CHAPTER 1

Chapter 1

Introduction

Contents

The present work gives a general introduction along with a literature review, describing the outline and scope of the present investigation in the background of known chemistry of niobium, with a special emphasis on general aspects and recent advances in the field of peroxo niobium chemistry.

1.1 Preamble

Peroxo complexes have been for the past several decades the object of intense investigation, due to their potential catalytic, biochemical and therapeutic applications [1-7]. A facile route to newer members of stable and structurally defined peroxometalllates opens the possibility of finding novel catalysts and biologically active agents. The work presented in this thesis is therefore, focused on synthesis and characterization of some new peroxide containing complexes of niobium, including peroxoniobates anchored to linear water soluble polymers, and exploration of their biochemical as well as catalytic activities. The contemporary interest in the chemistry of niobium essentially originates from the multiple utility of the element and its compounds in diverse domains ranging from catalysis to their uses in designing advanced materials for high technology applications [7-16].

In this Chapter we present a concise review of the following interrelated areas relevant to the work embodied in the thesis:

(i)   Selected aspects of chemistry of niobium.

(ii)   Salient features and applications of peroxo compounds of niobium.

(iii)   Immobilization of metal complexes on linear water soluble polymer matrices - synthesis and importance of soluble metal containing macromolecules in catalysis and biology.

1.2 Background information

1.2.1 Niobium – general comments

Niobium is a soft, grey, transition metal that belongs to Group V of the periodic table with ground state electronic configuration of [Kr] $4d^4$ 5s [17,18]. In the order of crustal abundance ascribed to the elements, niobium occupies 31st place [19]. It does not occur in nature in its free or native form and found in more than 60 independent minerals and nearly 90 in association with minerals of other elements which has been broadly classified into 15 mineral groups [20]. Complex oxides and hydroxides are dominating mineral groups over silicates and borate minerals in case of niobium abundance [20].

The spectrum of uses of niobium, mainly as an element of choice to generate materials for advanced technology applications, is extremely broad. These include sophisticated multiphase steels, aeronautics and space machinery, medical treatment, and modern information technology [21]. Niobium-based materials are also of noteworthy interest in the domains of catalysis [22-24], gas sensing [25-27], electrochromism [28], dye sensitized solar cells (DSSCs) [29-32] and optical application [33].

Most importantly, Nb and its oxides have been known to display good biocompatibility and apatite-inducing capability [34-37]. Olivares-Navarrete *et al.* [38] studied the biocompatibility of niobium coatings and established that Nb is by nature a highly chemically stable, hypoallergenic, biocompatible and bioinert material, which makes it suitable for applications in biomedicine and for use in corrosion-resistant coatings for surgical tools [39]. Nb has been reported to be non-toxic to animals, with LD_{50} values in several thousands of milligrams per kilogram body weight in contrast to its lighter group 5 element vanadium, which is known to be moderately toxic [40]. Tissue reaction studies have also identified Nb along with Ti and Ta as non-toxic elements as they do not cause any adverse reaction in the human body [41]. Yamamoto *et al.* [42] further observed that niobium shows lower cytotoxicity (IC_{50} of niobium ions for MC3T3-E1 cells is 1.47×10^{-3} mol/L) when compared with other metal ions. Most importantly, it has been reported that Ti-Nb alloys can display an elastic modulus of about 50~60 GPa, which is much nearer to that of human bones when compared to other binary Ti-based alloys [43-45]. These findings are of particular interest in the context of application of artificial biomaterials as therapies for degenerative diseases of bones [46].

Niobium based systems as support for immobilization of enzymes or biomolecules has also become an interesting field of research which may provide long-term stability, easy recovery and recyclability of enzymes [47,48]. Intercalation of hemoglobin (Hb) at the galleries of layered niobate $HCa_2Nb_3O_{10}$ has been shown to enhance the activity of Hb [47]. Gao and Gao [48] have developed a $Hb-HCa_2Nb_3O_{10}$ modified electrode based on the stabilizing effect of the layered niobates and demonstrated that it can detect H_2O_2 in strongly acidic and basic solutions with pH of 1-12.

Compounds of Nb have also been documented to show anti-cancer activity [49-52] and niobium substituted heteropolytungstates were found to be potent anti-HIV-1 agents while being minimally cytotoxic [53]. An analogue of the anti cancer agent titanocene dichloride, niobocene dichloride (Cp_2NbCl_2) has been shown to be a highly potent cancerostatic agent against the Ehrich ascites tumour in CFI mice [49]. It has been established that the oxidation to Nb(V) reduces the tumor inhibiting properties but potentially could also reduce toxic effects [50].

Apart from the applications in sophisticated technology, multimetallic Nb-based oxides generate a great deal of interest as potential heterogeneous catalysts for several highly challenging industrial processes, like alkane oxidation [54,55], ammoxidation [56] and oxidation of sulfides [57]. Thus fundamental research on Nb co-ordination compounds that could be used as molecular precursors for preparation of such catalysts, has been assuming increasing importance in recent years.

The chemistry of niobium ranges from oxidation states +V to −III with no species of oxidation state −II identified until recently [58]. Nb is actually very resistant to acids but can be dissolved in HNO_3-HF mixtures, and displays very little cationic behavior [7]. Aqueous solution chemistry of high valent metals such as Nb(V) is indeed complicated as such species are extremely sensitive to hydrolysis, leading to precipitation and undesired phase segregation [58]. In fact, aqueous chemistry of niobium is known to be rather restricted to a very few available water soluble precursors which also includes its peroxo derivatives [7]. It is therefore not surprising that one of the most fascinating domains of niobium chemistry, which has been garnering a great deal of contemporary interest, is its peroxo chemistry.

1.2.2   Peroxo complexes of niobium – salient features

Interest in the d^0 transition metal peroxo species of V(V), Mo(VI) W(VI) and Nb(V) in general, seems not to be diminishing. Besides their scientific significance, such systems are attractive as potential catalysts in biological [1,2,6,7,51,60-63] and industrial processes or as simple models [3-5,64-67]. Furthermore, knowledge regarding the active involvement of peroxovanadium compounds in haloperoxidases [68-70], and their enzyme inhibitory [69], antineoplastic [71] and insulino-mimetic properties [6,62,72-80]

have led to an upsurge in interest in these complexes. Transition-metal peroxides correspond to a vital class of reactive intermediates in catalytic oxidations, as they can be obtained upon interaction of molecular oxygen, hydrogen peroxide, and inorganic or organic peroxides with metal salts or complexes [65]. One very remarkable reactivity feature of peroxo metal complexes is that they generally act as 1,3-dipolar reagents and can react with both electrophilic and neucleophilic substrates [81].

A peroxo (p) transition metal species, as rationalized by Vaska [82], consists of a covalently bound dioxygen resembling O_2^{2-} in a peroxo configuration. There are varieties of ways, ranging from symmetrical bidentate to a terminal monodentate mode as shown in **Fig. 1.1**, in which the electron rich peroxo group can be expected to co-ordinate to metals (M). Reynolds and Butler [83] studied the metal-peroxo bonds with *ab initio* calculations and semi emperical computations and described these as δ-interactions between the metal d_{xy} orbital and an in-plane peroxo δ* orbital.
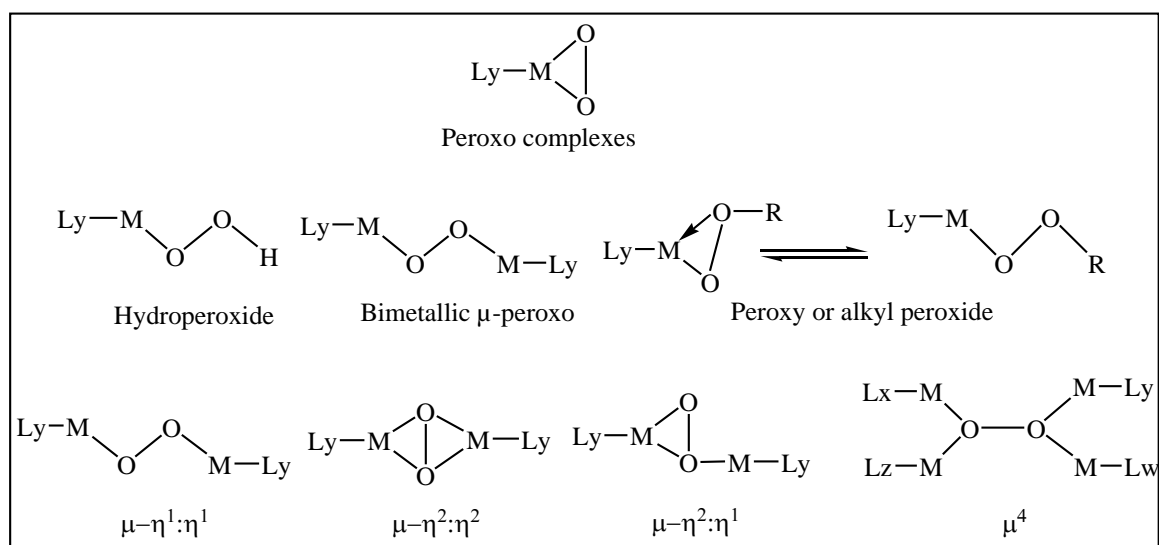
Fig. 1.1 Structural classification of metal-dioxygen complexes (L = Ligand) [82].

All the peroxide complexes of Nb metal reported in the literature exclusively contain one or more O_2^{2-} ligand(s) bound in a η^2 coordination mode [7]. As far as their peroxo chemistry is concerned, Nb(V) and Ta(V) peroxides display a clear isostructural and isoelectronic relationship and quasi identical chemical behaviour which is very different from that of vanadium, which also belongs to the same Group 5 [84]. Vanadium has a general tendency to form oxo-peroxo species [84]. The great majority of peroxo-

type complexes of V(V) described in the literature displays one or more vanadyl bonds [73,85]. In addition, bridging vanadium peroxo derivatives form very easily [84]. Furthermore, while vanadium generally displays 6- or 7- fold co-ordination, the co-ordination number around Nb and Ta in peroxo compounds has been reported to be eight [7,84].

The composition of pNb species formed in aqueous solution has been found to be influenced by various factors including pH, niobium and peroxide concentration, ionic strength and reaction temperature [7]. A variety of peroxo complexes ranging from homoleptic tetraperoxo to heteroleptic mono, di- and tri peroxo Nb complexes in different ligand environment have been synthesized and characterized over the last couple of decades [7]. The chemistry of Nb and Ta peroxo compounds was most systematically and comprehensively reviewed by Bayot and Devillers [7].

1.2.2.1 Homoleptic peroxo complexes of niobium

Balke and Smith [86], more than a century ago identified for the first time, the homoleptic peroxoniobium in the form of tetraperoxoniobate (**TpNb**) anion $[Nb(O_2)_4]^{3-}$, with the highest possible content of peroxo groups, in a solution of niobium hydroxide in hydrogen peroxide. Several salts of the **TpNb** anion with alkaline cations like sodium [86,87], potassium [86,88-91], rubidium [86,92] and cesium [86] have been subsequently developed, most of which are thermally unstable. Other than alkaline counter cations, **TpNb** systems with guanidinium (gu) [93] and ammonium ion [93-95] have also been generated. Three general synthetic pathways have been developed in recent years in order to obtain the tetraperoxoniobate complexes: (i) the fusing of the niobium pentoxide, Nb_2O_5 with the respective metal hydroxide (Na, K) [86-88] or carbonate (Rb) [92] followed by the dissolution of the melt in a solution of H_2O_2; (ii) the reaction of $NbCl_5$ with H_2O_2 and NH_3 [94]; and finally, (iii) the dissolution of the niobic acid in a concentrated H_2O_2 solution in the presence of NH_3 or gu_2CO_3 [93].

The crystal structures of several **TpNb** complexes have been reported [87,91-93] which revealed a tetrahedral arrangement of four η^2-O_2^{2-} ligands around the niobium atom of the $[Nb(O_2)_4]^{3-}$ anion representing an eight-fold co-ordination resulting in a dodecahedral geometry (D_{2d}) of the complex (**Fig. 1.2**).
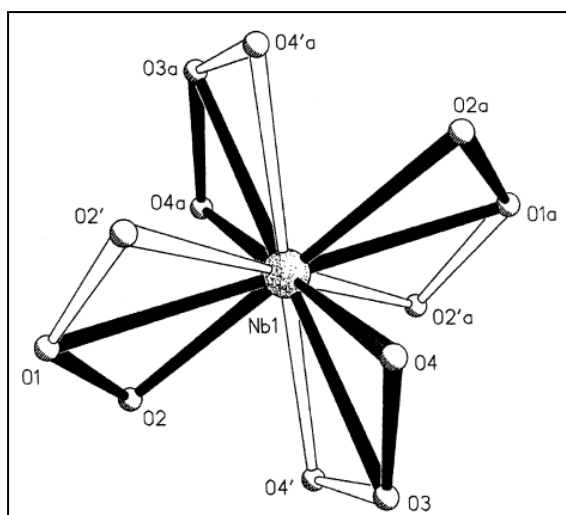
Fig. 1.2 The structure of the $[Nb(O_2)_4]^{3-}$ anion in $Na_3[Nb(O_2)_4]\cdot13H_2O$ showing the disorder in the peroxo oxygen atom positions. Two different conformations are shown in black and white lines [87].

1.2.2.2 Heteroleptic pNb complexes

It has been possible to synthesize a variety of halide containing heteroleptic pNb complexes with diverse compositions by dissolving the tetraperoxo precursor complex, the principal species in an alkaline solution of Nb and excess H_2O_2, in the presence of halide ion and appropriately adjusting the pH [96]. As illustrated in **Scheme 1.1** these studies show that the number of peroxo group per Nb atom increases with alkalinity [96].

pH	Complex separated from solution	
1		
	$[Nb(O_2)F_5]^{2-}$	1:5
3		
	$[Nb(O_2)_2F_4]^{3-}$	2:4
5		
7		
	$[Nb(O_2)_4]^{3-}$	
9		

Scheme 1.1 pH-dependence of the substitution of fluoro ligands by peroxo groups in niobate complexes [96].

The coordination geometry for the monohydrate potassium salt of the monoperoxopentafluoro complex of niobium, $K_2[Nb(O_2)F_5] \cdot H_2O$ was observed to be a monocapped octahedron by Geetha *et al.* [97]. For other monoperoxopentafluoro compounds reported by Stomberg [98-102], the polyhedron was described as pentagonal bipyramidal where the symmetry of the anion is almost C_{2v}.

A plethora of halide free heteroleptic diperoxo and triperoxo niobate complexes has been derived by the substitution of one or two peroxo groups from the precursor complex, $[Nb(O_2)_4]^{3-}$ by monodentate or bidentate ligands [7]. A variety of carboxylate containing species *viz.,* oxalic acid to polyaminocarboxylate ligands to N-containing heterocycles as well as Schiff bases of the type listed in **Table 1.1**, have been synthesized and many of these complexes have been structurally characterized [7]. Geometrical parameters like Nb-O and O-O coordination distances for some reported crystal structures are shown in **Table 1.1** [7].

Nearly in all the halide-free heteroleptic complexes, Nb exhibits coordination number of eight [7]. There are some exceptions, such as $[Nb(O_2)_2(L)]$ [103] and $K[Nb(O_2)_2OH(L)] \cdot 2H_2O$ [103,104] with L = 8-quinolinolate (hq), for which a coordination number of six or seven, respectively, has been reported. The commonly observed environment of Nb in the heteroleptic pNb complexes, as summarized by Bayot and Devillers [7], are illustrated in **Fig. 1.3**. In the developed crystals of pNb coordinated to either carboxylate or polyaminocarboxylate, the coordination polyhedron has been described as a dodecahedron which is highly distorted on one side [93,105-109]. A series of compounds of stoichiometry, $K[Nb(O_2)_3(dipy)]$, (phen = 1,10-phenantroline) [110], $K[Nb(O_2)_3(dipy)]$, (dipy = dipyridyl) [110], $K[Nb(O_2)_2(hq)_2] \cdot 2H_2O$ [103,104], $(gu)_2[Nb(O_2)_3(L)]$, {L = picolinato (pic$^-$) or picolinato N-oxide ligand (picO$^-$)} [107] and $(gu)_3[Nb(O_2)_3(pzdc)] \cdot H_2O$, {pyrazine 2,5-dicarboxylate (pzdc)} [107], has been developed in which the heterocyclic ligands are always bidentate *via* nitrogen and/or oxygen atoms.

Infrared and Raman spectra have been found to be highly informative and essential tools for characterization of pNb compounds. Three IR active modes are typically observed for peroxo metallates when peroxide group co-ordinate in a side-on bidentate fashion creating a local C_{2v} symmetry [114]. These bands originate from

Table 1.1: Some homoleptic and heteroleptic peroxoniobate (pNb) complexes described in the literature [7]

Types	Compounds	Nb-O (A°)	O-O (A°)	Ref
Tetraperoxo niobate	$Na_3[Nb(O_2)_4] \cdot 13H_2O$	1.954(6), 2.057(5)	1.568(6), 1.632(6)	[87]
	$KMg[Nb(O_2)_4] \cdot 7H_2O$	2.026(3) ± 0.040	1.500(4) ± 0.005	[91]
	$K_3[Nb(O_2)_4]$	--	--	[86]
Flouride	$(C_{12}H_{10}N_2)[Nb(O_2)F_5]$	1.884(5)	1.483(8)	[101]
	$(C_9H_8NO)_2[Nb(O_2)F_5] \cdot 3H_2O$	1.956(13) [170 K], 2.00(2) [275 K]	1.471(19) [170 K], 1.35(4) [275 K]	[102]
Carboxylates	$(gu)_2[Nb(O_2)_3(quin-2-c)] \cdot H_2O$	1.980, 2.000, 1.983, 1.961, 1.978, 1.998	1.506, 1.485, 1.502	[109]
	$(gu)_3[Nb(O_2)_2(ox)_2] \cdot 2H_2O$	1.978(2)	1.482(3)	[93]
	$(gu)_5[Nb_2(O_2)_4(tart)(Htart)] \cdot 6H_2O \cdot 1H_2O_2$	2.002(3), 1.992(3), 2.000(3), 1.997(4)	1.493(2), 1.500(2)	[105]
	$(NH_4)_3[Nb(O_2)_3(H_2tart)] \cdot 1.5H_2O$	--	--	[93]
	$K_6[Nb_2(O_2)_6(tart)] \cdot 2H_2O$	--	--	[88]
	$K_3[Nb(O_2)_3(H_2tart)] \cdot H_2O$	--	--	[88]
	$K_3[Nb(O_2)_3(glyc)] \cdot 2H_2O$	--	--	[88]
	$K_3[Nb(O_2)_3(Hmal)] \cdot H_2O$	--	--	[88]
	$K_3[Nb(Asc)(O_2)_3] \cdot 4H_2O$	--	--	[51]

Types	Compounds	Nb-O (A°)	O-O (A°)	Ref
Polyaminocarboxylates	$(gu)_3[NbTa(O_2)_4(dtpaO_3)]\cdot2.5H_2O$	--	--	[111]
	$(gu)_3[NbTa(O_2)_4(HtthaO_4)]\cdot2H_2O$	---	--	[111]
	$(gu)_3[Nb_2(O_2)_4(HtthaO_4)]\cdot2H_2O$	--	--	[111]
	$(gu)_3[Nb_2(O_2)_4(dtpaO_3)]\cdot3H_2O$	--	--	[111]
	$(gu)_3[Nb(O_2)_2(edtaO_2)]\cdot3H_2O\cdot H_2O_2$	1.966(5), 1.968(5), 1.977(5), 1.992(5)	1.478(7), 1.483(7)	[106]
	$(gu)_3[Nb(O_2)_2(pdtaO_2)]$	1.973(2),1.988(2)	1.488(3)	[106]
	$(NH_4)_3[Nb(O_2)_2(edtaO_2)]\cdot H_2O\cdot H_2O_2$	--	--	[106]
N-heterocycles	$(gu)_2[Nb(O_2)_3(picO)]$	2.024(5),2.011(5), 2.009(4), 1.967(4), 2.001(5), 2.011(5)	1.518(7), 1.491(6), 1.520(6)	[107]
	$K[Nb(O_2)_3(phen)]\cdot3H_2O$	1.98, 2.01	1.50, 1.47	[108]
	$K[Nb(O_2)_3(phen)]$	--	--	[110]
	$(gu)_3[Nb(O_2)_3(pzdc)]\cdot H_2O$	--	--	[107]
Schiff bases	$K[Nb(O_2)_2(salen)]\cdot8H_2O$	-	-	[112]
	$K[Nb(O_2)_2(H_2O)(hphpd)]\cdot8H_2O$	-	-	[112]
	$K[Nb(O_2)_2(hntrien)]\cdot8H_2O$			[112]
Organometallic	$(\eta^5\text{-}C_5H_5)_2Nb(O\text{-}O)Cl$	1.97, 2.00	1.47	[113]
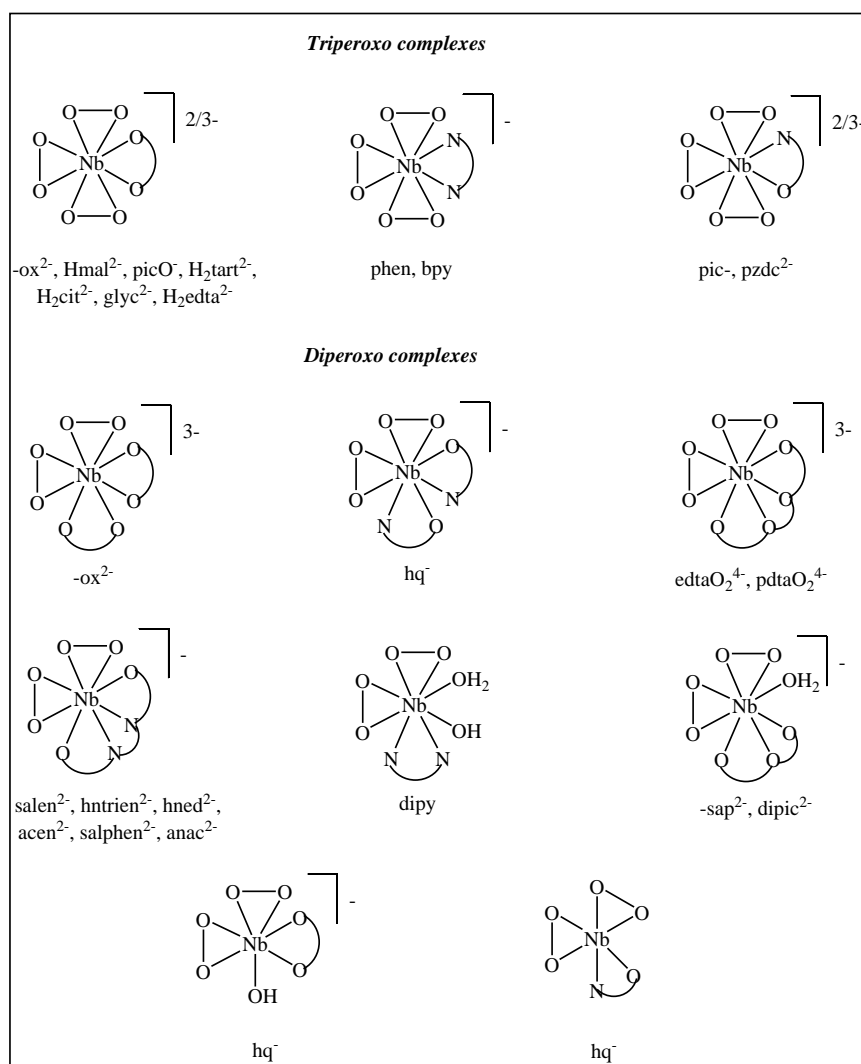
Fig. 1.3 Environment of the metal atom reported for halide-free homometallic heteroleptic peroxo complexes of niobium derived from the corresponding tetraperoxoniobate [7].

symmetric O-O stretching, symmetric metal-peroxo stretching and antisymmetric metal-peroxo stretchings, $\nu_s[\text{Nb-(O}_2)]$ and $\nu_{as}[\text{Nb-(O}_2)]$, which occur in the regions 900-800, 500 and 600 cm^{-1}, respectively [7,114]. The $\nu_s(\text{O-O})$ is the most sensitive and intense band. All the three IR active modes are also Raman active and thus the results of Raman spectral studies not only complement the IR results but also augment them. Interestingly, in the case of pNb complexes, two and three $\nu(\text{O-O})$ bands are usually observed for diperoxo and triperoxo species, respectively [7]. It has been possible to establish an empirical rule correlating the number of such stretching bands to the number of peroxo ligands present in the co-ordination sphere, which has been further validated by

theoretical investigations. The appearance of three v(O-O) bands for the triperoxo complexes was confirmed *via* DFT study by Maniatakou *et al.* [109]. The experimental data for crystal structure [Nb(O$_2$)$_3$(quin-2-c)]$^{2-}$ (**Fig. 1.4**) were compared with the bond lengths calculated from the density functional theory (DFT) approach to show that the geometrical parameters derived from the theoretical calculations are in close agreement with the reported crystallographic data [109].
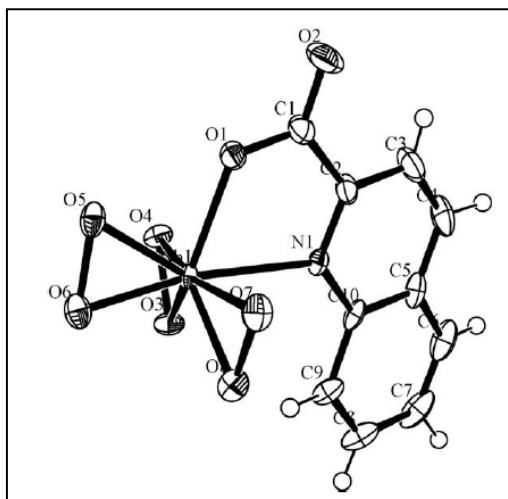
Fig. 1.4 Structure and atom numbering of [Nb(O$_2$)$_3$(quin-2-c)]$^{2-}$. Thermal ellipsoids are drawn at the 50% probability level [109].

Besides mononuclear peroxo complexes of niobium metal, dinuclear homo or heterometallic peroxoniobium complexes have also been prepared. The dinuclear homobimetallic species of pNb complexes *viz.,*(gu)$_5$[Nb$_2$(O$_2$)$_4$(tart)(Htart)]·6H$_2$O·1H$_2$O$_2$ (**Fig. 1.5**) with tartaric acid [105], and with *N*-oxidized polyaminocarboxylic acids, (gu)$_3$[Nb$_2$(O$_2$)$_4$(dtpaO$_3$)]·3H$_2$O and (gu)$_3$[Nb$_2$(O$_2$)$_4$(HtthaO$_4$)]·2H$_2$O [111], as well as their corresponding heterobimetallic complexes, (gu)$_5$[NbTa(O$_2$)$_4$(tart)(Htart)]·4H$_2$O [105], (gu)$_3$[NbTa(O$_2$)$_4$(dtpaO$_3$)]·5/2H$_2$O and (gu)$_3$[NbTa(O$_2$)$_4$(HtthaO$_4$)]·2H$_2$O [101] have been reported. In the molecular structure of the complex anion, [Nb$_2$(O$_2$)$_4$(tart)(Htart)]$^{5-}$ (**Fig. 1.5**), the tartrato groups serve as tetradentate ligands bridging the two diperoxoniobium(V) centres leading to eight-fold co-ordination around each Nb(V) [105].
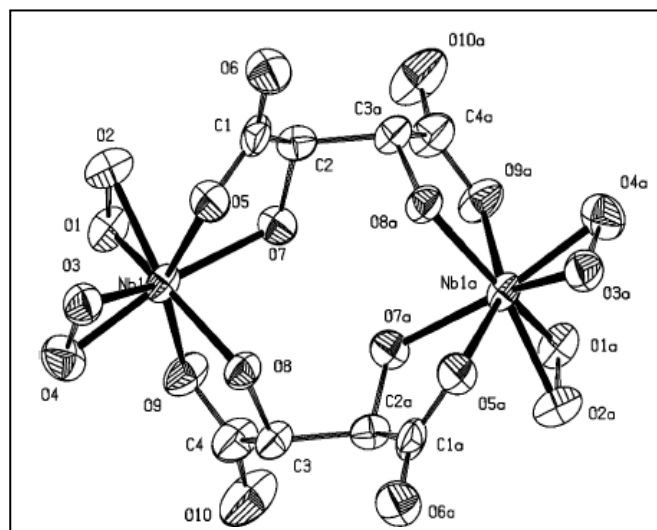
Fig. 1.5 ORTEP plot of the molecular anion, $[Nb_2(O_2)_4(tart)(Htart)]^{5-}$ (50% probability) [105].

Organometallic peroxoniobium complexes have also been developed with substituted cyclopentadienyl ligands *viz.,* $(R-Cp)_2Nb(O_2)Cl$ with R=H [113] or CH_3 [115]. The compounds were prepared from the corresponding dichloro compounds, $(R-Cp)_2Nb(V)Cl_2$, which reacted in CH_2Cl_2 medium with hydrogen peroxide affording the peroxo species. The crystal structure of the bis(cyclopentadienyl)peroxochloroniobium(V) complex, $[(Cp)_2Nb(O_2)Cl]$, has shown that the niobium atom is η^5-bonded to two Cp rings and the two oxygen atoms from the η^2-peroxo group (geometrical parameters are in **Table 1.1**) and the chlorine atom [Nb-Cl = 2.483(3) A°] are located in the plane which bisects the $(Cp)_2Nb$ bent sandwich system [113].

1.2.3 Applications of pNb compounds

Extensive applications of peroxoniobium compounds, as revealed by a survey of the literature, have so far been confined mostly to two exclusive areas (i) as catalysts for organic oxidations and (ii) as ideal water soluble precursors to attain Nb-based oxide materials *via* wet chemical solution routes [7].

In this context, it is pertinent to mention that transition metal peroxo compounds of other d^0 metals (V, Mo and W) have been investigated as biologically active agents as several of this class of compounds have been observed to display properties of clinical relevance [62,73,116-121]. The peroxo compounds of molybdenum (pMo) and tungsten (pW), besides peroxovanadates (pV), are now recognized as potential insulin mimics [1,6,62,72-80,121] and have been found to exhibit anti-neoplastic activity [71].

It is therefore intriguing to note that although Nb belongs to the same periodic group as vanadium, we have come across very few studies dealing with exploration of the biochemical potential of peroxo compounds of niobium [51,63]. Thomadaki and co-workers [51] investigated the anticancer activity of a pNb complex with ascorbate as co-ligand (**Fig. 1.6 B**). The compound was found to exert increased antiproliferative effect on human leukemia cells compared to ascorbic acid [51]. Maniatakou *et al.* [63] on the other hand, reported the insulinomimetic activity of pNb complexes *viz.,* $(gu)_3[Nb(O_2)_4]$ and $(gu)_2[Nb(O_2)_3(quin-2-c)]\cdot H_2O$ (**Fig. 1.6 A**).
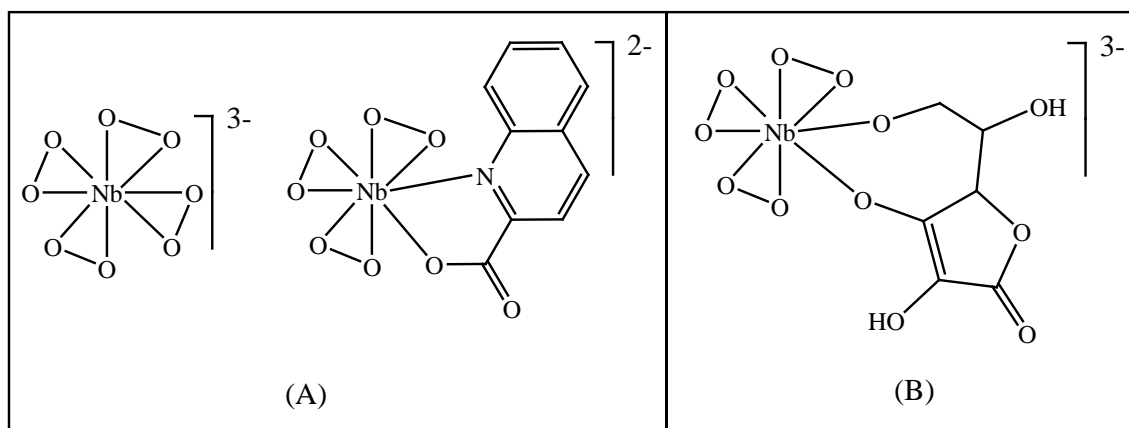
Fig. 1.6 The peroxoniobium complexes tested for their (A) insulin-like activity: $[Nb(O_2)_4]^{3-}$ and $[Nb(O_2)_3(quin-2-c)]^{2-}$ [63] and (B) anti-cancer activity: $[Nb(Asc)(O_2)_3]^{3-}$ [51].

There still remains a dearth of reports dealing with pharmacological potential of discreet synthetic peroxoniobium compounds or their effect on the activity of different enzyme functions including phosphohydrolases. Studies on enzyme inhibition by metal complexes are important in the context of gaining an insight into the mechanism of action of inorganic drugs and are an important area of current research [122,123].

1.2.3.1 Peroxoniobium compounds as molecular precursors to obtain Nb-oxide materials

Peroxoniobium compounds are of great interest as the molecular precursors for the preparation of oxide materials, for which the availability of well-defined water-soluble complexes is very limited [7]. The conventional way to prepare oxide materials is the "ceramic method" based on solid-state reactions between the binary oxides, which requires heat treatments classically beyond 1000 °C [105]. With the ever increasing emphasis on greener chemical approaches, there is a growing interest in designing alternative synthetic routes that enable lower temperature and selective phase synthesis to obtain alkali niobates such as $K_xNa_{1-x}NbO_3$, which represent environmentally friendly lead-free piezoelectric materials [13,124-128].

An efficient, simple, cost beneficial and environmentally benign synthetic protocol for the preparation of $K_{0.5}Na_{0.5}NbO_3$ nano sized powders from pure aqueous precursor solutions was successfully demonstrated by Stavber *et al.* [13] (**Scheme 1.2**). They used precursors based on the niobium(V)-peroxo-citrate and niobium(V)-peroxo-glycine intermediates in order to obtain stable Nb^{5+} ions in water and to establish compositional homogeneity and the fine particle size of the powders [13].
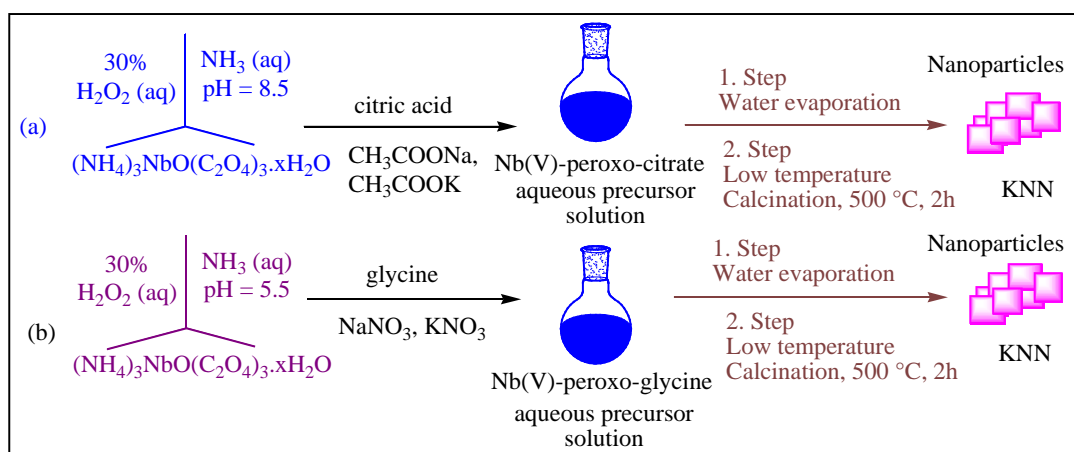
Scheme 1.2 An illustration of the green synthetic approach for preparation of KNN powders from aqueous solutions through (a) niobium(V)-peroxo-citrate (b) niobium(V)-peroxo-glycine precursors [13].

Using $(gu)_3[Nb(O_2)_2(edtaO_2)]\cdot 2H_2O$ and $(gu)_3[Ta(O_2)_2(edtaO_2)]\cdot 2H_2O$ species as molecular precursors, Bayot and Devillers [128] prepared multimetallic oxides of the general formula $(Ta_xNb_{1-x})_2O_5$, $Ta_xNb_{1-x}VO_5$ and $BiTa_xNb_{1-x}O_4$ $(0 < x < 1)$, under reasonably mild conditions and with specific morphology and textural properties. It has been demonstrated that the binuclear peroxo complexes containing niobium and tantalum have been used to prepare Nb-Ta mixed oxides from the heterobimetallic peroxo-tartrato and peroxo-PAC complexes of stoichiometry $(gu)_5[NbTa(O_2)_4(tart)(Htart)]\cdot 4H_2O$, $(gu)_3[NbTa(O_2)_4(dtpaO_3)]\cdot 5/2H_2O$ and $(gu)_3[NbTa(O_2)_4(HtthaO_4)]\cdot 2H_2O$ [105]. Work from the same laboratory also demonstrated peroxo-carboxylato compounds of the general formula $(NH_4)_3[NbO-(ox)_3]\cdot H_2O$ to be useful precursors for obtaining Nb-Mo oxide phases such as $Nb_2Mo_3O_{14}$ phase supported on silica, when combining them with analogous peroxo-carboxylato complexes of Mo(VI), $(NH_4)_2[MoO_3(ox)]\cdot H_2O$ [129]. In some studies, to generate niobates, "peroxo-niobic" solution was used which is prepared *in situ* from niobic acid dissolved in excess H_2O_2 medium, without additive [16,130,131] or in the presence of complexing agents like citric acid [15,132] or H4edta [133]. High purity Nb_2O_5 has been obtained from the hydrolytic decomposition [95] as well as from the thermal treatment [94] of $(NH_4)_3[Nb(O_2)_4]$. Using the triperoxoniobate complex, $Na[Nb(O_2)_3]\cdot 2H_2O$ as a precursor molecule, Dey *et al.* [134] synthesized pure crystalline $NaNbO_3$ by simple calcinations of the triperoxoniobate compound in air at reduced temperature of 400-500 °C. Narendar and co-workers [15] also developed a route for the formation of niobium oxide using the synthesized peroxo-citrato-niobium complex as precursor.

1.2.3.2 Application in catalysis

Many industrially significant selective oxidation reactions including oxidation of alkenes [11,12,135,136], alcohols [10] and sulfides [57,137,138] have been reported to be catalyzed by peroxoniobium species generated *in situ* in the presence of a variety of oxidants including H_2O_2, TBHP or urea-hydrogen peroxide (**Fig. 1.7**). Nb-containing mixed oxides, niobium pentoxide, and niobic acid have been studied as catalysts and supports for a wide range of heterogeneously catalyzed oxidation reactions [139-141]. Several applications also involve niobium-bearing compounds as promoters or support

for other metals, mainly due to their relatively high catalytic activity and chemical stability [142].

Among the peroxoniobium complexes, tetraperoxoniobate species, $Na_3[Nb(O_2)_4]\cdot13H_2O$ has been used as catalyst in the homogeneous epoxidation of cyclohexene with H_2O_2 as oxidant which provided good selectivity in epoxide with moderate activity [87]. Additionally, the $[Nb(O_2)_4]^{3-}$ anion was immobilized on a quaternary ammonium polystyrene anion-exchange resin and tested in the epoxidation of cyclohexene and oxidation of alcohols [87]. The diperoxo complexes of niobium, of general formula $K[Nb(O_2)_2(L)]\cdot nH_2O$ with Schiff bases ligands, were found to act as active catalysts in oxidation reactions, in the presence of t-butyl hydroperoxide, of secondary alcohols and in the epoxidation of cyclohexene, with moderate selectivity [112]. The $[Nb(O_2)_2L]$ (L = hq) complexes were reported to be highly efficient with respect to oxidation of both organic and inorganic substrates, olefins and phosphines
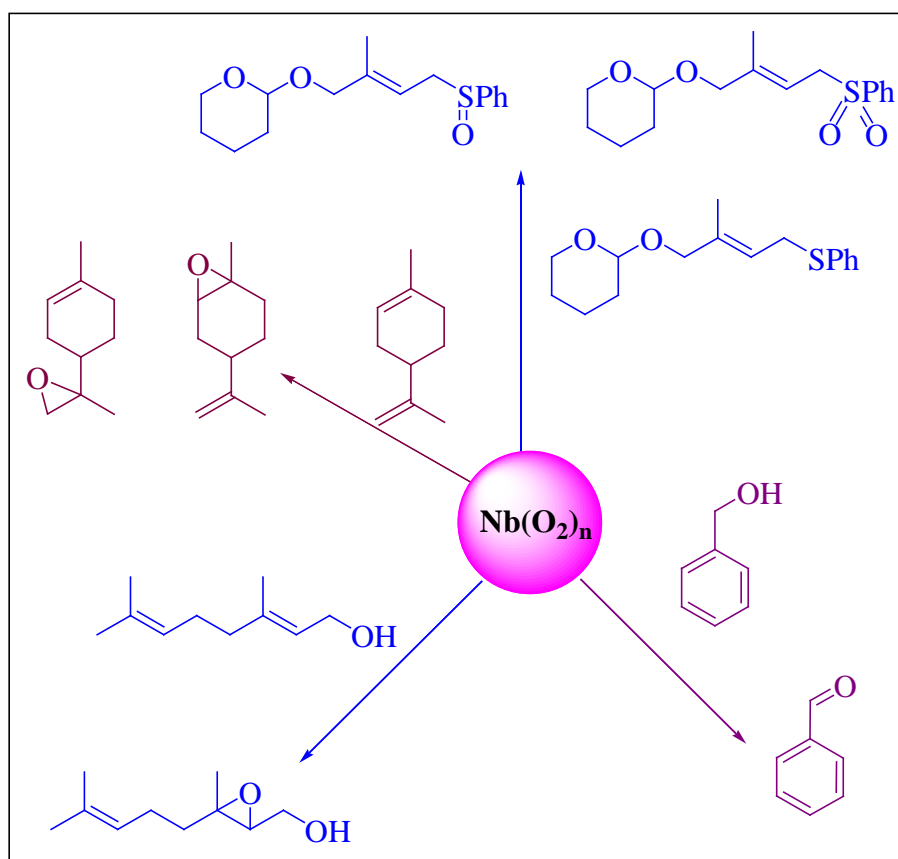
Fig. 1.7 Selected oxidations of organic compounds by Nb-peroxo systems in the presence of hydrogen peroxide [10-12,57].

[103]. Tarafder reported that the complex, [Nb(O$_2$)$_2$(C$_9$H$_6$NO)] can oxidize phosphines to their corresponding oxides and olefins to epoxides under stoichiometric conditions while, under catalytic conditions, *trans* stilbene is converted to α-hydroxyketone [103].

Interestingly, it has been demonstrated that the organometallic peroxo complexes of the type, (R-Cp)$_2$Nb(O$_2$)Cl (R = H or CH$_3$) could oxidize a variety of substrates such as (i) triphenylphosphine to its corresponding oxide (**Eq. 1**), (ii) sulfur dioxide to sulfate, affording the sulfato complex, (R-Cp)$_2$Nb(SO$_4$)Cl) (**Eq. 2**) and (iii) cyclohexene to cyclohexene oxide [115]. On the other hand, Colletti and Halterman tested (*R,R*)-(+)-bis[2,3-(1,1´-binaphtyl-2,2´-dimethyl)cyclopenta-2,4-dienyl]chloroniobium(V) peroxide and bis(η^5-indenyl)chloroniobium(V) peroxide as catalysts in the enantioselective epoxidation of unfunctionalized alkyl and aryl olefins [143].

$$(R\text{-}Cp)_2Nb(SO_4)Cl + PPh_3 \quad \rightarrow \quad (R\text{-}Cp)_2NbOCl + PPh_3O \qquad (1)$$

$$(R\text{-}Cp)_2Nb(O_2)Cl + SO_2 \quad \rightarrow \quad (R\text{-}Cp)_2Nb(SO_4)Cl \qquad (2)$$
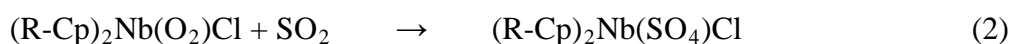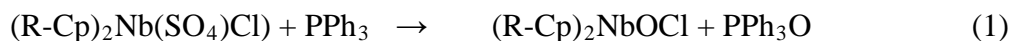
Peroxo complexes, formed in solution from NbCl$_5$ in H$_2$O$_2$ and in the presence of organic ligand such as phosphonic acid or 2,2-bipyridine, have been tested in the oxidation of benzylic alcohol, in biphasic conditions and in the presence of a phase-transfer catalyst, Bu$_4$NOH, which afforded benzaldehyde as the major product in very good yield [10]. Egami *et al.* [12] successfully employed *in situ* prepared Nb(salan) [salan = *N,N*'-bis(*o*-hydroxybenzyl)-1,2-diaminoethane (SaleanH$_4$)] complex to catalyze the highly enantioselective asymmetric epoxidation of allylic alcohol with a urea-hydrogen peroxide adduct in aqueous medium. It was observed that the catalyst did not catalyze the epoxidation of a simple olefin such as 1,2-dihydronaphthalene,which indicated that the pre-coordination of allylic alcohol is necessary for this epoxidation to occur [12]. The mechanism proposed for this reaction suggested the formation of a monomeric peroxo niobium species (a) with hepta-coordination as the possible intermediate during the epoxidation reaction (**Scheme 1.3**) [12].
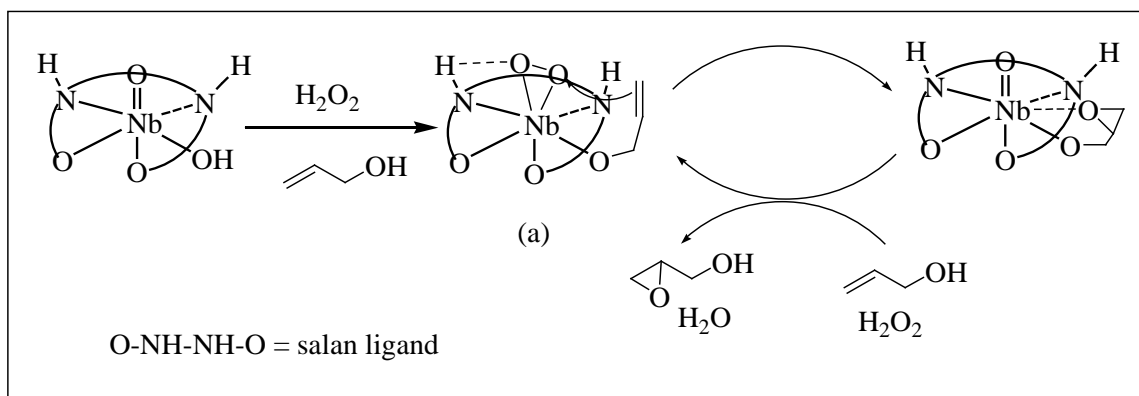
Scheme 1.3 Plausible mechanism for the epoxidation using pre-treated Nb(salan)(OiPr)$_3$ as a catalyst [12].

Scores of Nb and Ta oxide based systems have been reported as efficient catalysts in organic oxidations in presence of variety of oxidants. Very recently Thornburg *et al.* [142] illustrated that silica-supported niobium(V), Nb-SiO$_2$, can be an intrinsically good catalyst for electrophilic activation of H$_2$O$_2$ to oxidize alkene, and it has been established that the Group 5 catalysts (Nb and Ta) provided faster rates of oxidation compared to the more standard Ti-SiO$_2$ catalysts [144,145]. Particularly, Nb-based system has been observed to be a good catalyst as it could be synthesized to give stable, highly under coordinated sites in relatively high abundance and has been found to display excellent rates [142].

Chen *et al.* [8] developed peroxoniobates anion based ionic liquids (ILs) and used these as catalysts for epoxidation of various allylic alcohols. They also studied the mechanism using DFT calculations and proposed the hydrogen bonding mechanism for the reaction, in which OOH in [Nb(O-O)$_2$(OOH)$_2$]$^-$ serves as a highly active group to oxidize the C=C double bond of allylic alcohol while the peroxo group (O-O) can efficiently adsorb the substrate through H-bond interaction (**Scheme 1.4**) [8].

A highly active solid catalyst based on peroxo-niobium immobilized over iron oxide, produced *in situ* by treatment of Nb-doped iron oxides composites with H$_2$O$_2$ was reported by Silva *et al.* [9]. The innovative material was found to be highly active in the oxidation of organic dye in liquid phase [9].
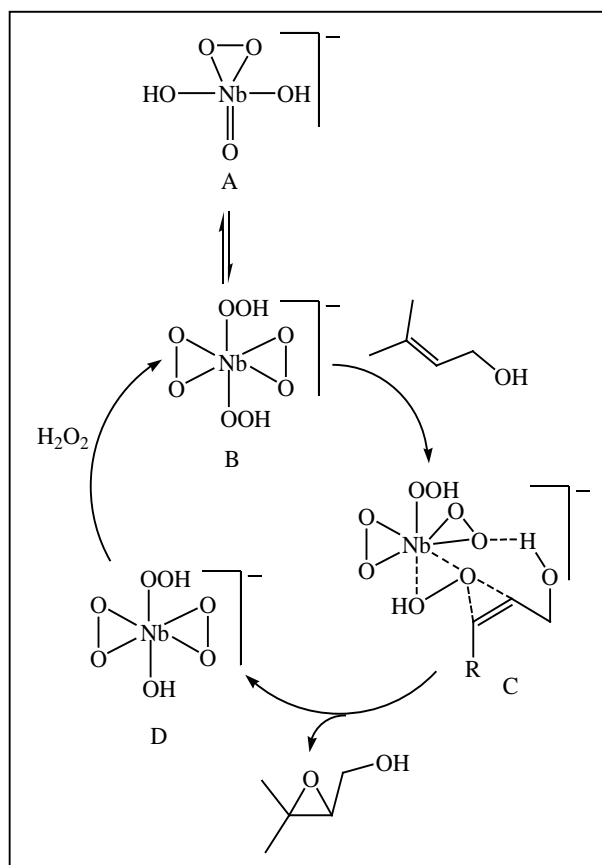
Scheme 1.4 Proposed mechanism for epoxidation of allylic alcohols with H_2O_2 catalyzed by the monomeric peroxoniobate anion of IL [8].

Notwithstanding these important progresses in the field of catalysis by supported pNb systems, no report appears to exist on preparation or use of polymer supported pNb compounds in organic oxidation. Most of the catalyst systems of these metals utilized porous siliceous oxide or other metal oxide supports (MCM-41 and SBA-15) which are known to be associated with certain limitations in terms of their activity and selectivity [145-148]. The reaction of appropriate polymers and reagents with catalytically active groups often confers catalytic activity to the polymer and generates a functional polymer [145]. There has been an increasing demand of application of polymer-supported catalysts in the production of bulk organic substances [149,150].

It is relevant in this context to mention that our group has a long standing interest in developing supported peroxometal complexes immobilized on soluble as well as insoluble polymer matrices which can serve as recoverable catalyst for organic oxidations under environmentally benign reaction conditions [116,151-154].

1.2.4 Polymer immobilized metal complexes – general aspects of macro complexes

It can be easily appreciated that attaching a metal complex or metal as part of a macromolecule can lead to the development of new materials with unique properties [155]. Metal containing polymers have been receiving tremendous attention during the past decades in light of their potential applications in diversified domains ranging from catalysis [156-161], superconducting materials [162], liquid crystals [163], ultra-high strength materials [164], bio-medical applications [165,166] and environment applications [167].

Organic co-polymers as supports for transition metal complexes can allow conjugating a controllable flexibility of the matrix with the possibility to fine-tune the physical properties of the material by appropriate arrangement of co-monomers and cross-linkers [161]. Haag and Whitehurst [168] proposed the first example of an organic polymer supported metal complex in 1969 that consisted of sulfonated polystyrene bearing Pt(II) complexes.

Diverse synthetic approaches to prepare polymer supported complexes in different combinations of metal complexes or metals with organic, inorganic and semi-organic macromolecules have been reported [155]. Moreover, a variety of terms for describing supporting processes have been proposed such as immobilization, anchoring, attachment or "heterogenization of homogeneous complexes" [148]. Based on the kind of interaction a metal complex or metal has with a macromolecule, Wöhrle *et al.* [155,169] classified metal containing macromolecules in the following ways:

Macromolecular Metal Complexes (**Type I**) **(Fig. 1.8):** This class of compounds are formed when a metal complex or a metal ion is linked to a chain of a linear or cross-linked organic polymer *via* a covalent bond or coordinative (at the metal), a complex (at the ligand of a complex), an ionic, or a π-bond formed as illustrated in **Fig 1.8**.
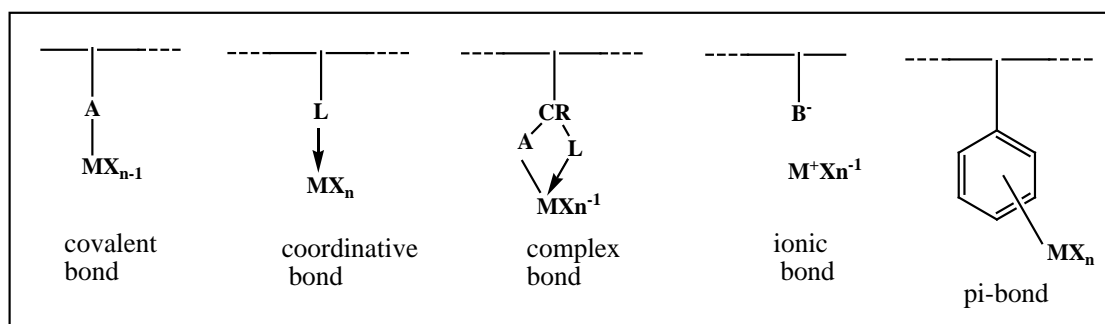
Fig. 1.8 Type I: Metal ions, complexes, chelates at macromolecules [155].

Ligand Macromolecular Complexes (Type II): This type of complexes, in which the ligand of a metal complex is a part of a macromolecular chain or network (**Fig. 1.9 A**), are usually obtained either by direct synthesis from low molecular weight precursors or by metallation of pre-formed macromolecular ligand.

Metal Macromolecular Complexes (Type III): In such compounds, metals or metal complexes exist as part of a macromolecular chain or network (**Fig. 1.9 B**). This class includes co-ordination polymers, π-complexes in the main chain with a metal, cofacially stacked polymer metal complexes, polycatenanes, and dendrimers with metals. Usually the metal is attached with another element such as C, N, O, S *via* a covalent, a coordinate, an ionic, or a π-bond.

Macromolecule Incorporated Metal Complexes (**Type IV**): The physical inclusion and stabilization of metal clusters or metal complexes in macromolecular milieu (**Fig. 1.9 C**) often provides an access to novel composite materials.
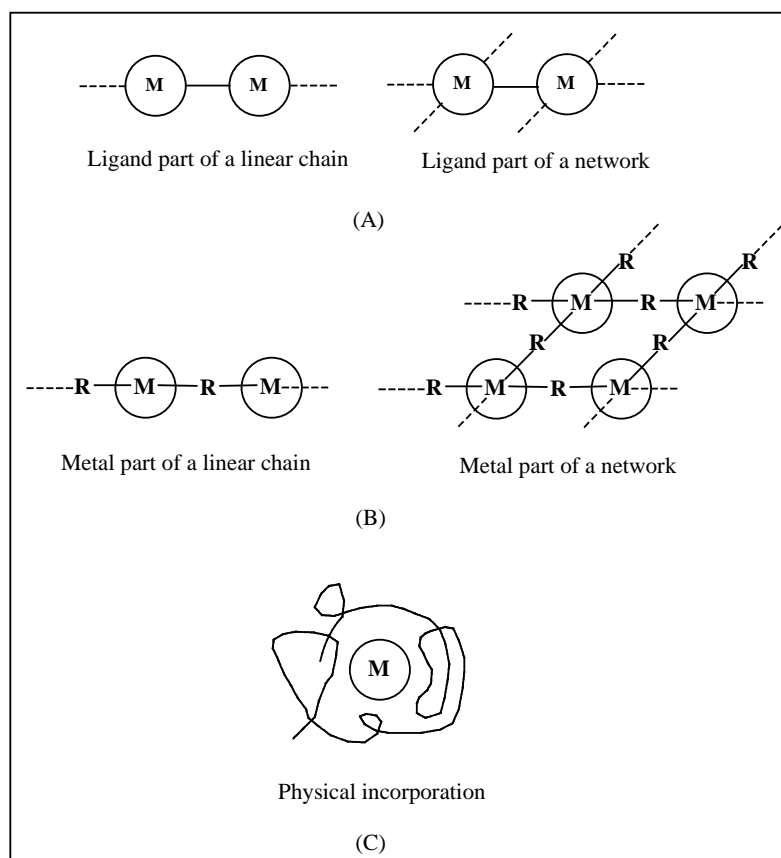
Fig. 1.9 (A) Type II: Ligand of metal complexes, chelates as part of linear or crosslinked macromolecules. (B) Type III: Metal as part of a linear chain or network. (C) Type IV: Physical incorporation of metal complexes, chelates [155].

The anchoring of a specific metal with a specific macromolecule results in both active and selective properties with high performance and stability [155]. A variety of natural as well as synthetic polymeric materials have been employed as matrices to anchor metal complexes [170]. The active transition metal complex may be supported on insoluble or soluble polymeric supports with each type of the support being associated with some advantages as well as disadvantages [149]. In general, the macromolecular metal complexes with linear or branched organic polymers are soluble in organic solvents and their structures can be identified rather easily [116]. The bridged macromolecular metal complexes are less soluble and are more stable with less defined structures [116]. On the other hand, the complexes with intermolecular bridge bonds are difficult to characterize and are insoluble. Some of the reported combinations of metal complexes with the available macroligands and their various catalytic applications, as summarized by Pomogailo [170], are listed in **Table 1.2**.

Table 1.2 The summary of combinations of metal complexes and macroligands, as well as catalyzed reactions most commonly used in practice [170].

Polymer support	Functional group	MX_n	Catalyzed reaction
Phosphinated CSDVB	$-PPh_2$	$RhCl(PPh_3)$ $[CODRhCl]_2$ $Rh(CO)_2(PPh_3)_2$ $PdCl_2(PPh_3)$ $RuCl_2(CO)_2(PPh_3)_3$ $RhHCO(PPh_3)_3$ $[CODRhCl]_2$ $CoCl_2(PPh_3$ $Mo(CO)_2(PPh)_2$ $Fe(CO)_4PPh_3$	Hydrogenation Hydroformylation Deuterium/hydrogen exchange Isomerisation Oligomerisation Cyclooligomerisation
PA	-	Ni(napht)	PhA hydrogenation
PEI/SiO2	NH	Pd^0	nitrobenzene
PE-gr-P4VP	Py	$PdCl_2(PhCN_2)$	p-Nitrochlorobenzene hydrogenation
Polymer support	Functional group	MX_n	Catalyzed reaction
PMMA	$-COOCH_3$	Pd^0	Nitrocompound hydrogenation
PE-gr-PAAc	$-COOH$	Co(AcAc)	Cyclohexene oxidation
PAN	$-C\equiv N$	$M(AcAc)_2(M=Mn, Co)$	Ethyl benzeneIsoprpyl benzene oxidation
Poly(2-vinylpyridine-co-styrene)		Fe^{3+}, Co^{2+}, phthalocyanines	H_2O_2 oxidation
Copolymer of styrene and acrylic acid	$-COOH$	$Ni(napht)_2$	1,4-cis-butadiene polymerisation
Thioacetalderivatives of poly(4-amino-styrene)	$-CH_2$ $-NH_2$	$-Mo(NMe_2)_4$ -	Nitrogen reduction Photocatalytic hydrogen formation

1.2.4.1 Metal complexes anchored to water soluble polymers (WSP)

Water being the basic solvent for natural macromolecules, such as proteins and DNA, coordination compounds of metal ions with soluble macromolecular ligands find relevance in designing biomimetic models [167,171]. Also in the field of organic synthesis, particularly from the perspective of green chemistry, there has been growing emphasis on use of environmentally benign solvents such as water. The concept of anchoring metal species to linear soluble polymers, in general, is receiving great deal of attention, as synthetic WSP have been finding wide use in diverse fields including separation processes [172,173], biomedical [174,175] and environmental applications [176,177]. The use of soluble polymers to recover catalyst and ligands in synthetic approaches to peptide and oligopeptide synthesis were developed by Merrifield as well as Letsinger and Wagner in the 1960's [178,179]. These discoveries revolutionized the synthesis of biomolecules [180]. They provided impetus for research in industrial and academic laboratories that was directed toward developing immobilized or heterogenized homogeneous catalysts.

Examples of soluble polymers bearing different functional groups available which are used as support for metal anchoring are presented in **Fig. 1.10** [160]**.** The commonly occurring ligands in these polychelatogens include amines, carboxylic acids, amides, alcohols, amino acids, pyridines and thiourea [167,181].

1.2.4.2 WSP supported metal complexes as catalysts

The first example where a soluble polymer was used as an alternative to a cross-linked insoluble polymeric resin to support a chiral ligand, was reported in 1976 by Bayer and Schurig [182]. A linearpolystyrene-bound version of DIOP [4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane] ligand was allowed to react with $HRh(CO)-(PPh_3)_3$, and the resulting polymer-bound Rh complex was used to hydroformylate styrene [182]. An important progress in soluble polymer support occurred with the report of Han and Janda [183] on supported chiral catalysts for asymmetric dihydroxylation of olefins, in the year 1996.

Although the use of WSP in catalysis appears to be a relatively new concept, transition metal complexes attached to a soluble non-cross-linked polymer is essentially a
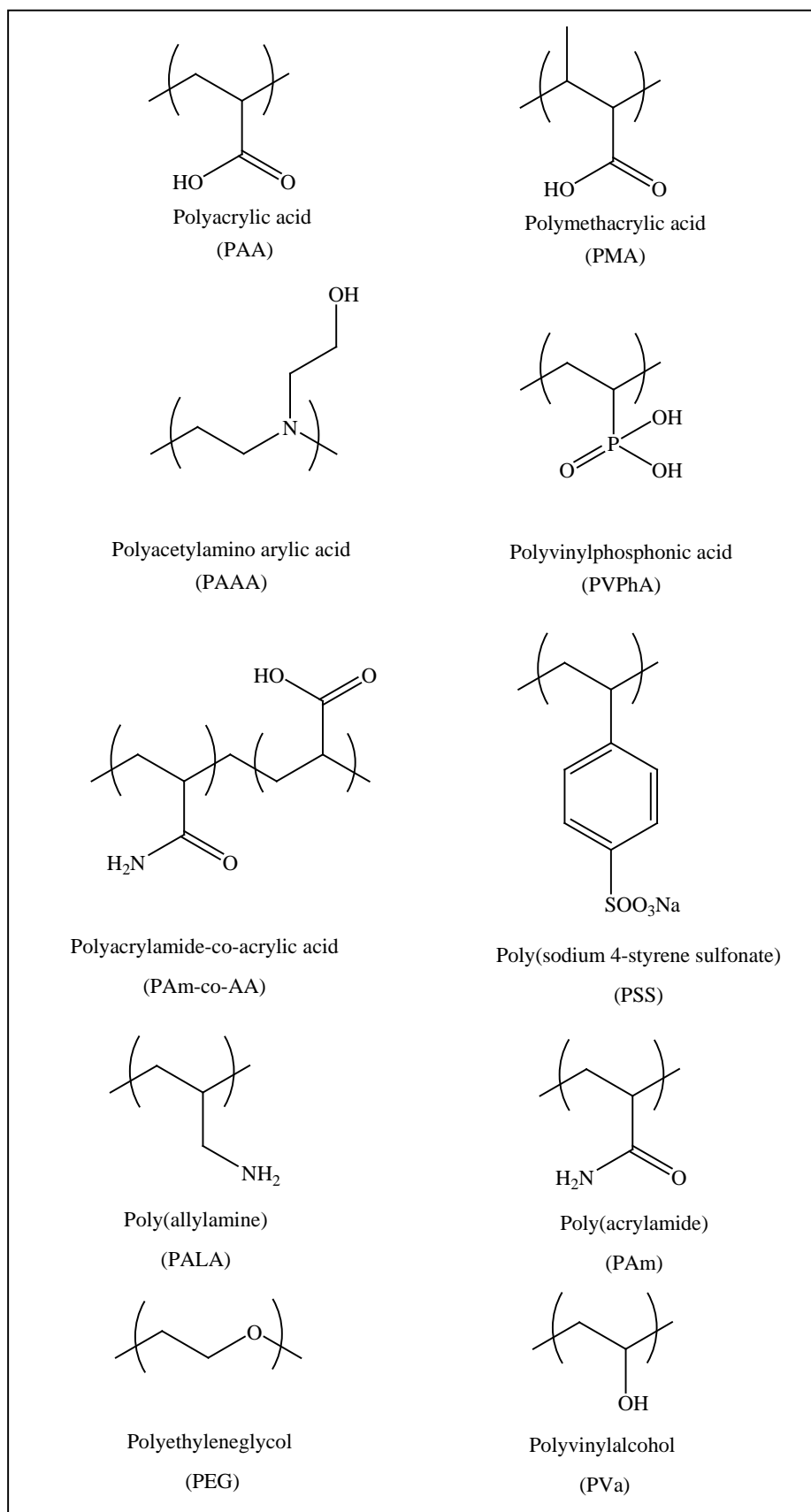
Fig. 1.10 Some water-soluble polymers used for metal ion interaction [160].

homogeneous catalyst with macromolecular ligands [116]. In fact, immobilized catalysts combine the main features of homogeneous, heterogeneous and enzymatic catalysts such as high activity and selectivity, specific character, and stability in operation which enhances their efficiency [149]. The use of polymer groups as ligands permits the ligand surroundings to be varied and regulation of the catalytic properties of the complexes become possible because of the flexibility of the macromolecular chains and their ability to adopt various conformations. Depending on the chemical nature of initial components, immobilized complexes can be soluble or insoluble in the reaction mixtures, therefore it is possible to transform homogeneous into heterogeneous catalysts and *vice versa*, which is a remarkable feature of such systems [170].

Despite the myriad advantages of insoluble supports, there are several shortcomings in the use of these resins due to the heterogeneous nature of the reaction conditions [160]. The limitations involving insoluble polymer support include nonlinear kinetic behaviour, unequal distribution or access to the chemical reaction, solvation problems associated with the nature of the support and synthetic difficulties in transferring standard organic reactions to the solid phase [160]. A possible way to overcome such issues is to use low molecular weight soluble linear polymers as supports [159,160,184-186] which reinstated the familiar reaction conditions of classical organic chemistry [160]. An additional advantage is that the chemical reactions performed on such polymers can be monitored by high resolution solution phase ^{1}H and ^{13}C NMR spectroscopy [187,188].

The recovery of the polymer supported catalyst can be achieved by temperature or solvent-induced precipitation followed by filtration [159,160]. Soluble polymers, till recently, have received less attention as polymeric supports compared to their insoluble counterparts due to the difficulty in isolation of the polymer from all other reaction components [116]. In practice, however, the homogeneous polymer solution is simply diluted with an appropriate solvent that induces precipitation of the support, followed by filtration to isolate the polymer [159,160]. Besides the solvent-induced precipitation technique, crystallization, dialysis and centrifugation methods could also be applied for the separation of polymer from reaction mixtures [159,160].

Among the various types of soluble polymers, non-cross-linked linear polystyrene and poly(ethylene glycol) (PEG), also known as poly(ethylene oxide), poly(oxyethylene) and polyoxirane, are some of the popular examples used in the preparation of soluble polymer-supported catalysts [160]. The modified poly(ethylene oxide) catalyst is widely used in catalysis for hydrogenation [189,190], Sharpless asymmetric dihydroxylation reaction [183,191], hydroformylation [192], Wacker oxidation [193,194], hydroxylation of aromatic compounds [195] and epoxidation [160,196]. Additionally, PEG is also well known for its ability to act as a phase transfer catalyst [160,197]. For instance, anchoring of rhodium to PEG was reported which catalyze hydrogenation of various olefins in water [189]. Polycarboxylic acid and its derivative are often used to synthesize soluble ligands and complexes. In this aspect, reports are available on manganese, cobalt, iron, copper or chromium complexes anchored on poly(acrylic acid) for autooxidations of cumene to cumene hydroperoxides [198-200]. Furthermore, a poly(acrylic acid)-Rh(II) complex was reported which has very high catalytic activity for the hydrogenation of olefins in homogeneous solution [201,202]. Besides poly(acrylic acid), poly(pentenoic acid) has also been used to produce phosphine containing ligands [203]. Polyacrylamide modified with optically active phosphine containing ligands and Rh catalysts were used for asymmetric hydrogenation of prochiral amides [204]. Wilson and Whitesides [205] used a water soluble natural polymer - a protein as support to prepare an asymmetric Rh(I) hydrogenation catalyst. Bayer and Schumann [206] described the use of linear polymers such as poly(vinylpyrrolidinone), polyethylenimine, polyacrylonitrile, and poly-(ethyleniminodiacetic acid) as polychelatogens with Rh, Pd, Pt and Ni as efficient hydrogenation catalysts. After reaction completion, the phases were allowed to separate and the aqueous catalyst solution could be reused directly.

1.2.4.3 Biological applications of soluble macro complexes

Immobilized complexes can be considered as models of biological catalysts because they can carry out multi-centre activation of a substrate like the metal enzyme [207]. The polymer bound metal complexes were shown to act as models for several metalloproteins and metalloenzymes including catalase, peroxidase, cytochrome P_{450}, myoglobin, hemoglobin, vitamin B12, proteolytic and other enzymes [149,170].

Recently, Kubota *et al.* [208] developed a polymer-bound Mn-porphyrin system as an artificial active center of catalase and it is reported to be the first water-soluble polymer-bound Mn-porphyrins as an artificial catalase model that is active at physiological pH.

Application of polymer-metal adducts provided new strategies in the development of pharmaceutical formulations and many other biological studies [209]. It has been reported that the polymer-metal ion complexes show a reduced genotoxic activity compared with free metal ions [209]. Binding of active drug molecules to water-soluble polymeric drug carriers offers a variety of merits including improved drug pharmacokinetics, lower toxicity to healthy organs, possible facilitation of preferential uptake by targeted cells and programmed drug release profile [210,211]. In addition, water-soluble polymer makes it possible to solubilize hydrophobic drugs, simplifying the formulation to administer intravenously [212].

A variety of polymers are used in the development of pharmaceutical formulations and other biomedical applications such as poly(acrylamide) [213], poly(4-vinylpyridine) [213], derivatives of poly(aspartamide) [213], poly(ethyleneimine) [213] and derivatives of poly(methacrylamide) with dextrane [213], polyphosphazenes [214], derivatives of poly(methacrylic acid) [215,216], synthetic poly(aminoacids) [217,218], analogues of nucleic acids [219,220], poly(ethylene oxide) [221], copolymers of vinyl pyrrolidone [222], polyamides [223], and polyamines [223]. A remarkable improvement has been achieved in case of platinum based anti-cancer drugs by anchoring it to soluble polymers [210]. It has been found that the polymer drug conjugates are more active and effective in suppressing ovarian tumor growth *in vivo* compared to their low molecular weight analogue [211]. Valente and Zinck [212] explained the advantages offered by drug conjugation to water-soluble polymers. As illustrated in **Fig. 1.11** such a system usually confines cellular uptake to the endocytic route permitting tumour-specific target of low molecular weight chemotherapeutic agents, at the same time preventing the access of the conjugate to the normal sites of toxicity [211]. In view of these advancements, it appears likely that metal containing polymers would be a rich source of potential future therapeutic agents [224].
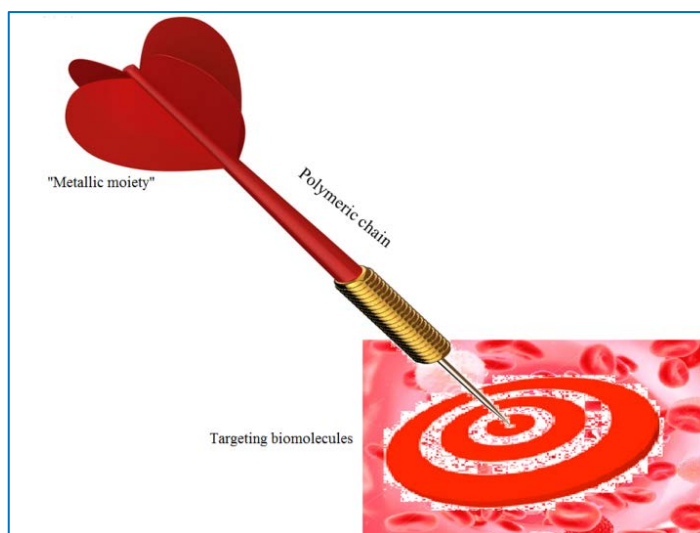
Fig. 1.11 "Metallic-arrows" tailored with targeting vectors which will efficiently shot to the cancer cells [211].

The majority of metal-containing polymers, particularly the transition metal-containing polymers, showed fascinating antimicrobial and antiviral properties [225]. Rivas and his co-workers introduced Ag(I) based water-soluble complexes supported on poly(4-ethylene azide) N-alkylated, poly(diallyldimethylammonium chloride) (PDDA) or poly[((3-methacryloylamino)propyl)trimethylammonium chloride] (PMPTA) which served as bactericidal agent against both Gram-positive and Gram-negative bacteria [209]. It is observed that the polymer based anti-bacterial agents being non-volatile, chemically stable, can reduce the loss associated with volatilization, photolytic decomposition and transportation [226,227]. Previous work from our group reported the antibacterial activity of peroxovanadium compounds anchored to poly(acrylate) and poly(methacrylate) against E. coli and S. aureus [227]. It is notable that WSPs were used for the first time in our laboratory to immobilize peroxo metal derivatives, which led to development of a series of pV, pMo and pW containing macro complexes with interesting bio-relevant features [116,119,120,228].

From the foregoing discussion based on survey of relevant literature, it is clear that despite the multitude of pNb complexes synthesized and studied in recent years and the tremendous advancement in the domain of metal containing polymers, no report appears to exist on design, synthesis and application of pNb compounds immobilized on polymer matrices, although polymer anchored complexes of other d^0 transition-metals

viz., V, Mo and W are available and have been extensively investigated [116,119,120,170,228,229]. Moreover, we have come across only few reports on heteroleptic pNb complexes containing biogenic species as ancillary ligands [13,230]. There is also a paucity of information on exploration of biochemical potential of peroxo-niobium compounds.

In line with the scope highlighted above, the present research programme has been undertaken which is focused on three basic goals: (i) to gain an access to peroxoniobium compounds with biologically important attributes such as hydrolytic stability and low toxicity, (ii) to investigate interaction of pNb derivatives with certain enzyme functions and (iii) to develop newer pNb based catalysts and eco-compatible routes for organic oxidative transformations.

Chapters **3** to **8** of the thesis present interpretative accounts of the findings of our investigations on the aforementioned aspects of peroxoniobium chemistry. Each of these Chapters has been so designed as to make it a self-contained one with brief introduction, sections on experimental, results and discussion and conclusions followed by relevant bibliography. The majority of new results have been either published or are under communication.

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