# ABSTRACT

The results and findings of the research work being presented in this thesis are based on the following aspects of inorganic and coordination chemistry of vanadium(V), molybdenum(VI), copper(I), manganese(III) and iron(III). While the work on copper and manganese involves the synthesis and characterisation of some fluoro compounds of these two metals in the oxidation states mentioned above, the investigation on vanadium and molybdenum includes the ability of their peroxo-intermediates to generate the active bromine species $Br_3^-$ from $Br^-$, leading to the development of novel synthetic protocols and reagents for bromination of organic substrates. The investigation on iron(III) is concerned with the role of iron(III) chloride, $FeCl_3$ as a catalyst in the bromination by TBATB, and evidence for involvement of “$Br^+$” in the process.

The text is distributed over seven chapters:

**Chapter I:** *Introduction and scope of the work*

**Chapter II:** *Details of elemental analyses and description of the instruments/ equipment used for characterisation and structural evaluation of the compounds*

**Chapter III:** *Some fluoro compounds of copper(I) and manganese(III): Synthesis of* $CuF(PPh_3)_3.2ROH$ *(R = Me or Et) and* $(NH_4)_3[MnF_6]$

**Chapter IV:** *An environmentally friendly biomimetic synthetic methodology for the bromination of organic substrates by tetrabutylammonium bromide (TBAB) promoted by* $V_2O_5$—$H_2O_2$

**Chapter V:** *An acid assisted peroxo-molybdate(VI) catalyzed methodology for in situ bromination of organic substrates by tetrabutylammonium bromide (TBAB)*

**Chapter VI:** *Cetyltrimethylammonium tribromide (CTMATB),* $C_{19}H_{42}NBr_3$*: A new environmentally favourable synthesis and studies of its reaction profile involving a few selected substrates*

**Chapter VII:** *Isolation of* $[(C_4H_9)_4N][FeCl_3Br]$ *from the reaction of* $FeCl_3$ *with* $(C_4H_9)_4NBr_3$ *(TBATB) and evidence for* $FeCl_3$ *as a catalyst in environmentally clean bromination by TBATB*

An outline of the content of each chapter is given below:

## I. Introduction and scope of the work

A general introduction to all the topics being included in the thesis has been presented in this chapter along with citation of relevant literature. To begin with a brief report has been presented on the importance of halo, especially the fluoro compounds of copper(I) and manganese(III) emphasising the problems associated with their syntheses. This has been followed by peroxo-chemistry of metals viz., vanadium(V) and molybdenum(VI), particularly in respect of their reactivity to oxidise halide to active halogen species. Mention has been made of the discovery of *V-BrPO*, a vanadium(V) containing enzyme that catalyses the bromide oxidation in marine animals and the consequent biomimetic studies carried out to design the models for *V-BrPO*. Some of the limitations of most of the customary methods of bromination have been identified and the need for development of environmentally cleaner yet highly effective routes to bromoorganic compounds emphasised. The importance of synthesis of such compounds has been underscored. Also highlighted were the advantages of metal assisted bromination over the conventional reagents especially in terms of environmental compatibility and economic viability in so far as the production of bromoorganics is concerned.

Based on the aforementioned background, scope of the work constituting the basis of the present Ph. D. research was identified.

## II. Details of elemental analyses and description of the instruments /equipment used for characterisation and structural evaluation of the compounds

Detailed procedures adopted for the quantitative determination of different constituents and relevant features of the instruments/ equipment used for physico-chemical studies have been provided. Reference has been made to the techniques involved in the structural assessment of the newly synthesized compounds including brominating reagents and bromo-organics.

## III. Some fluoro compounds of copper(I) and manganese(III): Synthesis of $CuF(PPh_3)_3.2ROH$ (R = Me or Et) and $(NH_4)_3[MnF_6]$

In this chapter the synthesis and characterization of copper(I)-fluoro complexes viz., $CuF(PPh_3)_3.2ROH$ (R= Me or Et) as well as a manganese (III)-fluoro complex i.e., $(NH_4)_3[MnF_6]$ have been reported. For convenience the results have been divided into two parts (**IIIa** and **IIIb**).

## IIIa Fluoro-compounds of copper(I): An easy access to $CuF(PPh_3)_3.2ROH$ (R= Me or Et )

The copper(I) fluoro compounds as well as other halo compounds find wide range of applications in the catalysis of a variety of organic transformations. Some fluoro-copper(I) species are also known to be involved in a few synthetically important transmetallation reactions. Having realized the importance of fluoro-compounds of copper(I) and the challenge associated with their synthesis particularly due to weak interaction of soft acid copper(I) and hard base fluoride, we decided to develop a direct yet efficient synthesis of fluorocuprates(I) containing triphenylphosphine, $Ph_3P$.

A solution of $CuSO_4.5H_2O$ when treated with $NH_2OH.HCl$ produced $Cu_2O$, which on being reacted with $Ph_3P$ and aqueous HF (48%) in MeOH or EtOH afforded $CuF(PPh_3)_3.2ROH$ (R= Me or Et) in good yield. The compounds were

$$CuSO_4.5H_2O + NH_2OH.HCl \xrightarrow{\text{dil. NaOH}} Cu_2O$$

$$Cu_2O + \text{aq. HF} + Ph_3P \xrightarrow{\text{MeOH}} CuF(PPh_3)_3.2MeOH$$

$$Cu_2O + \text{aq. HF} + Ph_3P \xrightarrow{\text{EtOH}} CuF(PPh_3)_3.2EtOH$$

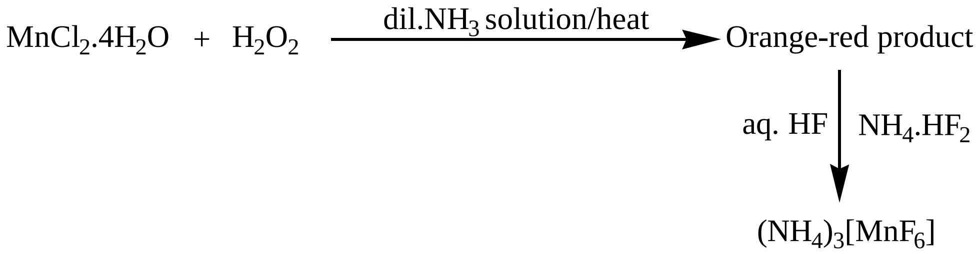
characterised by different spectroscopic techniques in addition to chemical analyses and solution electrical conductance measurements. The advantages of the present work over the earlier methods have been highlighted. In order to assess the thermal stability of fluorocuprates(I), TG analysis on $CuF(Ph_3P)_3.2MeOH$ as a typical example was carried out. TG profile reveals that the compound loses the solvent molecules and triphenylphosphines in the temperature range of 118 – 274 °C, yielding ‘CuF’ at 274°C.

Results emerged out of the present studies on fluorocopper(I) compounds provide an easy access to the title compounds and reveal an interesting thermal property of the compounds.

### IIIb. Hexafluoromanganate(III): A new synthetic route to $(NH_4)_3[MnF_6]$

In view of the biological and chemical importance of fluorine containing organic molecules, rapid development of new reagents and methods for fluorofunctionalization of organic molecules has taken place in the last few decades. Fluoro compounds of manganese(III) are known to be potential sources of fluorinating agents. Moreover, Mn(III) compounds draw special attention not only because it is difficult to stabilize in aqueous medium but also many of its complexes demonstrate unusual magnetic properties and structural features. We have developed a direct and easy method of synthesis of $(NH_4)_3[MnF_6]$. Reported in a part of this chapter are its synthesis and characterisation by physico-chemical techniques.

The treatment of an aqueous solution of $MnCl_2.4H_2O$ with $H_2O_2$ and dil. $NH_3$ solution resulted in the formation of a brown flocculent precipitate, which upon heating at *ca*. 70°C produced an orange-red product. The isolated product on being reacted with $NH_4HF_2$ and aqueous HF (48%) followed by concentration of the reaction solution yielded the title compound in good yield. The compound is insoluble in most of the common solvents and in water it undergoes hydrolysis to give hydrated manganese(III) oxide. The compound was characterised by IR and reflectance spectroscopies, magnetic susceptibility measurements and TG analysis in addition to chemical determination of



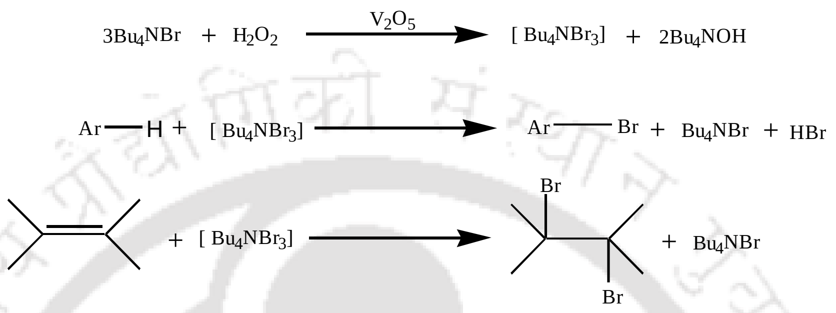
$$\begin{tikzcd} MnCl_2.4H_2O + H_2O_2 \arrow[r, "dil.NH_3\ solution/heat"] & \text{Orange-red product} \arrow[d, "aq.\ HF"', "NH_4.HF_2"] \\ & (NH_4)_3[MnF_6] \end{tikzcd}$$

manganese and fluoride. The chemical determination of oxidation state of manganese, which is considered to be important, supported the occurrence of Mn(III) in the compound. In order to gain knowledge of thermal behaviour of the compound, thermogravimetric analysis (TGA) was conducted. The thermogram revealed that the compound is stable up to 250°C and thereafter it loses $NH_4F$ between 250 and 315°C affording $MnF_3$ at 315°C.

## IV. An environmentally friendly biomimetic synthetic methodology for bromination of organic substrates by tetrabutylammonium bromide (TBAB) promoted by $V_2O_5$—$H_2O_2$

This chapter reports the development of a new biomimetic synthetic protocol for bromination of a variety of organic substrates by TBAB and $H_2O_2$ promoted by vanadium(V). Coordination to the metal center activates the peroxide towards oxidation of bromide, generating *in-situ* the active bromine species tribromide, $Br_3^-$ (a "$Br^+$" equivalent), in the reaction solution. The $Br_3^-$ thus formed then brings about bromination of the chosen organic substrates.

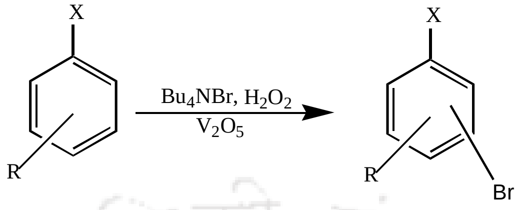
A typical reaction involved the addition of TBAB to an aqueous-acetonitrile suspension of vanadium pentoxide, $V_2O_5$, and hydrogen peroxide followed by the addition of the organic substrate. The resulting mixture when stirred for a specific period of time afforded bromo derivative of the substrate in a very high yield. The reactions were monitored by TLC and GC.



Generation of TBATB and bromination of organic substrates

A variety of substrates were brominated by this methodology with yields generally varying between 70 and 90%. The products were characterized by comparison with authentic compounds, while for a few samples IR and $^1$H NMR spectroscopic techniques were also used. Included in this chapter are the substrates drawn from activated aromatic compounds, namely, aniline, phenol, and 2-naphthol, polycyclic aromatic compound, viz., anthracene, cyclic alkene, viz., cyclohexene, α,β-unsaturated alcohol, i.e., crotyl alcohol and a ketone i.e., cyclohexanone. The environmental compatibility stems from the choice of $V_2O_5$ to be the metal promoter and $H_2O_2$ as the oxidant. Incidentally $H_2O_2$ is regarded as a green oxidant. The other notable feature is the regioselectivity of the protocol. Majority of the substrates gave a single regioisomer. As for example, anthracene, aniline, and 2-naphthol, afforded exclusively 9,10-

dibromoanthracene, 4-bromoaniline and 1-bromo-2-naphthol, respectively. A remarkable aspect of the methodology is the redundancy of the use of acid.



X = H, $CH_3$
R = OH, $NH_2$

The high to very high yields of most of the products obtained under mild reaction conditions with the other advantages mentioned above make the methodology a desirable alternative to traditional reagents and protocols for bromination.

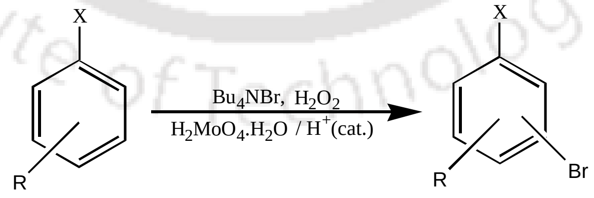
### V. An Acid assisted peroxo-molybdate(VI) catalyzed *in situ* bromination of organic substrates by tetrabutylammonium bromide (TBAB) and $H_2O_2$

In the methodology reported earlier the amount of $V_2O_5$ was used in considerable excess to generate sufficient acidity to afford products in high yields. Consequent upon this and taking into consideration the requirement of a reasonably strong acidic medium in the metal mediated *in situ* bromination of organic substrates, development of a metal catalyzed bromination protocol was considered to be a worthwhile exercise. Accordingly, we designed an acid assisted bromination protocol for organic substrates using $MoO_4^{2-}$ as the catalyst. There is a striking resemblance between various aspects of peroxo-chemistry of vanadium and molybdenum. Molybdenum(VI) (*c.f.* vanadium(V)) is also known to activate hydrogen peroxide through its coordination to the dioxygen. These led to the selection of molybdenum(VI) as the catalyst for $O_2^{2-}$ activation to bring about *in situ* oxidation of $Br^-$ to $Br_3^-$ (an ‘$Br^+$’

equivalent ) in the presence of a catalytic amount of an acid. This in turn gave rise to a protocol for bromination of organics substrates. The reactions were monitored by GC and TLC.

A typical reaction involved the activation of peroxide through its coordination to the molybdenum(VI). The activated peroxide then oxidizes the bromide to tribromide in presence of an acid. The tribromide thus formed brominates the chosen organic substrates.

The results of this methodology are quite similar to those of the previous methodology reported in **chapter IV**. The points of difference are the use of molybdenum(VI) as the catalyst and the requirement of catalytic amount of an acid. The environmental friendliness, high yield and selectivity and the other advantageous features of this methodology over the conventional protocols and reagents are reported in details in this chapter. One of the notable aspects of this methodology is that the product selectivity observed in the present case is different from that of earlier methodology. It has been shown with the help of the results obtained by other collaborators that for some of the substrates namely anthracene and phenol, the products



X = H, $CH_3$

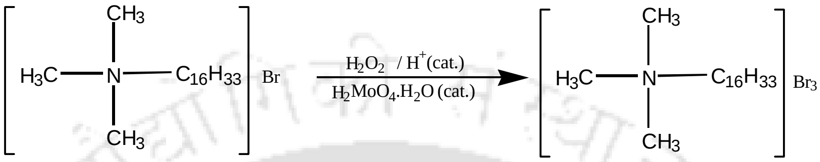
R = OH, $NH_2$

are different from what were obtained by peroxo-vanadium(V) promoted methodology, suggesting a distinct difference in regioselectivity with the change of the metal activator.

## VI. Cetyltrimethylammonium tribromide (CTMATB), $C_{19}H_{42}NBr_3$: A new environmentally favourable synthesis and studies of its reaction profiles involving a few selected substrates

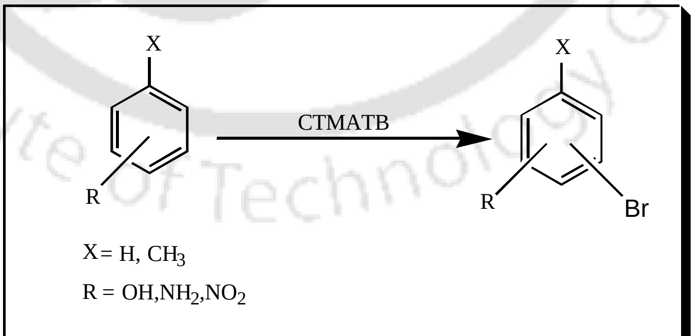
In our continued effort to develop new and improved methodologies for reagents and protocols for bromination, we embarked on to develop an environmentally safe synthetic route to an organic ammonium tribromide, cetyltrimethylammonium tribromide, $C_{19}H_{42}NBr_3$ (CTMATB). Organic ammonium tribromides have been proved to be extremely versatile brominating reagents in recent times. A number of tribromides are known and their efficacy as brominating agents have been appreciated. Cetyltrimethylammonium tribromide (CTMATB), $C_{19}H_{42}NBr_3$, appears to be mentioned in the literature but its preparation as reported only in a patent involves the use of molecular bromine whose use is rather hazardous from safety point of view. Interestingly, the usefulness of CTMATB as a brominating reagent was not reported to the best of our knowledge. The present study is based on the ability of a peroxo-molybdenum system to oxidize bromide to tribromide. Taking a cue from this cetyltrimethylammonium tribromide (CTMATB) was prepared from the corresponding bromide and its reaction profile was investigated.

The preparation involved the oxidation of CTMAB to the corresponding tribromide by $H_2O_2$, catalyzed by $H_2MoO_4.H_2O$, in the presence of a catalytic amount of $H_2SO_4$. The use of two molar equivalents of potassium bromide (ostensibly to increase the yield), as the consumable source, afforded the product in 93% yield. The product thus obtained was recrystallised from acetonitrile. The recrystallised product registered a sharp melting point at 94°C. The product has been found to be stable for a prolong period.



Formation of CTMATB from CTMAB

The efficacy of CTMATB as a brominating reagent was established by conducting bromination of a few selected substrates. The substrates chosen were mostly moderately activated aromatic compounds like phenol, cresols, aniline and phluroglucinol. The yields of majority of the products were high to very high (60-85%). Environmental implication of the preparation of the reagent has been highlighted. One of the inherent advantages of the reagent is its phase transfer property. Thus, it can be used very effectively in a biphasic reaction condition thereby enlarging the scope of bromination of a wide variety of substrates.



Reactivity of CTMATB

Moreover, the reagent is highly selective, as exemplified by the formation of 4-bromophenol and 2,4-dibromoanilne from phenol and aniline, respectively, as the major isomers. Similarly *o*-cresol and *m*-cresol afforded selectively 2-bromo and 4-bromo derivatives, respectively. For *o*-nitroaniline and phluroglucinol (1,3,5-trihydroxy benzene) the products obtained were 4-bromo *o*-nitroaniline and 2,4-dibromophluroglucinol. Additionally, the reagent is cost-effective and capable of brominating a wide range of substrates. These features together with its safer might be good enough reasons to render it a sought-after reagent for bromination for organic substrates.

## VII. Isolation of $[(C_4H_9)_4N][FeCl_3Br]$ from the reaction of $FeCl_3$ with $(C_4H_9)_4NBr_3$ (TBATB) and evidence for $FeCl_3$ as a catalyst in environmentally clean bromination by TBATB

Taking into consideration of the similarity of products profile of the bromination of aromatics by $Br_2$ and TBATB, it was conjectured that both the reagents might involve similar attacking species in their reactions. Recollecting the catalytic role of iron(III) chloride, $FeCl_3$, in the bromination of aromatics in which $Br_2$ is activated by the salt to generate '$Br^+$' as the active species with the formation of $[FeCl_3Br]^-$, it was thought to react $FeCl_3$ with TBATB in acetonitrile and then to ascertain the product obtained thereof. If the reaction would lead to the formation of a salt of $[FeCl_3Br]^-$ then it would be quite logical to believe that '$Br^+$' was also formed in the reaction in the bromination by TBATB. Assuming a positive outcome, it was logical to believe that $FeCl_3$ would be able to catalyse the bromination by TBATB. To this end, $FeCl_3$ catalyzed brominations of a few aromatic substrates including chalcone were conducted.

Brominations of aniline, phenol and chalcone were conducted by TBATB in acetonitrile in presence of catalytic amount of $FeCl_3$. The reaction times, ratio of substrates to catalyst, products and yields along with the results of the control reactions have been summarized in **Table 1**.

**Table 1**

| Substrate | Amount of catalyst | Reaction time (min) | Product [a] | Yield (%) [b] |
|---|---|---|---|---|
| Chalcone | 5 mol% | 30 | Threo-dibromochalcone | 70 |
| Chalcone | 0 | 30 | Threo-dibromochalcone | 10 |
| Aniline | 5 mol% | 2 or 3 | 2,4,6-tribromoaniline | 65 |
| Aniline | 0 | 5 | 2,4,6-tribromoaniline | 20 |
| Phenol | 5 mol% | 10 | 2,4,6-tribromophenol | 73 |
| Phenol | 0 | 10 | 2,4,6-tribromophenol | 15 |

[a] products were characterized by comparison with the authentic samples, [b] isolated yields

A comparison of the results of the catalytic reactions (**Table 1**) with those of uncatalysed reactions clearly suggests that $FeCl_3$ catalyses the bromination reactions by TBATB.

These results along with the isolation of $[FeCl_3Br]^-$ provides an evidence for the involvement of $Br^+$ in the bromination by TBATB.

The characterization of synthesised compounds including bromo-organics being reported in different chapters were made by a combination of variety of physical techniques, viz., IR and electronic spectroscopies, solution electrical conductance and magnetic susceptibility measurements, $^1H$ NMR spectroscopy, thermal analyses, and gas chromatography. In addition to the physical techniques mentioned above, microanalyses of carbon, hydrogen and nitrogen and chemical determination of a few other constituents were made by standard chemical procedures.