SOME CONTRIBUTIONS
TO
THE CHEMISTRY OF OXOFLUORO AND HETEROLIGAND PEROXO COMPOUNDS OF VANADIUM (V) AND (IV)
AND
SYNTHESIS AND STRUCTURAL ASSESSMENT OF BIS (ACETYLACETONATO)-FLUOROVANADATE (III) AND A NOVEL SYNTHESIS OF TRIS (ACETYLACETONATO)-IRON (III)

Abstract

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I certify that the thesis entitled "Some contributions to the Chemistry of Oxofluoro and Heteroligand Peroxo Compounds of Vanadium(V) and (IV) and Synthesis and Structural Assessment of Bis(acetylacetonato)fluorovanadate(III) and a Novel Synthesis of Tris(acetylacetonato)iron(III)" submitted by Mr. Soumitra Kumar Ghosh 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 Ph.D. Degree. This work has not been submitted for any Degree of any other University.

Date. 18 Jan. 1984
Place: Shillong

Mihir Kanti Chaudhuri

Signature of the Supervisor

Abstract

Chapter 1 of the thesis describes the synthesis, characterization and structural assessment of alkali-metal and ammonium oxotetrafluorovanadates(V), A $[VOF_4]$ (A = K, Rb, Cs or NH_4). I.R. and ^{19}F N.m.r. spectroscopy, molar conductance, magnetic moments and chemical analyses show that A $[VOF_4]$ are the principal products of the reactions of V_2O_5 with 40% HF and alkali-metal and ammonium bifluorides AHF_2 in presence of a small amount of ethanol at steam-bath temperature. While the i.r. spectra suggest square pyramidal C_{4v} structures for the solid A $[VOF_4]$ compounds, the ^{19}F N.m.r. spectrum shows stereochemical non-rigidity owing to rapid fluorine rearrangement between C_{4v} and the trigonal bipyramidal C_{2v} stereochemistry of the $[VOF_4]^-$ ion in solution.

Synthesis and spectroscopic studies of a new oxofluorovanadate(IV) complex, $[VOF_3]$, constitute the subject matter of Chapter 2. Blue crystalline hydrazonium oxotrifluorovanadate(IV), N_2H_5 $[VOF_3]$, has been synthesised by the reaction of V_2O_5 with an excess of 99% hydrazine hydrate in the presence of 40% HF. The alkali-metal and ammonium salts, of the complex anion, A $[VOF_3]$ (A = Na, K or NH_4), have been prepared by metatheses between N_2H_5 $[VOF_3]$ and an excess of AF

in an aqueous medium. Characterization of the compounds was made from the results of chemical analyses, chemical determination of the oxidation state of vanadium, molar conductance and magnetic susceptibility measurements, infrared, electronic and esr spectroscopic studies. The molar conductance values of the hydrazonium, and alkali-metal and ammonium salts of $[VOF_3]^-$ ion suggest a 1:1 electrolytic nature of each of them, and their i.r. spectra show the multiple nature of the V-O bond and the absence of water. The magnetic moments of the compounds lie between 1.51 and 1.53 B.M. The solution electronic spectrum of $N_2H_5[VOF_3]$ shows absorptions at 11,950 and 16,000 cm^{-1}, without exhibiting any notable change with the addition of an excess of F^- ions, owing to the two d-d transitions characteristic of an oxovanadium(IV) species. The esr spectra of $N_2H_5[VOF_3]$ in an aqueous solution at 100K indicate that the complex species, $[VOF_3]^-$, has a distorted octahedral structure in solutions, through the coordination of two H_2O molecules to the oxovanadium(IV) centre in addition to the three coordinated fluoride ions. In the solid state, the complex ion, $[VOF_3]^-$ may have a polymeric structure through weak V-O...V and V-F...V interactions.

Chapter 3 describes the results of studies on alkali-metal and ammonium oxodiperoxofluorovanadates(V), $A_2[VO(O_2)_2F]$ (A = Na, K, Rb, Cs or NH_4). It has been shown that the reaction of vanadium pentoxide, V_2O_5, with hydrogen peroxide in an alkaline medium in the presence of alkali-metal and ammonium fluorides, AF (A = Na, K, Rb, Cs or NH_4) gives alkali-metal and ammonium oxoperoxofluoro-vanadates(V), $A_2[VO(O_2)_2F]$, in very high yields. Characterization of the compounds was made from the results of chemical analyses, magnetic susceptibility measurements and infrared spectroscopic studies. IR spectrometry showed the peroxo ligands to be bonded to the vanadium(V) centre in a triangular bidentate(C_{2v}) manner. The complex species $[VO(O_2)_2F]^-$ may be a hexacoordinated monomer, or it may have a polymeric structure through a weak V-O...V or a weak V-F...V bridging.

The studies involving alkali-metal and ammonium triperoxofluorovanadates(V), $A_2[V(O_2)_3F]$ (A = Na, K or NH_4), form the subject matter of Chapter 4. Blue alkali-metal and ammonium triperoxofluorovanadates(V), $A_2[V(O_2)_3F]$ (A = Na, K or NH_4) have been synthesised by reacting V_2O_5 with fluoride AF and hydrogen peroxide in a highly alkaline medium (much higher than that used for the synthesis of $[VO(O_2)_2F]^{2-}$ complex). The compounds have

been characterised by elemental analyses, magnetic susceptibility measurements, and IR spectroscopic studies. The compounds do not permit molar conductance measurements. The IR spectra of the compounds suggest the presence of triangularly bonded chelated peroxo ligands. The complex species $[V(O_2)_3F]^{2-}$ may be a seven-coordinated monomer, or it may have a polymeric structure through a weak V-F...V bridging. The basicity of peroxo ligands increases with the increase in the number of peroxo groups coordinated to the vanadium(V) centre.

Synthesis, and assessment of structures of the first chloroperoxovanadate(V) compounds, and evidence for diperoxovanadate(V) —— triperoxovanadate(V) interconversion constitute the basis of Chapter 5. Alkali-metal and ammonium salts of yellow oxodiperoxochlorovanadates(V), $A_2[VO(O_2)_2Cl]$, and blue triperoxochlorovanadates(V), $A_2[V(O_2)_3Cl]$ (A = Na, K or NH_4), have been synthesised, for the first time, by reacting V_2O_5 with alkali chloride, ACl, and hydrogen peroxide in varying concentrations of alkaline media. The three salts of the anion $[VO(O_2)_2Cl]^{2-}$ are comparatively more stable than those of the complex anion $[V(O_2)_3Cl]^{2-}$. Characterization of the compounds have been made from the results of elemental analyses,

magnetic susceptibility measurements and infrared spectroscopic studies. The IR spectra suggest that the peroxo groups are bonded to vanadium(V) in a triangular bidentate manner, and that the O-O bond order of peroxo ligands decreases with the increase in the number of peroxo groups coordinated to the metal centre. The conversion of $[VO(O_2)_2Cl]^{2-}$ to $[V(O_2)_3Cl]^{2-}$, and the reverse provide good evidence for the facile diperoxovanadate(V) ——— triperoxovanadate (V) interconversion. The complex species $[VO(O_2)_2Cl]^{2-}$ may be a hexacoordinated monomer or it may as well be a polymer through a weak V-O-V or a weak V-Cl-V bridging. Similarly the complex species $[V(O_2)_3Cl]^{2-}$ may be a heptacoordinated monomer or it may have a polymeric structure through a weak V-Cl-V interaction.

Chapter 6 of the thesis reports the synthesis, characterization and structural assessment of alkali-metal and ammonium diaquofluoro-oxoperoxovanadate(IV) complexes, $A[VO(O_2)F(H_2O)_2]$ (A = K, Rb, Cs or NH_4). These compounds are the first peroxovanadate(IV) compounds to be obtained in the solid state. Orange-red alkali-metal and ammonium diaquofluorooxoperoxovanadates(IV), $A[VO(O_2)F(H_2O)_2]$, have been synthesised by the reaction of alkali-metal and ammonium tetrafluorooxovanadate(V), $A[VOF_4]$

($A = K, Rb, Cs$ or NH_4) with H_2O_2 in the molar ratio 1:12 followed by precipitation with ethanol. Characterization of the compounds was made from the results of chemical analyses, chemical determination of oxidation state of vanadium, i.r. and electronic spectroscopic studies and magnetic susceptibility measurements. I.r. spectra suggest that the peroxo-ligand is bonded to the V^{4+} centre in a triangular bidentate fashion. The complex species $[VO(O_2)F(H_2O)_2]^-$ may have a polymeric structure through V-F-V bridging; however, the possibility of a weak V-O-V interaction can not be ruled out completely.

Chapter 7 describes the synthesis and assessment of structure of bis(acetylacetonato) fluorovanadate(III), $VF(acac)_2$, a novel neutral compound of vanadium(III). It has been shown that vanadium pentoxide, V_2O_5, undergoes a ready reaction with an excess of hydrazine hydrate in the presence of 40% HF to give $N_2H_5[VOF_3]$, which on being treated with acetylacetone affords blue-green crystalline bis(acetylacetonato) fluorovanadate(III), $VF(C_5H_7O_2)_2$, in a very high yield. The compound $VF(C_5H_7O_2)_2$ has been characterized on the basis of the results of chemical analyses, chemical determination of oxidation state of vanadium, magnetic susceptibility measurement, infrared

and mass spectrometric studies. EI induced mass spectrometry showed the compound to be monomeric in the vapour state; however, the compound may have a hexacoordinated polymeric structure, through a weak V-F...V interaction, in the solid state.

A novel synthesis of tris(acetylacetonato) iron(III), $Fe(acac)_3$, and its mass spectrometric studies constitute the subject matter of Chapter 8. The reaction of iron(III) hydroxide with acetylacetone, in the absence of any buffer, readily gives highly crystalline tris(acetylacetonato) iron(III), $Fe(acac)_3$, in a very high yield. The pH of the solution recorded immediately after the formation of the compound was found to be ca. 5. Its mass spectrum provides evidence for rearrangement to give $Fe-CH_3$ species.

The work described in Chapters 1, 3, 4 and 8 have been published, while those of Chapters 5, 6 and 7 are in press.

Chapter 1

Synth. React. Inorg. Met.-Org. Chem., 63, 12, 1982.

Chapter 3

Polyhedron, 553, 1, 1982.

Chapter 4

Inorg. Chem., 4020, 21, 1982.

Chapter 5

Inorg. Chem., in press.

Chapter 6

J. Chem. Soc. Dalton Trans., in press.

Chapter 7

Inorg. Chem., in press.

Chapter 8

J. Chem. Soc. Dalton Trans., 1983, 839.

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