STUDIES ON
PEROXO AND HETERO-LIGAND-PEROXO COMPLEXES OF VANADIUM(V)
AND
FLUORO AND MIXED-LIGAND-FLUORO COMPLEXES OF IRON(III)

ABSTRACT

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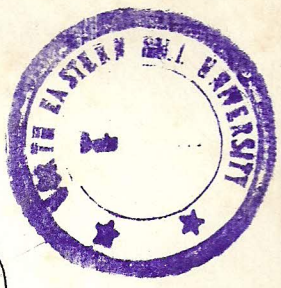

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ABSTRACT

The present thesis deals with the results of studies involving syntheses, assessment of structure, and reactivity of some peroxo and heteroligand-peroxo complexes of vanadium(V), as well as synthesis and physico-chemical studies of fluoro and mixed-ligand-fluoro complexes of iron(III). Further, the optimum conditions for oxidation of SCN^- to SO_4^{2-} by hydrogen peroxide are also described in the thesis, as these became necessary in the context of some other work related to the present research. The contents of the thesis has been distributed over six chapters,

Chapter 1 presents a brief introduction pertaining to the work embodied in the thesis. The importance of and the interest in peroxo-metal chemistry in general, and peroxo and hetero-ligand peroxovanadium(V) compounds in particular are highlighted. Also emphasised in this chapter are the lack of information concerning the reactions of highly peroxygenated-metal species with inorganic substrates and the relevance of such studies in the context of contemporary interest involving metal-dioxygen chemistry.

Apart from the importance of studies on peroxovanadium chemistry, attention has also been drawn to the current interest on the study of fluoro-metal compounds together with the difficulties in getting an access to them. As a case in point the problems encountered in the reported synthesis of hexafluoroferrates(III) and also the absence of any reported existance of mixed-ligand-fluoroferrates(III) are stressed herein. Further, the synthetic utility of the reaction of SCN^- oxidation to SO_4^{2-} by hydrogen peroxide is mentioned in Chapter 1. This Chapter also projects the scope of work on the chosen aspects of vanadium and iron chemistry.

Chapter 2 describes the details of the methods of elemental analyses, and instruments/equipment used for characterisation and structural assessment of the newly synthesised compounds.

Chapter 3 of the thesis presents the details of first isolation in the solid state, characterisation, and structural assessment of alkali oxodiperoxovanadate(V) complexes, $A[VO(O_2)_2]$ (A = NH_4, Na or K). This Chapter also provides an account of the results of reactions of vanadium(V) with alkali sulphate or thiocyanate and hydrogen peroxide.

Alkali oxodiperoxovanadates(V), $A[VO(O_2)_2]$ (A = NH_4, Na or K), have been synthesised from the reaction of V_2O_5 with 30% hydrogen peroxide at pH 7-8 maintained by the addition of corresponding alkali hydroxide, AOH, or aqueous ammonia, in the concentration ratio V_2O_5:H_2O_2:AOH as 1:41.8:5.3-6.6.

Compounds were precipitated with ethanol. $A[VO(O_2)_2]$ compounds were diamagnetic, and their molar conductances in water recorded at ambient temperatures, were found to lie between 130 and 140 $\Omega^{-1}cm^2mol^{-1}$. The results of infrared and laser Raman spectroscopic studies suggest that the complex, $[VO(O_2)_2]^-$ species, contains a terminally bonded V=O group, and that the peroxide (O_2^{2-}) ligands are bonded to the vanadium(V) centre in a triangular bidentate (C_{2v}) manner. The complex ion, $[VO(O_2)_2]^-$, may be a pentaco-ordinated monomer, however, a hexaco-ordinated structure through a weak -V=O....V=O....V=O.... interaction cannot be discounted. As an example of its reactivity, the potassium salt of the complex ion $K[VO(O_2)_2]$, has been shown to undergo facile reaction with KF, and 2,2-bipyridine(bipy) to produce $K_2[VO(O_2)_2F]$, and $K[VO(O_2)_2bipy]$, respectively.

In order to explore the reactions of vanadium(V) with alkali sulphate or thiocyanate in the presence of hydrogen peroxide, V_2O_5 was allowed to react with alkali sulphate or alkali thiocyanate in the molar ratio of $V_2O_5:A_2SO_4$ or ASCN as 1:2 and an excess of hydrogen peroxide ($V_2O_5:H_2O_2$::1:32) at pH 7-8, maintained by the addition of corresponding alkali hydroxide or aqueous ammonia. From the resulting yellow solution, yellow oxodiperoxovanadate(V) complexes containing sulphate were precipitated out by the addition of ethanol. The compounds were characterised by elemental analyses, molar conductance measurements, and IR and laser Ramanspectroscopic studies. These results showed that the compounds synthesised

were oxodiperoxovanadate(V) complexes containing ionic sulphate (T_d) and could be best formulated as $A[VO(O_2)_2].A_2SO_4$ (A = NH_4, Na or K). The peroxide has been shown to be bonded to the metal centre in a chelated fashion.

Chapter 4 of the thesis describes the first synthesis and structural assessment of hitherto unreported peroxovanadate(V) compounds containing an amino acid, namely glycine(GlyH), as the heteroligand.

The synthesis of alkaliglycineoxodiperoxovanadate(V)-monohydrates, $A[VO(O_2)_2GlyH].H_2O$ (A = NH_4 or K), has been achieved by reacting vanadium pentoxide, V_2O_5, with a hydrogen peroxide solution of glycine at pH 3-4 maintained by the addition of aqueous ammonia or KOH. The molar ratio of V_2O_5:GlyH:H_2O_2 was maintained as 1:2:32. The reaction was carried out an an ice-bath temperature and the precipitation of the compounds were brought about by the addition of ethanol. The yellow glycine-oxodiperoxovanadate(V)monohydrate, $A[VO(O_2)_2GlyH].H_2O$, complexes are hygroscopic in nature. The IR spectra of the compounds exhibit bands characteristic of ν (V=O), ν (O-O), and ν (V-O_2) in addition to the absorptions originating from the presence of co-ordinated glycine(GlyH). The amino acid (GlyH) occurs in the compounds in its zwitterionic form and co-ordinates with the metal centre through its carboxylic oxygen atom. The spectra also provide strong evidence for the presence of a triangularly bonded (C_{2v}) peroxide (O_2^{2-}) in each of the complexes. The compounds are diamagnetic in nature in conformity with the presence of vanadium(V)

Reported in Chapter 5 are the first synthesis, isolation in the solid state, and structural assessment of blue alkali-metal triperoxovanadates(V), $A[V(O_2)_3]$ (A = Na or K). Also reported in this Chapter are the results of studies of reactivity of $A[V(O_2)_3].3H_2O$ with $SO_2(g)$.

Blue alkali-metal triperoxovanadate(V) complexes, $A[V(O_2)_3]$ (A = Na or K), have been synthesised from the reactions of vanadium pentoxide with hydrogen peroxide in the presence of concentrated alkaline media, with the molar ratio of V_2O_5:H_2O_2:AOH being maintained as 1:42.5:10-12, followed by precipitation with ethanol. The $A[V(O_2)_3]$ compounds are relatively more stable than the corresponding heteroligand triperoxovanadates(V), and permit molar conductance measurements. The compounds are diamagnetic. The IR and laser Raman spectra suggest that the peroxo ligands are bonded to the vanadium(V) centre in a triangular bidentate (C_{2v}) manner with the structure of the complex, $[V(O_2)_3]^-$ ion, being similar in the solid state as well as in a solution. The electronic spectra of $A[V(O_2)_3]$ exhibit absorptions at 560 and 192 nm. The compounds are obtained as $A[V(O_2)_3]$ if the final products are dried over P_4O_{10} for a prolonged period, however, they are otherwise obtained as trihydrates, $A[V(O_2)_3].3H_2O$ when they are dried over conc. H_2SO_4.

The reactions of $A[V(O_2)_3].3H_2O$ (A = Na or K) with $SO_2(g)$ were carried out in an aqueous medium. The deep blue $A[V(O_2)_3].3H_2O$ compounds were dissolved in a minimum volume of water and $SO_2(g)$ was bubbled through it. The $A[V(O_2)_3].3H_2O$ reacts readily with

$SO_2(g)$ and first generates a yellow colour which ultimately turns into a permanent green-blue solution. Our endeavour to isolate products at each stage of colour change was successful.

The yellow microcrystalline product, potassium aquooxo-diperoxovanadate(V), $K[VO(O_2)_2(H_2O)]$, was thwarted out from the yellow solution, pH of which was ca 6, when $K[V(O_2)_3].3H_2O$ reacted with $SO_2(g)$. The product was characterised by elemental analyses, conductivity measurements, and ESR, IR, and LR spectroscopic studies. The compound was ESR silent suggesting that the metal centre did not undergo any reduction. The molar conductance recorded at ambient temperatures were found to be 130 $\Omega^{-1}cm^2mol^{-1}$. The significant features of IR spectrum of the yellow $K[VO(O_2)_2H_2O]$ compound involve the bands due to co-ordinated peroxide bonded to the vanadium(V) centre in a triangular bidentate fashion, terminally bonded V=O, and co-ordinated water. The results were further augmented by LR spectroscopic studies. Attempts to isolate the sodium salt of yellow $[VO(O_2)_2(H_2O)]^-$ species, from the reaction of corresponding $Na[V(O_2)_3].3H_2O$ with $SO_2(g)$, were futile.

The deep blue $A[V(O_2)_3].3H_2O$ (A = Na or K) reacts with $SO_2(g)$ to generate ultimately a permanent green-blue solution (pH ca 2) from which a blue complex was obtained. The compounds were characterised as salts of triaquobis(sulphato)oxovanadate(IV) complex, $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ (A = Na or K). The molar conductances of the complexes at ambient temperatures were found to lie between 235 and 262 $\Omega^{-1}cm^2mol^{-1}$. The room temperature magnetic moment of the compounds were found to be 1.51 - 1.53 μ_B. The ESR

spectra of the compounds in aqueous solution recorded at room temperature and also at 77°K showed signals characteristic of oxovanadium(IV) species. The IR and LR spectra exhibited the characteristic absorptions of co-ordinated SO_4^{2-} ligand, co-ordinated and lattice water, and the V=O stretching. The IR and LR spectral studies further showed the occurrence of SO_4^{2-} ligand bonded to the metal centre in a unidentate (C_{3v}) manner. It is evident from the compounds isolated from the reactions of $A[V(O_2)_3].3H_2O$ with $SO_2(g)$, that it is one of the co-ordinated peroxide groups which participates in an electron transfer reaction preferentially over vanadium(V), which is also otherwise known to undergo ready electron-transfer reaction.

Newer information concerning the reactivity of co-ordinated dioxygen may be anticipated from further studies on similar highly peroxygenated metal systems.

The reactions of $A[V(O_2)_3].3H_2O$ with $SO_2(g)$ conducted in the presence of alkali fluoride, AF, taken in a molar ratio between V:F as 1:2 afforded a novel blue coloured ternary complex vanadate(IV), $A_4[VO(SO_4)_2F_2(H_2O)].2H_2O$ (A = Na or K). The compounds are hygroscopic in nature and soluble in water. The molar conductances of the complexes were recorded to be 510-522 $\Omega^{-1}cm^2mol^{-1}$. The ESR spectra in aqueous solution at room temperature as well as at 77°K exhibit signals characteristic of oxovanadium(IV) species with g_{av} = 1.996. The IR and LR spectra of the compounds, $A_4[VO(SO_4)_2F_2(H_2O)].2H_2O$, resemble those of $A_2[VO(SO_4)_2(H_2O)_3].H_2O$ closely and show absorptions of co-ordinated SO_4^{2-}, co-ordinated

H_2O, and V=O stretching. In addition, the absorption at ca 520 cm^{-1} has been attributed to ν_{M-F} of co-ordinated F^- ligands. The SO_4^{2-} ligands are co-ordinated to the vanadium(IV) centre in a unidentate (C_{3v}) manner. This reaction serves as a paradigm for the synthesis of ternary complexes of vanadyl, VO^{2+}, and may provide an easy access to such compound for further studies.

The direct synthesis of alkali-metal and ammonium hexafluoroferrates(III), A_3FeF_6 (A = NH_4, Na or K), the results of studies concerning optimum conditions for quantitative conversion of SCN^- to SO_4^{2-} through electron-transfer reaction between H_2O_2 and SCN^- along with the scope of this reaction, and a detailed account of the first reported synthesis of fluoro(sulphato)ferrate(III) complexes, $(NH_4)_2[Fe(SO_4)F_3]$ and $K_3[Fe(SO_4)F_4]$, as well as their characterisation and structural assessment form the subject matter of Chapter 6 which is indeed the concluding Chapter of the thesis.

The reaction of iron(III) hydroxide with alkali metal or ammonium fluoride and 48% hydrofluoric acid in the presence of hydrogen peroxide, followed by the addition of ethanol, directly gives alkali metal or ammonium hexafluoroferrates(III), A_3FeF_6 (A = Na, K or NH_4), in very high yields. The compounds were characterised and their identity established from the results of chemical analyses, magnetic susceptibility measurements, and IR and LR spectroscopy.

The optimum conditions for oxidations of SCN^- to SO_4^{2-} by the reaction between SCN^- and H_2O_2 have been determined. Ammonium or potassium thiocyanate and 30% H_2O_2, in the molar ratio of SCN^- to H_2O_2 at 1:8-10 was allowed to react at pH 7-8 to yield quantitatively the corresponding sulphate. While the pH > 8 reduced the yield of A_2SO_4 (A = NH_4 or K), the pH < 6 has not been found conducive to the quantitative conversion of SCN^- to SO_4^{2-}. Likewise, the SCN^-:H_2O_2 molar ratio 1:6, at a pH 7-8, did not produce SO_4^{2-} in more than 90% yield, and an excess of H_2O_2 (SCN^-:H_2O_2 as 1: > 10) was found to be redundent. The knowledge obtained from the study of this reaction has been of some practical utility in the context of the synthesis of fluoro(sulphato)ferrates(III) complexes.

An investigation of the reaction of ammonium or potassium thiocyanate and 48% HF with iron(III) hydroxide in the presence of hydrogen peroxide has been carried out. Sulphate has been obtained as the oxidation product of SCN^-, without involving reduction of iron(III), and providing an access to fluoro(sulphato)-ferrates(III) of the types $(NH_4)_2[Fe(SO_4)F_3]$ and $K_3[Fe(SO_4)F_4]$. Similar reactions with sulphates in lieu of thiocyanates, either in the presence or in the absence of H_2O_2, do not afford fluoro(sulphato)ferrates(III), however. IR and Laser Raman spectroscopy provide evidence for a chelated sulphate in each of the fluoro(sulphato)ferrates(III). The magnetic moment of the compounds were found to be ca 5.7 μ_B.

The results of studies described in Chapters 3 and 6, and a part of the results described in Chapter 5 have been published, while rest of the results incorporated in Chapter 5 and those included in Chapter 4 are now under communication.

Chapter 3

Transition Met. Chem., 1985, 10, 333;

J. Ind. Chem. Soc., 1985, 62, 815.

Chapter 5

Inorg. Chem., 1985, 24, 2706.

Chapter 6

Inorg. Chem., 1986, 25, 3749; Ind. J. Chem., 1985, 24A, 447.