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

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, $Ni(C_5H_7O_2)_2 \cdot 2H_2O$, 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, $A_3[V(O_2)_3CO_3].3H_2O$ (A = Na or K). The blue $A_3[V(O_2)_3CO_3].3H_2O$ 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 $A_3[V(O_2)_3CO_3].3H_2O$ 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, $Ni(C_5H_7O_2)_2.2H_2O$, 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 $Ni(C_5H_7O_2)_2.2H_2O$ using the literature reported method, two direct procedures have been developed for the synthesis of $Ni(C_5H_7O_2)_2.2H_2O$. 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 Chapter 7. The complexes $A_2[NiF_4]$ (A = K, Rb or NH_4) have been synthesised from the reaction of bis(acetylacetonato)nickel(II) dihydrate, $Ni(C_5H_7O_2)_2 \cdot 2H_2O$, 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.