated by the method described in our earlier papers(3).

Results and Discussion

Very recently neyer method have been developed for the syntheses of metal acetylacetonates(7). In the course of our studies it was observed that the metal-oxygen bonds could be easily cleaved with aqueous hydrofluoric acid, which suggested that an excess of F^- ions would lead to fluorometallate complexes. Accordingly, $Ni(acac)_2 \cdot (H_2O)_2$ was allowed to react with 40% HF and MF (M = NH_4, Na or K) and led to the syntheses of alkali metal trifluoronickelate(II) monohydrates, $MNiF_3 \cdot H_2O$, in very high yield. It is believed that similar procedures could be used to synthesise analogous compound of other transition metals. Indeed, alkali metal trifluoromanganate(II) monohydrates, $MMnF_3 \cdot H_2O$, can be easily prepared by analogous methods.

Characterisation of the compounds

The alkali metal trifluoronickelate(II) monohydrates are all light green stable products. Analyses are in excellent agreement with formulae containing one molecule of water per formula weight of each compound. Moreover, prolonged heating of the compounds at 120°C did not remove the water.

The i.r. spectra of $MNiF_3 \cdot H_2O$ (M = NH_4, Na or K) closely resemble each other, showing absorptions at *ca.* 3455, *ca.* 1640, and *ca.* 450 cm^{-1} which are assigned to ν(O–H), δ(H–OH) and ν(Ni–F) modes, respectively. The i.r. spectra also suggest, in line with the earlier observations(1), that the water molecule is most probably not co-ordinated to the nickel centre, an argument which is supported further by the occurrence of ν(O–H) at *ca.* 3455 cm^{-1} characteristic of the presence of lattice water(8). The three extra vibrations at 3160m, 3040s, and 1400s cm^{-1}, in the spectrum of $NH_4 \cdot NiF_3 \cdot H_2O$, are assigned to the ν_3, ν_1 and ν_4 modes of NH_4^+. The ν(Ni–F) mode at *ca.* 450 cm^{-1} compares very well with that observed elsewhere(9).

The room temperature (300 K) magnetic moments of $NH_4NiF_3 \cdot H_2O$, $NaNiF_3 \cdot H_2O$ and $KNiF_3 \cdot H_2O$ were found to be 3.2, 2.9 and 2.4 BM respectively in agreement with values observed previously by Machin and Nyholm(1). In an attempt to assess the identity of the compounds, magnetic susceptibilities of $NaNiF_3 \cdot H_2O$ and $KNiF_3 \cdot H_2O$ were measured in the 300–80 K range. The results are consistent with those observed previously(1). Thus, while $NaNiF_3 \cdot H_2O$ behaves ferromagnetically $KNiF_3 \cdot H_2O$ is antiferromagnetic. The antiferromagnetism in $K \cdot NiF_3 \cdot H_2O$ is most probably due to super-exchange interaction through a –Ni–F–Ni–F– chain in the crystal lattice in a manner analogous to that in $KNiF_3$ (perovskite).

Acknowledgements

We thank the Council of Scientific and Industrial Research, New Delhi for awarding fellowships (to S.K.G. and Z. H.).

References

(1) D. J. Machin and R. S. Nyholm, *J. Chem. Soc.*, 1500 (1963). – (2) M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Das Gupta and D. T. Khathing, *J. Chem. Soc., Dalton Trans.*, 2587 (1981); M. K. Chaudhuri, H. S. Das Gupta, S. K.Ghosh and D. T. Khating, *Synth. React. Inorg. Met.–Org. Chem.*, *12*, 63 (1982); M. K. Chaudhuri and N. Roy, *Synth. React. Inorg. Met.-Org. Chem.*, *12*, 879 (1982); M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Das Gupta, N. Roy and D. T. Khathing, *Synthesis*, 588 (1982); M. K. Chaudhuri, S. K. Ghosh and Z. Hiese, *J. Chem. Soc., Dalton Trans.*, 1763 (1984). – (3) M. K. Chaudhuri and S. K. Ghosh, *Polyhedron*, *1*, 533 (1982); *Inorg. Chem.*, *21*, 4020 (1982); *J. Chem. Soc., Dalton Trans.*, 507 (1984); M. N. Bhattacharjee, M. K. Chaudhuri, R. N. Dutta Purkayastha, *J. Chem. Soc., Dalton Trans.*, ~~in press (1984)~~. – (4) M. N. Bhattacharjee, M. K. Chaudhuri, S. K. Ghosh, Z. Hiese and N. Roy, *J. Chem. Soc., Dalton Trans.*, 2561 (1983). – (5) A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Longman-Green, London, 479 (1962). – (6) Ref. 5, p. 561. – (7) M. N. Bhattacharjee, M. K. Chaudhuri and D. T. Khathing, *J. Chem. Soc., Dalton Trans.*, 669 (1982); M. K. Chaudhuri, N. Roy and D. T. Khathing, *Synth. React. Inorg. Met.-Org. Chem.*, *12*, 715 (1982); M. K. Chaudhuri, S. K. Ghosh, *J. Chem. Soc., Dalton Trans.*, 839 (1983). – (8) N. F. Curtis, *J. Chem. Soc. A*, 1584 (1968). – (9) R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 2762 (1959).

409 (1985)

(Received November 8th, 1984) TMC 1260

Table 1. Reagents used to prepare $MNiF_3 \cdot H_2O$ (M = NH_4, Na or K).

Compound	Yield/g (%)	$Ni(acac)_2 \cdot (H_2O)_2$/g (mmol)	MF/g (mmol)	40% HF cm³ (mmol)
$NH_4NiF_3 \cdot H_2O$	0.4 (77)	1.0 (3.41)	0.51 (13.77)	15 (300)
$NaNiF_3 \cdot H_2O$	0.5 (92)	1.0 (3.41)	0.58 (13.81)	15 (300)
$KNiF_3 \cdot H_2O$	0.5 (85)	1.0 (3.41)	15 (300)	

0.8
(13.77)

Table 2. Analytical data, magnetic moments, Curie or Neel temperature and structurally significant i.r. bands of $MNiF_3 \cdot H_2O$ (M = NH_4, Na or K).

Compound	μ_{eff} BM[a]	Curie[b] or Neel[c] temp., K	Found (calcd.) %			I.r. (cm⁻¹)	~~Assignment~~
			M	Ni	F		Assignment
$NH_4NiF_3 \cdot H_2O$	3.2	–	9.4[d] (9.2)[d]	38.9 (38.7)	12.7 (12.5)	450m 1630m 3460s	ν(Ni–F) δ(H–O–H) ν(O–H)
$NaNiF_3 \cdot H_2O$	2.9	145[b]	14.4 (14.7)	37.9 (37.5)	12.4 (12.1)	450m 1640m 3450s	ν(Ni–F) δ(H–O–H) ν(O–H)
$KNiF_3 \cdot H_2O$	2.4	230[c]	22.3 (22.6)	33.6 (34.0)	11.25 (11.0)	445m 1640m 3455s	ν(Ni–F) δ(H–O–H) ν(O–H)

[a] Measured at 300 K; [b] Curie Temperature; [c] Neel Temp.; [d] Analysis for N.

Date 85/03/05 Länge 720 mm

Note

First Synthesis and Structural Assessment of Alkali-metal Carbonatodioxoperoxouranate(VI) Monohydrates, $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$, and Carbonato-oxodiperoxovanadate(V) Trihydrates, $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$

Jayanta K. Basumatary, Mihir K. Chaudhuri,* Ranendra N. Dutta Purkayastha, and Zavei Hiese
Department of Chemistry, North-Eastern Hill University, Shillong 793003, India

The complexes $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ (A = Na or K) have been synthesised from the reaction of the product obtained by treating $UO_2(NO_3)_2\cdot 6H_2O$ with AOH and $AHCO_3$ (ratio $U:CO_3^{2-} = 1:4$) with an excess of 30% H_2O_2 at pH 7—8, and $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ (A = Na or K) have been synthesised by treating V_2O_5 with A_2CO_3 (ratio $V:CO_3^{2-} = 1:1.5$) and an excess of 30% H_2O_2 at pH *ca.* 7. They were precipitated with ethanol. The occurrence of *trans* O=U=O and terminal V=O in the $[UO_2(O_2)(CO_3)]^{2-}$ *and* $[VO(O_2)_2(CO_3)]^{3-}$ *ions respectively, and the presence of triangular* bidentate O_2^{2-} and chelated bidentate CO_3^{2-} groups, have been ascertained from i.r. and laser Raman spectra. The complexes $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ can be dehydrated at *ca.* 100 °C, a temperature at which $A_3[VO(O_2)_2)]\cdot 3H_2O$ starts to decompose.

The complexity involved in the field of peroxouranates is an acknowledged problem.[1,2] Few examples of peroxouranates have been reported $[NH_4]_2[UO_2(O_2)(CO_3)]\cdot 2H_2O$ [3] being the only one for which the synthesis is available. In contrast, relatively more is known about complex peroxovanadates,[4,5] and some peroxovanadates containing co-ordinated N-heterocyclic ligands have been very well characterised.[5] However, $[VO(O_2)_2C_2O_4]^{3-}$ is to our knowledge the only peroxovanadate having an oxygen-containing ligand.[5,6] Attempts to co-ordinate SO_4^{2-} with V^V in the presence O_2^{2-} were unsuccessful,[7] however, the simultaneous co-ordination of CO_3^{2-} and O_2^{2-} to V^V appeared to be possible under appropriate conditions.

Experimental

The chemicals used were all reagent-grade products. Magnetic susceptibilities and the pH of the reaction solutions were measured as described earlier.[4,8] Molar conductances were measured using a Philips PR 9500 conductivity bridge. I.r. spectra were recorded on a Perkin-Elmer model 983 instrument. The laser Raman spectra were recorded at ambient temperatures on a SPEX Ramalog 1403 spectrometer using the line at 4 880 Å from a Spectra Physics model 165 argon laser as the excitation source. The sample was held either in a quartz capillary or in the form of a pressed pellet.

Synthesis of Alkali-metal Carbonatodioxoperoxouranate(VI) *Monohydrates*, $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ (A = Na *or* K).—Powdered $UO_2(NO_3)_2\cdot 6H_2O$ (1 g, 1.99 mmol) was dissolved in hot water (20 cm^3) and a 20% solution of AOH (A = Na or K) was added slowly with stirring until a yellow product ceased to appear. The solution was filtered while hot and the yellow product washed free from alkali. To a stirred water suspension of the product, $AHCO_3$ (8 mmol; ratio $U:CO_3^{2-} = 1:4$) was added and stirring continued for *ca.* 20 min. An excess of 30% H_2O_2 (30 cm^3, 264.7 mmol) was added until a clear yellow solution was obtained. The pH of the solution was found to be 7—8. The solution was filtered and then cooled in an ice-bath for *ca.* 30 min. Addition of pre-cooled ethanol (*ca.* 50 cm^3) led to the precipitation of a yellow microcrystalline solid which was filtered off, washed 3—4 times with ethanol, and then dried *in vacuo* over concentrated H_2SO_4. The yields of $Na_2[UO_2(O_2)(CO_3)]\cdot H_2O$ and $K_2[UO_2(O_2)(CO_3)]\cdot H_2O$ were 0.7 (82) and 0.8 g (88%) respectively.

Synthesis of Alkali-metal Carbonato-oxodiperoxovanadate(V) *Trihydrates*, $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ (A = Na *or* K).—In a typical synthesis a mixture of V_2O_5 (1 g, 5.5 mmol) and A_2CO_3 (16.5 mmol; ratio $V:CO_3^{2-} = 1:1.5$) was dissolved in 30% H_2O_2 (15 cm^3, 132.4 mmol) giving a clear yellow solution. The solution was filtered and the filtrate cooled in an ice-bath for *ca.* 15 min. An excess of pre-cooled ethanol was added with stirring until the yellow microcrystalline $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ (A = Na or K) was completely precipitated. The stirring and cooling were continued for another 30 min. The compounds were isolated, purified, and dried similarly to the peroxouranates. The yields of $Na_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ and $K_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ were 3 (87) and 3.2 g (80%) respectively.

Elemental Analysis.—The determinations of uranium,[8] and of vanadium, peroxide, carbon, sodium, and potassium,[4] were as described earlier. The elemental analyses, molar conductances, and structurally significant i.r. and Raman bands are summarised in the Table.

Results and Discussion

The importance of the pH for the successful synthesis of peroxometal compounds has been emphasised,[4,9,10] and it was shown very recently that a relatively high pH favoured co-ordination of O_2^{2-} with UO_2^{2+} (ref. 8) and VO^{3+}.[4,10] In the present case, pH > 6 was considered conducive in order to prevent the reaction $CO_3^{2-} + 2H^+ \longrightarrow CO_2 + H_2O$. Thus pH *ca.* 7 was found to be suitable for the syntheses. It is imperative that the products isolated at pH 4 or 5 either did not show the presence of CO_3^{2-} at all or did to a very small extent, indicating that co-ordination of the CO_3^{2-} ligand might have just commenced. However, the reaction of UO_2^{2+} with hydrogen peroxide and $AHCO_3$ (A = Na or K) at pH 7—8, and that of V_2O_5 with H_2O_2 and A_2CO_3 at pH 7, followed by the addition of alcohol with facilitated precipitation, afforded $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ and $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ respectively in very high yields. Attempts to synthesise the ammonium salts of the complex ions were not successful. Corresponding salts of Rb^+ and

Table. Analytical data, molar conductances structurally significant i.r. and laser Raman bands of $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ and $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ (A = Na or K)

Compound	Molar conductance[a]/ Ω^{-1} cm^2 mol^{-1}	Analysis[b]/(%)				I.r. (cm^{-1})	Laser Raman (cm^{-1})	Assignment
		A	U or V	O[c]	C			
$Na_2[UO_2(O_2)(CO_3)]\cdot H_2O$	225(20)	10.45	56.2	7.8	2.85	1 580s	1 570	$\nu(C-O)\ \nu_1, A_1$
	-	*(10.8)*	*(55.85)*	*(7.5)*	*(2.8)*	1 325m		$\nu(C-O) + \delta(O-C-O)\ \nu_3, B_2$
						920s	930	$\nu(O{=}U{=}O)$
						890s	880	$\nu(O-O)\ \nu_1$
						615m	600	$\nu(U-O_2)\ \nu_3$
						550s	550	$\nu(U-O_2)\ \nu_2$
$K_2[UO_2(O_2)(CO_3)]\cdot H_2O$	245(20)	17.3	52.25	7.2	2.6	1 570s	1 570	$\nu(C-O)\ \nu_1, A_1$
		(17.1)	(51.94)	(7.0)	(2.6)	1 330m		$\nu(C-O) + \delta(O-C-O)\ \nu_3, B_2$
						925s	930	$\nu(O{=}U{=}O)$
						885s	885	$\nu(O-O)\ \nu_1$
						610m	600	$\nu(U-O_2)\ \nu_3$
						550s	540	$\nu(U-O_2)\ \nu_2$
$Na_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$	370(7)	23.2	16.7	20.65	3.85	1 580s	1 580	$\nu(C-O)\ \nu_1, A_1$
		(21.95)	(16.2)	(20.4)	(3.8)	1 340s		$\nu(C-O) + \delta(O-C-O)\ \nu_3, B_2$
						940s	940	$\nu(V{=}O)$
						865s	870	$\nu(O-O)\ \nu_1$
						620s	600	$\nu(V-O_2)\ \nu_3$
						525s	530	$\nu(V-O_2)\ \nu_2$
$K_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$	375(7)	32.6	14.55	18.2	3.35	1 585s	1 580	$\nu(C-O)\ \nu_1, A_1$
		(32.4)	(14.05)	(17.65)	(3.3)	1 335s		$\nu(C-O) + \delta(O-C-O)\ \nu_3, B_2$
						945s	940	$\nu(V{=}O)$
						865s	865	$\nu(O-O)\ \nu_1$
						625s	600	$\nu(V-O_2)\ \nu_3$
						520s	530	$\nu(V-O_2)\ \nu_2$

[a] Temperature (°C) in parentheses. [b] Calculated values are in parentheses. [c] Peroxo-oxygen.

Cs^+ could be obtained by the method analogous to that used for Na^+ and K^+. Strong desiccation of the compounds over concentrated H_2SO_4 did not remove the water of crystallisation. Pyrolysis of $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ at 100 °C expelled the water molecule without changing the composition of the complex ion, while at the same temperature the $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ started to decompose through the loss of both O_2^{2-} and H_2O.

The molar conductances of $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$, lying in the range 240—255 Ω^{-1} cm^2 mol^{-1} at room temperature, are as expected and attest to the stability of the complexes. The room-temperature molar conductances of $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ were higher than the expected values, indicating rapid decomposition. The values obtained at *ca.* 7 °C *ca.* 370 Ω^{-1} cm^2 mol^{-1} were, however, as expected, suggesting that the complex peroxovanadates are stable in solution only at low temperatures.

The complexes $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ and $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ tend to absorb moisture slowly. The compounds are diamagnetic, in conformity with the occurrence of U^{VI} and V^{V} respectively. The results of the peroxide estimations, by redox titrations[4,8,10] involving separate standard potassium permanganate and cerium(IV) solutions, suggest the presence of one peroxide per U^{VI} and two peroxides per V^{V} in the corresponding complexes.

The i.r. spectra of $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ shows bands at *ca.* 920s, *ca.* 890s, and *ca.* 610m and *ca.* 550s cm^{-1} due to $\nu(O{=}U{=}O$, *trans*),[8,11] $\nu(O-O)$, and $\nu(U-O_2)$ modes[8,10,12] respectively, at *ca.* 1 580s, *ca.* 1 330m, *ca.* 1 050s, *ca.* 750m, *ca.* 675m, and *ca.* 415 cm^{-1} due to $\nu(C-O)$, $\nu(C-O) + \delta(O-C-O)$, $\nu(C-O)$, ring deformation + $\nu(U-O)$, $\delta(O-C-O) + \nu(U-O)$, and $\nu(U-O)$ respectively originating from the co-ordinated bidentate carbonate,[13] and at *ca.* 3 455m, and *ca.* 1 630s cm^{-1} due to $\nu(O-H)$ and $\delta(H-O-H)$ modes of unco-ordinated water. The laser Raman spectra, recorded in the solid state because of low solubility, exhibited peaks at *ca.* 930 cm^{-1} assigned to $\nu(O{=}U{=}O)$,[8,11] at 880, *ca.* 600, and *ca.* 550 cm^{-1} due to $\nu(O-O, \nu_1)$, $\nu(U-O_2, \nu_3)$, and $\nu(U-O_2, \nu_2)$ respectively,[12] and at *ca.* 1 570 cm^{-1} due to $\nu(C-O)$ (ν_1, A_1) of co-ordinated CO_3^{2-}. The distinction between the ν_2 and ν_3 modes of $\nu(U-O_2)$ was made on the basis of the sharpness and intensity of the peaks, that at *ca.* 550 cm^{-1} being the sharpest and most intense. The i.r. spectra of $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ show $\nu(V{=}O$, terminal) at *ca.* 940s cm^{-1}, $\nu(O-O, \nu_1)$ at 865s cm^{-1}, and the two $\nu(V-O_2, \nu_2$, and $\nu_3)$ modes at *ca.* 525s and *ca.* 620s cm^{-1} due to co-ordinated O_2^{2-} groups. The bands at *ca.* 1 585s, *ca.* 1 340s, *ca.* 1 050s, *ca.* 740m, *ca.* 695w, and *ca.* 395m cm^{-1} have been attributed to $\nu(C-O)$, $\nu(C-O) + \delta(O-C-O)$, $\nu(C-O)$,ring deformation + $\nu(V-O)$, $\delta(O-C-O) + \nu(V-O)$, and $\nu(V-O)$ modes[13] respectively, while those at *ca.* 1 640s and *ca.* 3 450m cm^{-1} have been assigned to $\delta(H-O-H)$ and $\nu(O-H)$ modes of unco-ordinated water.[14] The laser Raman spectra of $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ exhibit a strong peak at 940 cm^{-1} assigned to $\nu(V{=}O)$, peaks at *ca.* 870, *ca.* 600, and *ca.* 530 cm^{-1} attributed to this $\nu(O-O, \nu_1)$, $\nu(V-O_2, \nu_3)$, and $\nu(V-O_2, \nu_2)$ modes[12] respectively of the co-ordinated O_2^{2-}, and a peak at *ca.* 1 580 cm^{-1} assigned to the $\nu(C-O, \nu_1, A_1)$ mode of co-ordinated CO_3^{2-}. The facile loss of water at 100 °C and the resemblance of the peak shapes and positions of $\delta(H-O-H)$ and $\nu(O-H)$ with those of unco-ordinated water[14,15] suggest that the water molecules are not co-ordinated. The typical pattern of absorptions due to the co-ordinated O_2^{2-},[4,8,12] and those due to co-ordinated CO_3^{2-},[13] especially the appreciable separation between $\nu_1(A_1)$ and $\nu_3(B_2)$ modes (Table 1) and also the appearance of a Raman peak at *ca.* 1 575 cm^{-1} due to $\nu(C-O, \nu_1, A_1)$, render it certain that both the peroxide (O_2^{2-}) as well as the carbonate (CO_3^{2-}) ligands are bonded to the metal centres in a bidentate chelated (C_{2v}) manner.

Acknowledgements

We thank the CSIR (New Delhi) for the award of senior research fellowships to (R. N. D. P. and Z. H.).

References

1 J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Chem. Radiochem.*, 1964, 6, 345.
2 S. Ahrland, K. W. Bagnall, D. Brown, R. M. Dell, S. H. Eberle, C. Keller, J. A. Lee, J. O. Liljenzin, P. G. Mardon, J. A. C. Marples, G. W. C. Milner, G. Philips, P. E. Potter, and J. Rydberg, 'The Chemistry of the Actinides,' Pergamon Texts in Inorganic Chemistry, vol. 10, Pergamon Press, Oxford, 1975, p. 249.
3 Ref. 1, p. 352.
4 M. K. Chaudhuri and S. K. Ghosh, *Inorg. Chem.*, 1984, 23, 534 and refs. therein.
5 N. J. Campbell, M. V. Capparelli, W. P. Griffith, and A. C. Skapski, *Inorg. Chim. Acta*, 1983, 77, L215.
6 N. Vuletić and C. Djordjević, *J. Chem. Soc., Dalton Trans.*, 1973, 1137.
7 M. K. Chaudhuri and N. S. Islam, *Transition Met. Chem.*, in the press.
8 M. N. Bhattacharjee, M. K. Chaudhuri, and R. N. Dutta Purkayastha, *J. Chem. Soc., Dalton Trans.*, 1985, 409.
9 Ref. 1, p. 292.
10 M. K. Chaudhuri and S. K. Ghosh, *Inorg. Chem.*, 1982, 21, 4020; *J. Chem. Soc., Dalton Trans.*, 1984, 507.
11 K. W. Bagnall, D. Brown, and J. F. Easey, *J. Chem. Soc. A*, 1968, 2223
12 W. P. Griffith, *J. Chem. Soc.*, 1963, 5345; 1964, 5248; W. P. Griffith and T. D. Wickins, *J. Chem. Soc. A*, 1968, 397.
13 K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' 2nd edn., Wiley-Interscience, London, 1970, pp. 169—172.
14 M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, and D. T. Khathing, *J. Chem. Soc., Dalton Trans.*, 1981, 2587.
15 N. F. Curtis, *J. Chem. Soc. A*, 1968, 1584.

Received 4th April 1985; *Paper* 5/576