SOME ASPECTS OF MIXED-LIGAND COMPLEXES OF MANGANESE, PEROXO COMPOUNDS OF MOLYBDENUM AND BIOMIMETIC CHEMISTRY OF VANADIUM BROMOPEROXIDASE

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

To

THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG
INDIA
APRIL 1996

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ACKNOWLEDGEMENTS

It is with the feelings of pleasure that I would like to place the acknowledgements. My heartfelt thanks are due to Prof. Mihir K. Chaudhuri for his guidance, constant encouragement and affection throughout my Ph.D. research.

I feel very happy to acknowledge the help, inspiration and good wishes of all those who bestowed on me during the period of my Ph.D. work. However, it is a formidable task to name them all. I should like to thank all my laboratory colleagues, friends, seniors as well as the Faculty Members of the Department of Chemistry, NEHU.

I am grateful to Dr. Manish Bhattacharjee for magnetic measurements, Prof. K. Wieghardt, Dr. Weyhermüller, Prof. A. Chakravorty, Dr. S. Chattopadhyay and Prof. P. K. Bharadwaj for X-ray structure determination of our compounds.

Thanks are due to the Dean, School of Physical Sciences, NEHU, Head, RSIC, NEHU, and the University authorities in general for permitting me to use all the research facilities. I also wish to thank all the non-teaching staff members of the Department of Chemistry as well as the technical staff of RSIC, NEHU, for their help. Research Fellowships(NET) received from the University Grants Commission, New Delhi, is gratefully acknowledged.

It will remain incomplete if I do not place on record the gratitude to my beloved parents for their blessings, encouragement and support. My profound thanks are also due to all other members of our family which they rightly deserve.

G. C. Mandal

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Date: 8.4.96

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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 manganese, peroxo and heteroligand peroxo complexes of molybdenum, and the oxidation of bromide to tribromide by titanium, vanadium, molybdenum, and uranium peroxo intermediates. The relevance of oxidation of bromide by transition-metal peroxides to the vanadium bromoperoxidase activity has been highlighted.

Chapter I gives a brief background information related to the types of problems selected for the present Ph.D. research. The importance of and interest in the coordination chemistry of manganese, peroxo complexes of molybdenum and the chemistry related to the vanadium bromoperoxidase activity has been underscored in this chapter.

Chapter II presents details of the methods adopted for the preparation of some starting materials, sources of ready-made reagents and elemental analyzes as well as the particulars of instruments/equipment used for the characterization and structural assessment of the compounds.

Chapter III provides an improved methodology for $K_2[MnF_3(SO_4)]$ based on redox reaction between $KMnO_4$ and $SO_2(g)$ in the presence of KHF_2. The compound bears an acknowledged importance because of its unusual structural and magnetic properties.

Also incorporated in this chapter is the study of some newer reactions of $Mn(acac)_3$ by the way of product isolation. Reactions of $Mn(acac)_3$ with H_2O_2 in the presence of 2,2'-bipyridine(bpy) or 1,10-phenanthroline(phen) have been performed. This has led to the generation of $[Mn(acac)_2(bpy)]$ 1 or $[Mn(acac)_2(phen)]$ 2, respectively. The reaction provides a rarely encountered example of the reduction of Mn(III) by H_2O_2. Further the treatment of $Mn(acac)_3$ with H_2O_2 in the presence of bpy or phen followed by the interaction of $Cl_2(g)$ has led to the oxidation of Mn(II) compounds formed *in situ* to $[MnCl_3(bpy)]$ 3 and $[MnCl_3(phen)]$ 4, respectively. Similar reaction sequence has been observed by using $KF.H_2O_2$ in place of H_2O_2. In separate reaction runs the interaction of $Cl_2(g)$ with 1 and 2 has brought about their oxidation respectively to 3 and 4. The compounds produced in the reactions have been isolated in good yields and characterized by analysis, IR, UV-Vis and EPR spectroscopies, magnetic susceptibility measurements, TG, DSC and cyclic voltammetry. The single crystal X-ray structure of [Mn(acac)$_2$(phen)] 2 has been determined. The compound has a distorted octahedral geometry and crystallizes in orthorhombic space group Pbcn.

Chapter IV is devoted to the stabilization of a combination of Mn(III) and chloride, bromide or iodide with salicylic acid, a biologically relevant coligand. Described in this chapter is the synthesis of $A_2[Mn_2X_2(salH)_4(sal)].nH_2O$ (A = NH_4, Na or K; X = Cl, n = 4; X = Br, n = 6) and $K[Mn_2I(sal)_3(H_2O)_4].2H_2O$. The syntheses have been achieved from the reaction of manganese oxide hydroxide, MnO(OH), with salicylic acid in the presence of corresponding halide salts at the molar ratio 1:1.25:14.1. Characterization of the compounds has been made by analysis, IR, laser Raman, UV-Vis spectroscopies, magnetic measurements, TG, DSC experiments, and cyclic voltammetry.

Chapter V reports the effect of fluoride on dimeric peroxomolybdates as well as the synthesis of newer heteroligand peroxomolybdenum compounds. The dimeric peroxomolybdates, $A(NH_4)[MoO_2O_3(O_2)_4(H_2O)_2].2H_2O$ (A = Na(1) or K(2)), have been synthesized by reacting $(NH_4)_2[MoO_4]$ with H_2O_2 at pH 6. The action of fluoride on the dimeric complexes has been investigated by product isolation. Similar reaction on being conducted in the presence of fluoride afforded monomeric fluoroperoxomolybdates, $A(NH_4)[MoO(O_2)_2F_2].3H_2O$ 4 and $K(NH_4)[MoO(O_2)_2F_2].H_2O$ 5. The reaction of NH_4HF_2 with 1 and 2 produced in each case

$(NH_4)_2[MoO(O_2)_2F_2].H_2O$ 3. New quaternary fluoroperoxomolybdenum complexes of the type $(NH_4)[MoO(O_2)_2F(L)]$ where L = glycine (6), alanine (7), valine (8) and leucine (9) have been synthesized from the reaction of $H_2MoO_4.H_2O$ with H_2O_2, aqueous HF and the corresponding organic heteroligands at pH 6. The corresponding reaction with L being oxinate, however, afforded $(NH_4)[MoO(O_2)_2(oxinate)]$ 10. Compounds are all diamagnetic and have been characterized by analysis, IR, laser Raman and electronic spectroscopies. In all cases peroxide is bonded in a side-on(C_{2v}) fashion. Vibrational spectra of compounds 6-9 showed the presence of amino acids in zwitterionic form and their coordination through carboxylate oxygen to the metal centre. In 10 oxine is ligated in a bidentate manner, through its -O and -N atoms to molybdenum. Two well resolved LMCT (O_2^{2-} ----> Mo) bands in the electronic spectra of these compounds have been observed. Transformation of a few chosen substrates involving some of these peroxo complexes have been accomplished.

Chapter VI, indeed the concluding chapter of the thesis, evidences the peroxo-metal mediated generation and trapping of tribromide, Br_3^-. This is important in understanding the nature of intermediate in the reactions catalyzed by vanadium bromoperoxidase (V-BrPO). Bromide has been oxidized by Ti-, V-, Mo- and U- peroxo complexes generated *in situ*. To trap the oxidized bromine species in aqueous solution NBu_4^+ was used as a heavy organic cation. That bromide is oxidized also by the other transition-metal intermediates, than that of vanadium alone, indicates that the V-BrPO activity may not be restricted to only vanadium, rather it is specific to such metals that are capable of forming peroxo compounds. Trapping of the tribromide has also been accomplished by precipitating with NEt_4^+ or $NCetMe_3^+$ (Cet = Cetyl group, $CH_3(CH_2)_{15}-$) from the titanium peroxomediated oxidation of bromide. The products have been isolated in good yields. This work provides an evidence that Br_3^- is one of the intermediates in V-BrPO catalyzed biomimetic reactions. The products have been characterized by analysis, UV-Vis, IR, laser Raman spectroscopies and solution electrical conductance measurements. NBu_4Br_3 has been characterized by X-ray crystallography. Bromination of some selected organic substrates has been carried out with NBu_4Br_3 to ascertain its efficacy as a brominating agent. It is anticipated that the present methodology for the generation of tribromide will have a tremendous potential in replacing the existing methods. The major advantages of the new protocol include ease of synthesis of the reagent and redundancy of use of the hazardous chemicals Br_2 and HBr.