SYNTHESIS, STRUCTURAL ASSESSMENT AND SOME REACTION PROFILES OF PEROXO COMPLEXES OF V, Mo AND UO_2^{2+}, A FLUORO COMPOUND OF Cr,

AND

MIXED-LIGAND MOLECULAR COMPLEXES OF THE TYPE M $(acac)_2(dmpz)_n$ [dmpz = 3, 5-dimethylpyrazole, M=Mn, Co, Ni; n=2, M=VO^{2+}; n=1, AND M=UO_2^{2+}; n=4]

ABSTRACT

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ABSTRACT

The thesis, consisting of six chapters, deals with the results of investigation on some chosen aspects of the chemistry of peroxo and heteroligand peroxo complexes of vanadium, molybdenum and uranium including peroxo-metal mediated oxidation of Br^- to Br_3^- leading to the synthesis of organic ammonium tribromide, and the synthesis and structural assessment of some mixed-ligand metal acetylacetonate complexes of manganese, nickel, cobalt, uranium and vanadium along with an easy synthesis of pyridinium fluorochromate, $C_5H_5NH[CrO_3F]$ (PFC).

Chapter I provides a brief background of the types of problems selected for the present Ph.D. research. The importance of and the interest in the chemistry of dioxygen, in general, and peroxo and heteroligand peroxo compounds of vanadium, molybdenum and uranium in particular are highlighted. Apart from the importance of studies of peroxo-chemistry, attention has been drawn to the study of mixed-ligand metal acetylacetonato complexes. Also emphasised in this chapter is the importance of chromium(VI) reagents as useful oxidants for organic substrates and some need for further studies. Scope of work in the chosen topics has been highlighted.

Chapter II presents details of the methods adopted for the preparation of starting materials, elemental analyses, and instruments/equipment used for characterisation and structural assessment of the newly synthesised compounds.

Synthesis, characterisation and structural assessment, and reactivity of heteroligand peroxovanadate and heteroligand peroxomolybdate constitute the basis of chapter III. Heretofore unreported dioxo diperoxo-μ-peroxotetrakis(3,5dimethylpyrazole)divanadium(V), $[V_2O_2(O_2)_3(dmpz)_4]$,and oxodiperoxo-bis(3,5-dimethylpyrazole)molybdenum(VI), $[MoO(O_2)_2(dmpz)_2]$, have been synthesised from the reaction of V_2O_5 with 30% H_2O_2 at pH 2 followed by addition of 3,5-dimethylpyrazole, and the reaction of $(NH_4)_6Mo_7O_{24}.4H_2O$ with 30% H_2O_2 at pH 5 followed by the addition of powdered 3,5-dimethylpyrazole, respectively. The compounds have been characterised from the results of elemental analyses, determination of molar conductance in water and methanol in case of $[V_2O_2(O_2)_3(dmpz)_4]$ and in water for $[MoO(O_2)_2(dmpz)_2]$, IR, Laser Raman and UV-Vis spectroscopies, TG and DSC experiments. In both the cases peroxide (O_2^{2-}) is bonded in a side-on (C_{2v}) fashion. Vibrational spectra of the compounds also show the co-ordination of 3,5-dimethylpyrazole through tertiary nitrogen atom, i.e. the pyridine nitrogen of the pyrazole nucleus. Two well resolved LMCT (O_2^{2-}—M) bands due to $\pi_h^* \rightarrow d_\sigma^*$ at *ca.*214nm and due to $\pi_v^* \rightarrow d_\sigma^*$ at *ca.*326nm have been observed in the electronic spectra of the compounds.

Oxidation of some organic substrates have been carried out separately with both the reagents to ascertain their efficacy as oxidising agents. The reagents are expected to be environmentally favorable owing to the presence of non toxic metals and peroxide.

Chapter IV describes an improved synthesis of $(NH_4)_2[UO_2(O_2)F_2].H_2O$, and $K_2[UO_2(O_2)F_2(H_2O)]$ along with the synthesis of new μ-peroxo-dimeric compounds of uranium, $A_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ ($A=NH_4^+$, K^+ or Na^+). $(NH_4)_2[UO_2(O_2)F_2].H_2O$, and $K_2[UO_2(O_2)F_2(H_2O)]$ have been synthesised by the reaction of $UO_3.4H_2O$ with 30% H_2O_2 in the presence of the corresponding bifluoride, AHF_2. Whereas the general synthesis of $A_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ has been based on the reaction of $UO_2(NO_3)_2.6H_2O$ with 30% H_2O_2 at pH 10 maintained by addition of the corresponding hydroxide. One of the significant features of the new syntheses of the fluoro-peroxo uranium compounds is the redundancy of the use of hydrofluoric acid. All the compounds were characterised by elemental analyses, IR spectroscopy and TG, DSC studies.

Chapter V provides evidences for the peroxo-vanadium mediated generation of Br_3^-. This is believed to be important in understanding the nature of the intermediate involved in the reactions catalysed by vanadium bromoperoxidase (V-BrPO). Tribromide thus generated *in situ* from bromide oxidation by vanadium-peroxo complexes was trapped in aqueous solution by a heavy cation, *viz.,* tetrabutylammonium ion. The tribromide has been characterised by elemental analyses, IR, UV-Vis spectroscopies and solution electrical conductance measurements. The major concern in the present context was to investigate its efficacy as an environmentally friendly brominating agent. Bromination of some selected organic substrates has thus been carried out to ascertain its efficacy. The major advantage of the new protocol lie in the ease of synthesis of the reagent and redundancy of the hazardous chemicals like Br_2 and HBr, and the ease in maintaining stoichiometry of the reagent.

Chapter VI, indeed the concluding chapter of the thesis provides information regarding the synthesis of mixed-ligand metal acetlyacetonato complexes starting from the corresponding metal-acetlyacetonato dihydrate as the precursors. The synthesis has been based on the reaction of $M(acac)_2.2H_2O$ (M=Mn, Ni, Co or UO_2^{2+}) with 3,5-dimethylpyrazole resulting to the formation of $M(acac)_2(dmpz)_2$ (M= Mn, Ni or Co) $UO_2(acac)_2(dmpz)_4$. The vanadium analog $VO(acac)_2(dmpz)$ was obtained by the reaction of $VOSO_4.H_2O$ with acetylacetone and 3,5-dimethylpyrazole in ethanol. The compounds were isolated in good yields, and were characterised by elemental analyses, IR, UV-Vis and ESR spectroscopies, TG and DSC studies. Apart from the mixed ligand metal acetylacetonate complexes, an easy synthesis of pyridinium fluorochromate (PFC), achieved by the reaction of CrO_3 with NH_4HF_2 and pyridine, has been reported.

The results of studies described in chapter V and chapter VI in part have been published, the work described in chapter IV is under revision, while the manuscripts based on the contents of chapter III and chapter VI in part are now being prepared.

Chapter IV

Inorg.Synth.(under revision)

Chapter V

Tetrahedron Letter, 1998, **39,** 8163.

Chapter VI

J Fluorine Chemistry, 1997, **81**, 211.