# CHAPTER 1

## Introduction

## 1.1 Preamble

The chemistry of niobium and its compounds have been garnering a great deal of contemporary interest, essentially owing to their multiple utility in diverse domains ranging from catalysis to their use in designing advanced materials for high technology applications [1-6]. The work presented in this thesis is mainly focused on the development of some new structurally defined niobium compounds, including peroxidoniobates immobilized on a range of polymer supports and investigation on their catalytic potential as well as their selected bio-relevant aspects. Transition metal peroxido complexes, in general, continue to remain the subject of intense research over the past decades due to their well-documented catalytic, biological and therapeutic applications [7-17]. Viable routes to newer members of peroxidometallates open the prospect of gaining an access to novel homogeneous and heterogeneous catalysts, as well as biologically active agents.

A concise review of the following interrelated areas relevant to the work embodied in the thesis is presented in this Chapter:

1) Selected features of niobium and its compounds.
2) Salient attributes of niobium(V) peroxido complexes.
3) Anchoring of metal complexes to various types of soluble and insoluble polymer supports and the significance of such macromolecular systems in catalysis and biology.

## 1.2 Background information

### 1.2.1 Niobium (Nb) – general comments

Niobium (Nb) is a group V transition element of the periodic table with an atomic number of 41, atomic mass of 92.91(2) units and ground-state electronic configuration of $[Kr]4d^4 5s$ [1,18]. The element was first discovered by an English chemist, Charles Hatchett, in the year 1801 [1]. Niobium is ranked 31st in the order of crustal abundance, with its assessed abundance being 12 ppm in the upper continental crust [19,20]. Due to the high charge to ionic radius ratio, niobium is insoluble in most of the geological fluids and behaves as a Pearson's acid that can only be complex with strong ligands, *viz.*, $O^{2-}$, $OH^-$ and $F^-$ [19]. Niobium does not occur as a pure metal in nature; however, it is concentrated in a range of comparatively rare oxide and hydroxide minerals and a few rare borate and silicate minerals as well [21,22]. Primarily, Nb is derived from the pyrochlore

group of complex oxides [(Na,Ca,Ce)$_2$(Nb,Ti,Ta)$_2$(O,OH,F)$_7$], found in some alkaline igneous rocks comprising of Na- or K-rich minerals and deficient or devoid of quartz [21], carbonatites which are found in some igneous rocks with a composition having more than 50% by volume of primary carbonate minerals [21] and columbite [(Fe/Mn)(Nb/Ta)$_2$O$_6$] [23]. $^{93}$Nb is the only stable isotope of niobium. Apart from that, Nb has eight radiogenic isotopes with an atomic mass range from 89 to 97 [19].

Niobium is a soft, lustrous, ductile, and grey metal possessing properties like high melting (2468 ℃) and boiling points (4744 ℃), relatively low density, thermal/chemical stability, and superconductivity [1,19,24]. The primary applications of niobium are based on its conductivity, hardness, and corrosion resistance [1,24]. Niobium is widely used in ferrous metallurgy to produce stainless steels for high temperature applications, including heat-resisting and combustion equipment, turbocharger systems, rocket subassemblies, gas turbines and jet engine components [1,21]. Presence of niobium enhances the corrosion resistance, tenacity, mechanical strength, and lightness of steel alloys [21]. Niobium alloys have also been utilized in the fabrication of superconducting magnets applied in the instruments of nuclear magnetic resonance (NMRI), tomographs for magnetic resonance imaging (MRI) and particle accelerators [1,21]. Multiple utilities of niobium-based oxides in the field of energy as electrodes for Li-, Na-ion batteries, supercapacitors, memristors, dye-sensitized solar cells, and solar fuel production are well-established [5,6,25]. The diverse range of potential applications of Nb-based materials are summarized in **Fig. 1.1**.
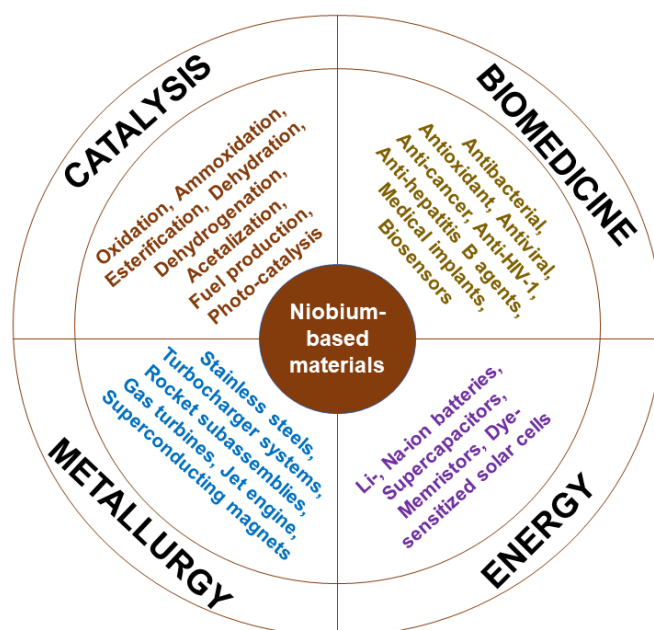


**Fig. 1.1** Application of niobium and various niobium-based compounds [1-6].

In the elemental state, niobium is known to be non-toxic to animals, with a very high $LD_{50}$ value compared to its lighter analog vanadium, which is reported to be moderately toxic in nature [26]. Therefore, Nb is the appropriate alternative alloying element for V in biomedical applications where the release of alloying element can cause fatal impact [27]. Significantly, niobium and its oxides are known to exhibit good biocompatibility and osteoconductivity [2,28]. According to the recent critical review by Safavi *et al.* [2], oxides of niobium are documented to be chemically, thermally and thermodynamically stable, highly corrosion-resistant, hypoallergenic, bioinert and biocompatible materials with great biological features aiding cellular attachment, growth, proliferation and metabolic activity making them suitable candidates for the applications in biomedicines as well as fabrication of synthetic medical implants and biosensors [3,29]. In addition, Nb-based compounds have widely been investigated for antibacterial [30], antioxidant [31], antiviral [32,33], and anticancer activities [4,30,31]. Pereira-Maia *et al.* reported a new class of polyoxoniobates (PONs) that can restrain the development of tumours by altering the electron density in the malignant cells and inhibiting their growth by oxidative stress [4]. The enhanced cytotoxic activity under UV irradiation and non-toxicity make PONs attractive for the application in photodynamic therapy [4]. Niobocene dichloride ($Cp_2NbCl_2$), as an analog to the cytostatic complex titanocene dichloride [34], exhibits impressive tumour-inhibiting properties against the Ehrlich ascites tumour in CFI mice [35]. However, the air oxidation of $Cp_2NbCl_2$ produces a less toxic binuclear Nb(V) complex but eventually reduces its cancerostatic property [35]. Apart from that, heteropolytungstates substituted with niobium were described as effective anti-hepatitis B [33] and anti-HIV-1 agents [32].

Niobium-based system as support for the immobilization of biomolecule or enzyme has also been an emerging area of research that may provide long-term stability, ease of recovery, and recyclability of enzymes [36,37]. Intercalation of haemoglobin (Hb) at the galleries of layered niobate $HCa_2Nb_3O_{10}$ has been displayed to improve the activity of Hb [36]. Gao and Gao [37] have developed a Hb-$HCa_2Nb_3O_{10}$ modified electrode based on the stabilizing effect of the layered niobates [**Scheme 1.1**] and established that it can exhibit electrocatalytic response to detect $H_2O_2$ in strongly acidic and basic solutions within the pH of 1-12 and thus, introduced a new class of biosensors.
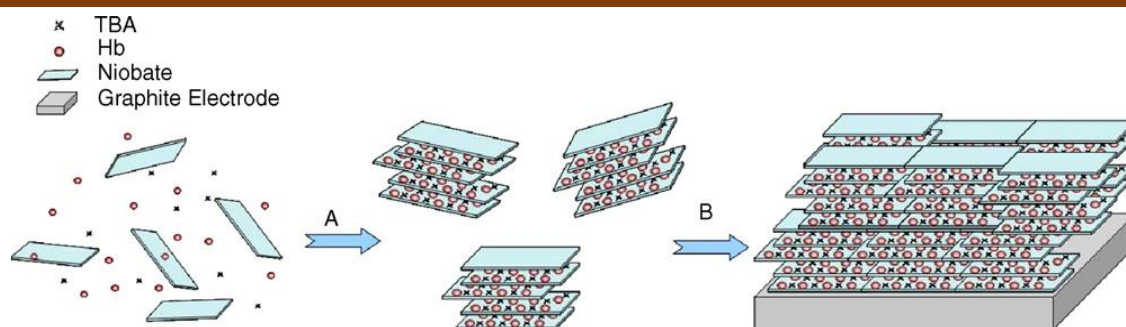
**Scheme 1.1** The preparation progress of Hb–HCa$_2$Nb$_3$O$_{10}$ modified electrode [37].

In addition to their application in advanced materials and biomedical research, Nb compounds have been extensively employed as homogeneous or heterogeneous catalysts [38-46], as catalytically active phase, or key promoters in catalyst formulation [47,48], or as catalyst support [49-52] in a variety of organic reactions. As catalysts, Nb-based materials have been investigated in the esterification of levulinic acid [53] and fatty acids [54], dehydration and oxidation of alcohols [45,55-58], selective epoxidation of alkenes [39,41,42,59-62], cycloaddition [63] and acetalization reactions [64] etc. Niobium-based catalysts have been reported to possess both Brønsted and Lewis acid sites with controllable ratios and retain their catalytic activity even under high temperatures and in polar solvents [40]. Niobium containing molecular sieves and mesoporous silica have been finding use in a range of organic reactions, including cyclohexanone-oxime conversion to caprolactam [65], liquid phase oxidation of olefins, organic sulfides, terpenes and glycerol with hydrogen peroxide [66-74], biodiesel production [75], etc. Ziolek *et al*. [47] elaborately discussed the role of Nb as a component supported on zeolites and molecular sieves and stated that modification of Nb-molecular sieves (Nb-MCF, Nb-SBA-3, Nb-MCM-41) or Nb$_2$O$_5$ with other transition metals like Cu, Pt, Au or thio- and amino-organosilanes introduces new surface properties and enhances the catalytic activity of the catalysts.

In the recent past, structurally well-defined metal-organic-frameworks (MOFs) composed of metal nodes and organic linkers have been attracting a great deal of importance as promising catalysts support [76,77]. Ahn *et al*. have reported grafting of the Nb(V) oxides onto the nodes of the Zr-based metal organic framework (MOF) NU-1000 *via* two different approaches, namely, AIM (vapor-phase atomic layer deposition in a MOF) and SIM (solution-phase grafting in a MOF) (**Fig. 1.2**) [76]. Their findings revealed

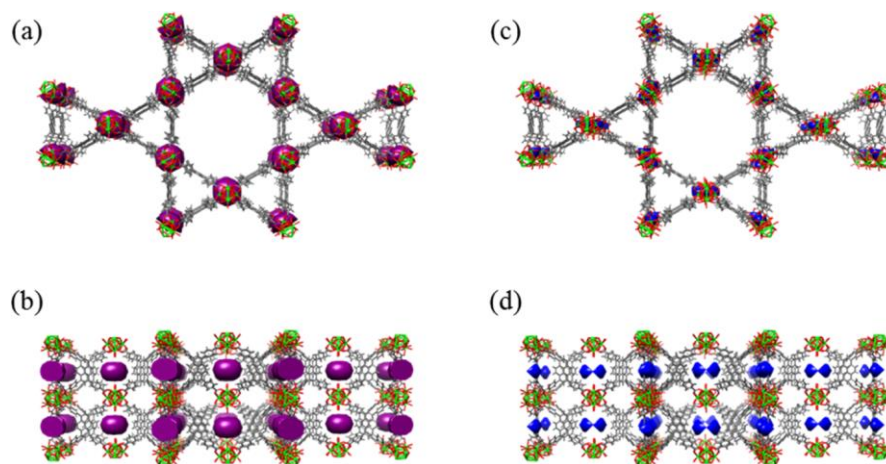that nearly all Nb(V) sites of the MOF-supported catalysts were active sites for alkene epoxidation [76].



**Fig. 1.2** Mapping of Nb-AIM (a) views along the c axis and (b) a axis and of Nb-SIM (c) views along the c axis and (d) a axis [76].

Application of niobium in various photocatalytic processes has also emerged as a highly promising area during the last few years [1,78,80]. Pure or doped $Nb_2O_5$ are documented to be capable of the photo-degradation of organic contaminants from wastewater and the production of fine chemicals [79]. In addition to $Nb_2O_5$, other Nb-based compounds such as $Li/Na/KNbO_3$ and $HNb_3O_8$ have been applied for the conversion of $CO_2$ to methane [80,81]. Nb-based perovskite oxynitrides with lower bandgaps could effectively be applied in the photocatalytic water-splitting reaction under visible light [82]. Recently, Islam and group comprehensively reviewed the structure, design, and efficiency of different niobium-based photocatalysts for the production of robust hydrogen ($H_2$) *via* water splitting reaction [83].

### 1.2.2 A quick glance at the coordination chemistry of niobium

Niobium displays a rich coordination chemistry with oxidation states ranging from −III to +V, although species with –II oxidation is yet to be identified [23]. Niobium chemistry is however dominated by its higher oxidation states, particularly +V. Examples of compounds of niobium with various coordination numbers and oxidation states and their geometries are listed in **Table 1.1**. Niobium has the propensity to form multiple bonds with nonmetals, *viz.*, O, S, N or C and construct hexanuclear clusters [23,84]. Nb can simultaneously bind to a large number of ligands and, thereby, show higher coordination numbers resulting in a dynamic and fluxional coordination sphere. Albeit hexa- and hepta-

coordination numbers are the most common for niobium, large coordination numbers like eight, nine or even ten have also been reported [23, 85,86].

**Table 1.1:** Common stereochemistry of Nb compounds in different oxidation states [23]

| Oxidation state | Coordination number | Idealized geometry | Examples of compounds |
|---|---|---|---|
| +V (d$^0$) | 4 | Tetrahedron | $NbO_4^{3-}$, $NbO[N(SiMe_3)_2]_3$ |
| | 5 | Trigonal bipyramid | $NbS(S\text{-}t\text{-}Bu)_4^-$, $NbCl_{5(vap)}$ |
| | 5 | Square-based pyramid | $Nb(NMe_2)_5$, $NbS(SPh)_4^-$ |
| | 6 | Octahedron | $NbAlCl_8$, $[Nb(OMe)_5]_2$ |
| | 6 | Trigonal prism | $Nb(CH_3)_6^-$, $[Nb(SC_2H_4S)_3]^-$ |
| | 7 | Capped octahedron | $NbOCl_3(PMe_3)_3$ |
| | 7 | Pentagonal bipyramid | $[NbO(C_2O_4)_3]^{3-}$, $NbOF_6^{3-}$ |
| | 8 | Capped trigonal prism | $NbF_7^{2-}$ |
| | 8 | Dodecahedron | $[Nb(\eta^2\text{-}O_2)_4]^{3-}$, $[Nb(\eta^2\text{-}O_2)_2(C_2O_4)_2]^{3-}$ |
| | 9 | – | $[NbCl_3(Cp)_2]_2O$ |
| +IV(d$^1$) | 4 | Tetrahedron | $Nb(NR_2)_4$, $Nb(NR_2)_2Cl_2$ |
| | 5 | Trigonal bipyramid | $[NbH_2(OSi\text{-}t\text{-}Bu_3)_2]_2$ |
| | 6 | Octahedron | $NbX_4L_2$, $NbCl_6^{2-}$ |
| | 7 | Pentagonal bipyramid | $NbF_7^{3-}$ |
| | 7 | Capped octahedron | $NbBr_4(PPhMe_2)_3$ |
| | 8 | Dodecahedron | $Nb[S_2P(OR)_2]_4$, $Nb(CN)_8^{4-}$ |
| | 8 | Square antiprism | $Nb(thd)_4$, $Nb(SCN)_4(bipy)_2$ |
| | 9 | – | $Nb(acac)_4(dioxane)$ |
| +III(d$^2$) | 4 | Tetrahedron (flattened) | $Nb(silox)_3(PMe_3)$ |
| | 6 | Octahedron | $NbCl_3(py)_3$, $Nb_2X_9^{3-}$ |
| | 8 | Dodecahedron | $Nb(CN)_8^{5-}$ (solid) |
| | 8 | Square antiprism | $Nb(CN)_8^{5-}$ (solution) |
| +II(d$^3$) | 6 | Octahedron | $NbCl_2(PMe_3)_4$, $t\text{-}NbCl_2(py)_4$ |
| +I(d$^4$) | 7 | 'Four-legged piano stool' | $Nb(CO)_4(\eta^5\text{-}Cp)$ |

*Continued…*

| Oxidation state | Coordination number | Idealized geometry | Examples of compounds |
|---|---|---|---|
| $+I(d^4)$ | 7 | Capped trigonal prism | $NbCl(CO)_3(PMe_3)_3$ |
| $0(d^5)$ | 6 | Octahedron | $Nb(dmpe)_3$, |
| | | | $Nb(CO)_2(NO)(PPP)$ |
| | 6 | Sandwich | $Nb(\eta^6\text{-arene})_2$ |
| $-I(d^6)$ | 6 | Octahedron | $Nb(CO)_6^-$, $HNb(PF_3)_6$ |
| $-III(d^8)$ | 5 | – | $Nb(CO)_5^{3-}$ |
| | 6 | – | $Nb(CO)_3(\eta^5\text{-Cp})^{2-}$ |

Niobium can directly combine with any of the halogens at high temperatures and form pentahalides [87]. The $NbX_5$ (X is a halogen) are known to be predominantly covalent and relatively volatile solids, where the metal is in hexacoordination state *via* the formation of halide bridges [23,87]. The heavier pentahalides form dimers, while the pentafluorides are tetramers [23]. Niobium-pentahalides are barely soluble in non-coordinating solvents and are easily prone to hydrolysis by water, moist air, or hydrolytic solvent [23]. The addition of various Lewis bases containing nitrogen, sulfur or oxygen to $[NbX_5]_n$ causes the breaking of the polynuclear structure and affords monomeric, octahedral, generally non-electrolytic coordination compounds that are usually soluble in chlorinated solvents [87]. Oxidohalo complexes of Nb with general formula $NbOX_3$ (X = F, Cl, Br, I) or $NbO_2X$ can be synthesized by the halogenation of the oxides or controlled oxidation of the pentahalides with dioxygen [23]. The monomeric oxido derivatives of nonhalide niobium complexes can be stabilized by using bulkier O- or N-donor ligands [23]. Niobium-oxygen systems are structurally very complicated and vast. Myriads of niobium oxides have been reported where niobium can have four oxidation states such as 0, +II, +IV and +V [88]. Notably, $Nb_2O_5$ is the most thermodynamically stable Nb-oxygen system with Nb in a +V oxidation state [88]. Niobium pentoxide reveals a structure based on $NbO_6$ octahedra with a slight distortion due to the type of linkage between the octahedra [88].

Furthermore, in aqueous solutions, Nb has a tendency to form orthoniobates ($NbO_4^{3-}$), metaniobates ($NbO^{3-}$), and polyoxoniobates (e.g. $[Nb_6O_{19}]^{8-}$) [23]. Apart from that, peroxido complexes of niobium are other known species derived from aqueous phase [12,23]. Orthoperoxidoniobates get precipitated from the alkaline solution of niobates

while treated with hydrogen peroxide [23,84]. However, the aqueous chemistry of high valent metals like Nb(V) is indeed complicated as such species are extremely sensitive towards hydrolysis, leading to precipitation and undesired phase segregation [23]. In fact, the aqueous phase chemistry of Nb is known to be rather limited to a very few available water-soluble precursors, including the peroxido derivatives [12].

### 1.2.3. Peroxido complexes of niobium – salient features

The chemistry of peroxido complexes of $d^0$ transition metal ions, in general, continues to attract tremendous research interest for the past several decades as they constitute a vital class of reactive intermediates mainly due to their well-documented implications in biologically and industrially important catalytic processes [7-17]. Numerous findings showing the active involvement of peroxidovanadates in V-haloperoxidases [89-91], their activity as enzyme inhibitors [15,16,90,92], antineoplastic [93-97] and insulino-mimetic agents [11,16,92,94,95,98,99] are also partly responsible for triggering a resurgence of interest in these systems.

Peroxido-metal complexes can serve as highly active catalysts in the oxidation of a range of organic substrates such as alcohols, olefins, sulfides, aliphatic and aromatic hydrocarbons, etc., because of their inherent ability to liberate active oxygen either chemically or on irradiation [8,9,17,100,101]. In most cases, peroxidometallates are soluble in water as well as in other organic solvents, contributing to their feasibility as precursors for the synthesis of various oxide materials [12,102-106]. Notably, peroxides of transition metals have been known as a significant group of reactive intermediates in catalytic oxidation processes formed by the interaction of inorganic or organic peroxides, hydrogen peroxide, or molecular oxygen with metal salt or complex [101]. Peroxido metal complex displays a remarkable reactivity aspect of behaving as a 1,3-dipolar reagent ($M^+$–O–O$^-$) with the positive charge confined on the metal and the negative charge on the terminal oxygen atom, thus, can react with both electrophilic and nucleophilic substrates [107].

The different coordination modes of the peroxido moiety to the metal center in a complex have been rationalized by Vaska [108], and based on the characteristics of the dioxygen ligands, all the $O_2$-metal complexes can primarily be categorized into two types, *viz.*, superoxido- and peroxido-complexes. Peroxido-metal complexes consist of a covalently bound dioxygen ligand to the metal resembling $O_2^{2-}$ in a peroxido configuration

[108]. There is a range of possible means, including symmetrical bidentate to a terminal monodentate mode, as shown in **Fig. 1.3**, by which the electron-rich peroxido groups can bind to the metals. Reynolds and Butler [109] investigated the interaction between the peroxido group and the metal ion using *ab initio* and semi-empirical computations and explained the bond as a σ-interaction between the $d_{xy}$ orbital of the metal and an in-plane π* orbital of the peroxido group.
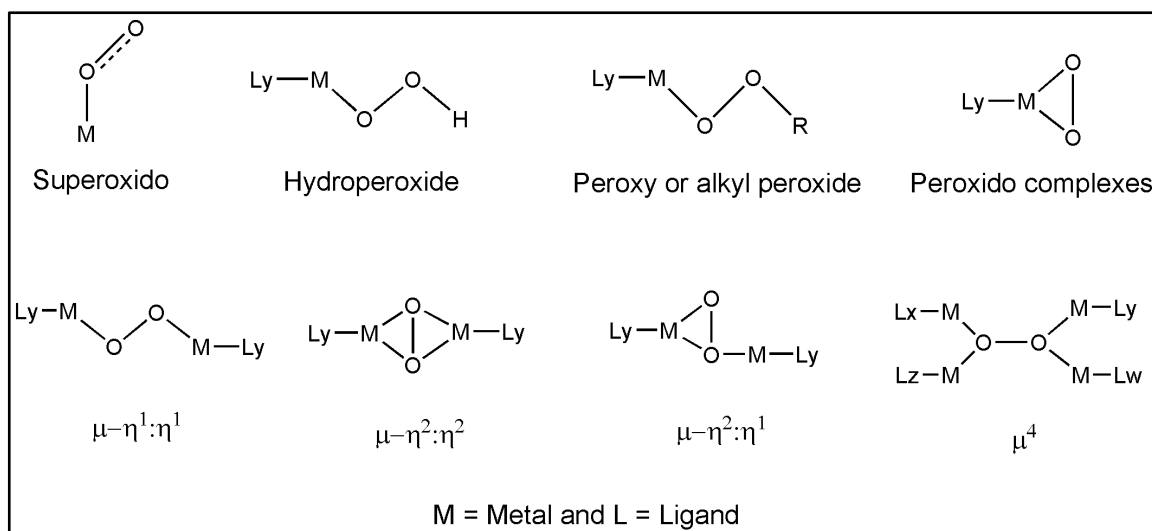


**Fig. 1.3** Structural classification of metal-dioxygen complexes [108].

The mode of oxidation reactions with $H_2O_2$ catalyzed by some of the group 4-6 transition metals originated from the work of Milas and co-workers' dates back to the 30s of the 20th century [8,110-113]. Over the subsequent decades, several interesting procedures were developed in this area and most of these have been utilized in industrial processes [8,114,115]. The accepted mechanism representing metal-catalyzed oxidations with peroxides is illustrated in **Scheme 1.2** [8]. As has already been established, peroxido metal complexes of the type shown in **Scheme 1.2** are much more reactive compared to the peroxide precursors, *viz.*, hydrogen peroxide or alkylhydroperoxide [8]. This fundamental feature has been recognized as the direct link between the chemistry of peroxido metal complexes and metal-catalyzed oxidations [8,108,111].

In case of the peroxidoniobate complexes reported so far, $O_2^{2-}$ groups have been observed to bind to the metal centre exclusively *via* $\eta^2$ mode of coordination [12]. An isoelectronic and isostructural relationship as well as a quasi-identical chemical behaviour, have been found to exist between peroxido complexes of Nb(V) and Ta(V), which is rather
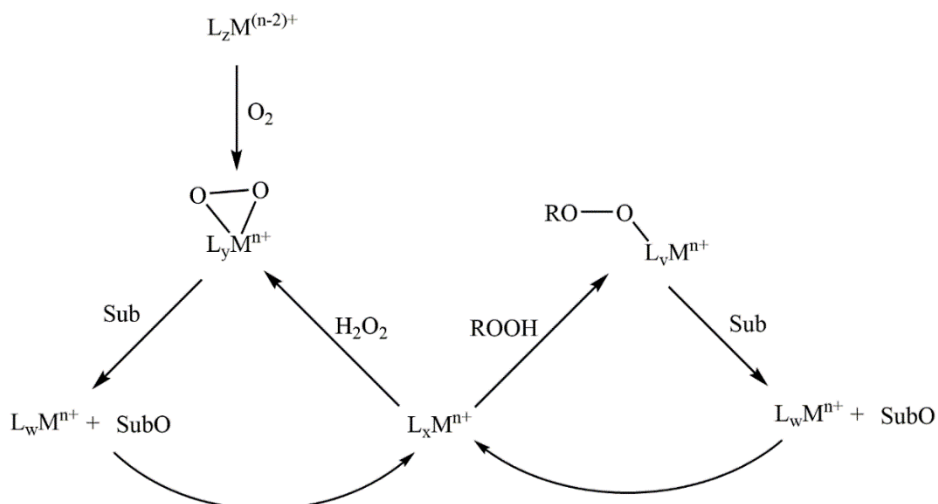
**Scheme 1.2** Metal-catalyzed oxidation with peroxides [8].

different from that of vanadium, the lighter group 5 analog [116]. As vanadium has a propensity to form oxido-peroxido species [116], a majority of the reported peroxido-type V(V) complexes possess one or more vanadyl bonds [90,117]. Moreover, vanadium can easily form bridging peroxido derivatives [116]. It is also notable that, Nb and Ta are known to display an eight-fold coordination in the peroxido compounds [12,116], whereas the coordination number around vanadium in structurally characterized peroxidovanadates (pV) has been reported to be six or seven.

The peroxido chemistry of Nb and Ta was extensively reviewed by Bayot and Devillers [12]. Various factors such as pH, the concentration of Nb and peroxide, ionic strength and reaction temperature influence the composition of the peroxidoniobium (pNb) derivatives formed in an aqueous solution [12]. A variety of peroxido complexes ranging from homoleptic tetraperoxido to mixed-ligand or heteroleptic mono, di- or triperoxido-Nb compounds in diverse ligand environments have been developed and characterized till date [12].

**1.2.3.1 Homoleptic and mixed-ligand/heteroleptic peroxido complexes of niobium**

More than a century ago, Balke and Smith reported for the first time the homoleptic tetraperoxidoniobate anion $[Nb(O_2)_4]^{3-}$ (**TpNb**) containing the highest possible numbers of peroxido groups, produced from an alkaline solution of niobic acid (niobium hydroxide) in hydrogen peroxide [118]. Since then a wide range of salts with $[Nb(O_2)_4]^{3-}$ ion has been developed by varying the alkaline counter cations, for example, $Na^+$ [100,118],

$K^+$ [118-122], $Rb^+$ [118,123] and $Cs^+$ [118]. Apart from that, compounds with ammonium ($NH_4^+$) and guanidinium ($gu^+$; $CN_3H_6^+$) cations, as well as double cationic compositions, were also reported [12,106,118,122,124,125]. Over the years, three general synthetic routes have been established for the preparation of tetraperoxidoniobate compounds namely: (i) fusing of $Nb_2O_5$ with metal hydroxide (Na or K) [100,118,119] or carbonate (Rb) [123] and subsequently dissolving the resulting melt in an aqueous $H_2O_2$ solution; (ii) reaction of $NbCl_5$ with $H_2O_2$ and $gu_2CO_3$ or $NH_3$ [124]; and (iii) dissolving niobic acid with concentrated $H_2O_2$ solution in the presence of $gu_2CO_3$ or $NH_3$ [106]. The crystal structures of tetraperoxidoniobium complexes have been reported to exhibit a dodecahedral geometry ($D_{2d}$) [100,106,122,123] in a tetrahedral arrangement of four $\eta^2$-$O_2^{2-}$ ligands surrounding the niobium satisfying an eight-fold coordination environment as shown in **Fig. 1.4**.
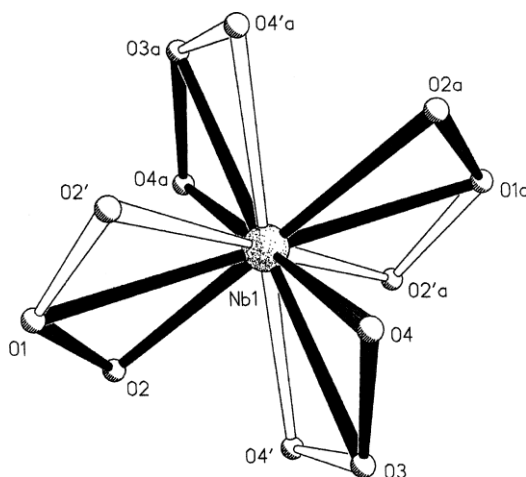


**Fig. 1.4** The structure of the $[Nb(O_2)_4]^{3-}$ anion in $Na_3[Nb(O_2)_4]\cdot13H_2O$ showing the disorder in the peroxido oxygen atom positions. Two different conformations are shown in black and white lines [100].

The homoleptic tetraperoxidoniobates are prone to hydrolysis under ambient conditions and, being thermally unstable, tend to decompose exothermally to the respective orthometallate or pentoxide [12]. On the other hand, heteroleptic peroxido complexes of niobium, synthesized by replacing one or more peroxido group(s) with some of the strong ligands like halides and O,O- or N,O- donor organic ligands, *viz.*, carboxylic acids [106,119,126], oxalate [106,127], DTPA [128], EDTA [125,129], *N*-heterocycles [127,130,131] as well as Schiff bases [132] were found to be significantly more stable *vis-à-vis* the homoleptic ones. Halide containing mixed-ligand peroxidoniobates with varied

compositions were prepared by the dissolution of the alkaline **TpNb** precursor in excess $H_2O_2$ in the presence of halide ions and maintaining the suitable pH [12]. **Scheme 1.3** depicts the dependency of the number of peroxido groups per Nb atom in these complexes on the increasing pH of the solution [12]. Generally, halogeno-peroxido complexes are stable under room temperature and easy to store or handle [12]. In the last few decades, the chemistry of halogeno-peroxido complexes has been expanded to a vast extent, and various halogeno-pNb species with organic ligands have been developed by the substitution of the halogen group with an organic ligand such as oxalate, pyridine-*N*-oxide, 2,2'-bipyridine, triphenylphosphine oxide, triphenylarsine oxide, and 2-aminopyridine, etc. [12,133,134]. Organic ligand-free halogeno-pNb complexes are soluble in water as well as in some of the organic media [12]. In contrast, those containing such organic ligands are soluble only in organic solvents [12].

| pH | Complex separated from solution | No. ratio of Nb:F |
|---|---|---|
| 1 | $[Nb(O_2)F_5]^{2-}$ | 1:5 |
| 3 | | |
| 5 | $[Nb(O_2)_2F_4]^{3-}$ | 2:4 |
| 7 | | |
| 9 | $[Nb(O_2)_4]^{2-}$ | |

**Scheme 1.3** pH-dependence of the substitution of fluoro ligands by peroxido groups in niobate complexes [12].

A large number of halide-free heteroleptic diperoxido and triperoxido niobium complexes has been obtained by replacing one/two peroxido groups from the **TpNb** precursor complex with mono- or bidentate ligands, and many among those complexes were structurally characterized [12]. **Table 1.2** illustrates some heteroleptic pNb complexes coordinated to a variety of auxiliary ligands along with their geometrical parameters like Nb-O and O-O bond lengths as reported in their crystal structures [12].

In most halide-free heteroleptic pNb complexes, niobium predominantly displays an eight-coordination number [12], although there are some exceptions. For example, the complexes of the type, $[Nb(O_2)_2(L)]$ [133] and $K[Nb(O_2)_2OH(L)]\cdot 2H_2O$ [131,133] with L = 8-quinolinolate (hq),  coordination numbers of six and seven, respectively, were

**Table 1.2:** Some homoleptic and heteroleptic peroxidoniobate (pNb) complexes described in the literature [12]

| Types | Compounds | Nb-O (A°) | O-O (A°) | Ref |
|---|---|---|---|---|
| **Tetraperoxidoniobate** | $Na_3[Nb(O_2)_4] \cdot 13H_2O$ | 1.954(6), 2.057(5) | 1.568(6), 1.632(6) | [100] |
| | $KMg[Nb(O_2)_4] \cdot 7H_2O$ | 2.026(3) ± 0.040 | 1.500(4) ± 0.005 | [122] |
| | $K_3[Nb(O_2)_4]$ | -- | -- | [118] |
| **Flourides** | $(C_{12}H_{10}N_2)[Nb(O_2)F_5]$ | 1.884(5) | 1.483(8) | [136] |
| | $(C_9H_8NO)_2[Nb(O_2)F_5] \cdot 3H_2O$ | 1.956(13) [170 K], 2.00(2) [275 K] | 1.471(19) [170 K], 1.35(4) [275 K] | [137] |
| **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 | [135] |
| | $(gu)_3[Nb(O_2)_2(ox)_2] \cdot 2H_2O$ | 1.978(2) | 1.482(3) | [106] |
| | $(gu)_5[Nb_2(O_2)_4(tart)(Htart)] \cdot 6H_2O \cdot 1H_2O_2$ | 2.002(3), 1.992(3), 2.000(3), 1.997(4) | 1.493(2), 1.500(2) | [126] |
| | $(NH_4)_3[Nb(O_2)_3(H_2tart)] \cdot 1.5H_2O$ | -- | -- | [106] |
| | $K_6[Nb_2(O_2)_6(tart)] \cdot 2H_2O$ | -- | -- | [119] |
| | $K_3[Nb(O_2)_3(H_2tart)] \cdot H_2O$ | -- | -- | [119] |
| | $K_3[Nb(O_2)_3(glyc)] \cdot 2H_2O$ | -- | -- | [119] |
| | $K_3[Nb(O_2)_3(Hmal)] \cdot H_2O$ | -- | -- | [119] |
| | $K_3[Nb(Asc)(O_2)_3] \cdot 4H_2O$ | -- | -- | [13] |

*Continued…*

| Types | Compounds | Nb-O (A°) | O-O (A°) | Ref |
|---|---|---|---|---|
| **Polyamino-** **carboxylates** | $(gu)_3[NbTa(O_2)_4(dtpaO_3)] \cdot 2.5H_2O$ | -- | -- | [128] |
| | $(gu)_3[NbTa(O_2)_4(HtthaO_4)] \cdot 2H_2O$ | -- | -- | [128] |
| | $(gu)_3[Nb_2(O_2)_4(HtthaO_4)] \cdot 2H_2O$ | -- | -- | [128] |
| | $(gu)_3[Nb_2(O_2)_4(dtpaO_3)] \cdot 3H_2O$ | -- | -- | [128] |
| | $(gu)_3[Nb(O_2)_2(edtaO_2)] \cdot 3H_2O \cdot H_2O_2$ | 1.966(5), 1.968(5), 1.977(5), 1.992(5) | 1.478(7), 1.483(7) | [125] |
| | $(gu)_3[Nb(O_2)_2(pdtaO_2)]$ | 1.973(2),1.988(2) | 1.488(3) | [125] |
| | $(NH_4)_3[Nb(O_2)_2(edtaO_2)] \cdot H_2O \cdot H_2O_2$ | -- | -- | [125] |
| *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) | [138] |
| | $K[Nb(O_2)_3(phen)] \cdot 3H_2O$ | 1.98, 2.01 | 1.50, 1.47 | [130] |
| | $K[Nb(O_2)_3(phen)]$ | -- | -- | [127] |
| | $(gu)_3[Nb(O_2)_3(pzdc)] \cdot H_2O$ | -- | -- | [138] |
| **Schiff bases** | $K[Nb(O_2)_2(salen)] \cdot 8H_2O$ | -- | -- | [132] |
| | $K[Nb(O_2)_2(H_2O)(hphpd)] \cdot 8H_2O$ | -- | -- | [132] |
| | $K[Nb(O_2)_2(hntrien)] \cdot 8H_2O$ | -- | -- | [132] |
| **Organometallic** | $(\eta^5-C_5H_5)_2Nb(O-O)Cl$ | 1.97, 2.00 | 1.47 | [139] |

reported. The frequently observed Nb coordination environments as well as ligand denticity in the hetero-ligand peroxido-Nb complexes, as described by Bayot and Devillers [12], are shown in **Fig. 1.5**. In the crystal structures of pNb bonded to carboxylate or poly-aminocarboxylate, the coordination polyhedra have been defined as a dodecahedron with high distortion on one side [106,130,135]. Furthermore, all the halide-free hetero-ligand pNb complexes are reported to be soluble in water and insoluble in organic solvents [12].
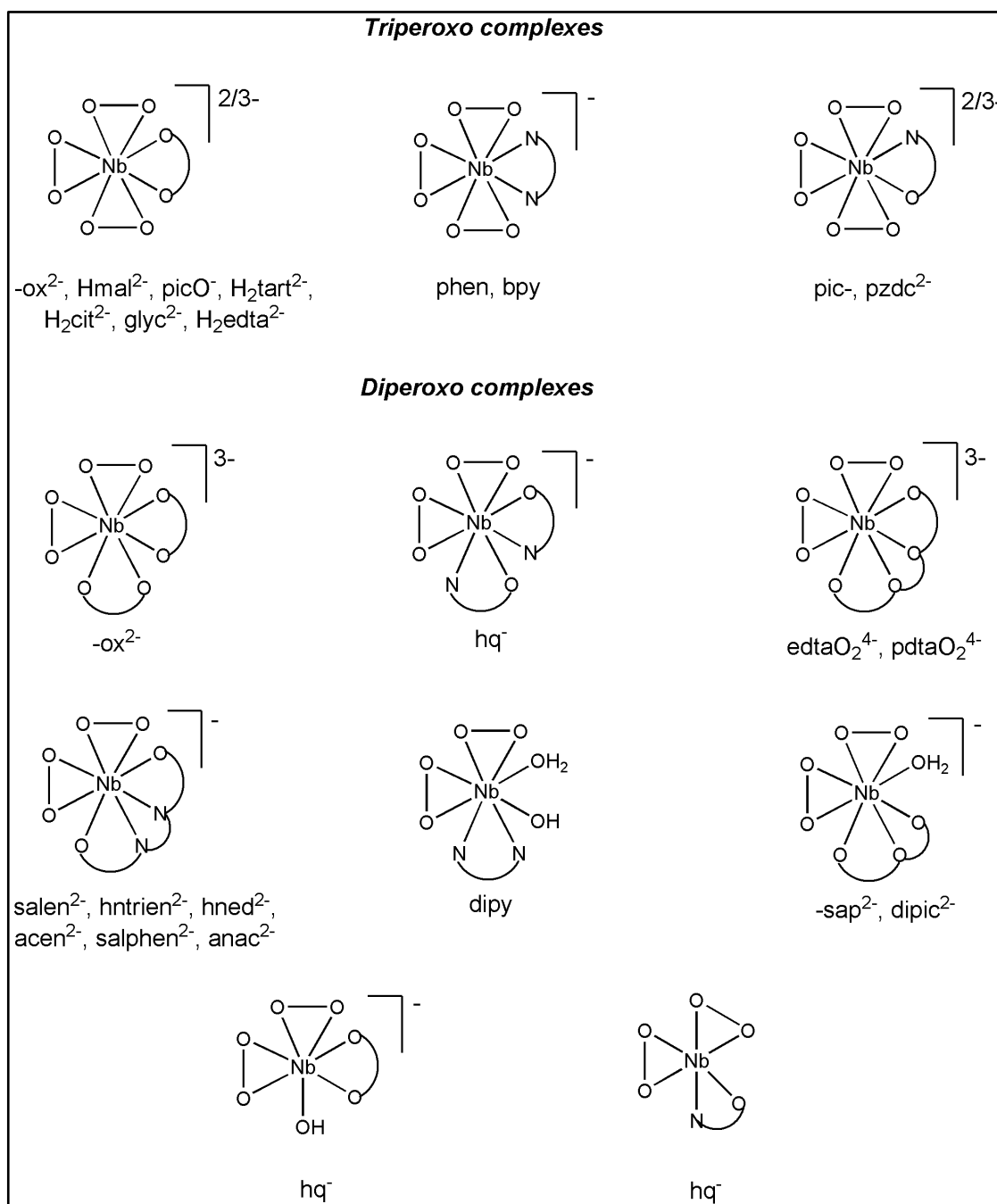


**Fig. 1.5** Environment of the metal atom reported for halide-free heteroleptic peroxido complexes of niobium derived from the corresponding tetraperoxidoniobate [12].

FTIR and Raman spectral analyses have been found to be highly informative and indispensable for the characterization of heteroleptic peroxidoniobium complexes. When a peroxido group coordinates to the metal center in a side-on $\eta^2$- manner generating a local $C_{2v}$ symmetry, characteristically, three IR active modes are observed for peroxidometallates [140]. These occur mainly due to the symmetric O-O stretching (at *ca.* 900-800 cm$^{-1}$), metal-peroxido stretching $v$(M-O$_2$) with symmetric and asymmetric metal-peroxido modes at nearly 500 and 600 cm$^{-1}$, respectively [12,140]. The $v$(O-O) is the most sensitive and intense band observed among them. Additionally, all of these IR active bands are Raman active too, and thus, the Raman spectra complement the IR spectra very well. In case of homoleptic tetraperoxidoniobates, as expected, a single intense band is observed corresponding to $v$(O-O) in both IR and Ramana spectra. On the other hand, diperoxido and triperoxido-Nb species generally show two and three bands, respectively, corresponding to $v$(O-O) stretching modes [12]. The observations have been interpreted on the basis of an established empirical rule correlating the number of stretching bands to the number of peroxido ligands present in the coordination sphere [12]. The presence of three $v$(O-O) bands for the triperoxido compounds was validated by density functional theory (DFT) study [135] carried out by Maniatakou *et al.* In addition, the bond lengths obtained from the DFT study of the complex [Nb(O$_2$)$_3$(quin-2-c)]$^{2-}$ concurred well with the results of the reported crystal structure (**Fig. 1.6**) [135].
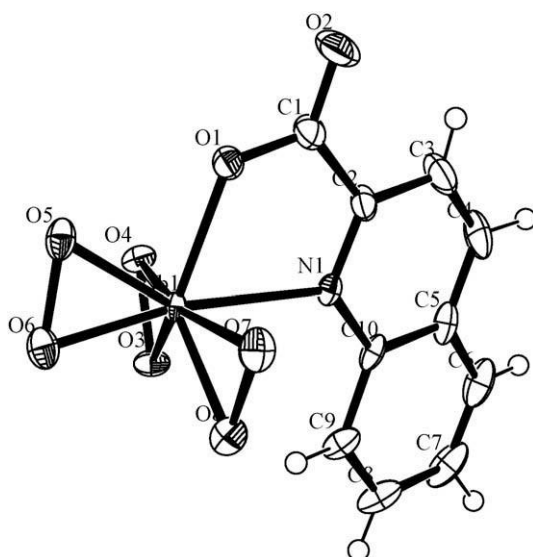


**Fig. 1.6** ORTEP representation of [Nb(O$_2$)$_3$(quin-2-c)]$^{2-}$. Thermal ellipsoids are drawn at the 50% probability level [135].

Binuclear homo- or hetero-bimetallic peroxidoniobium complexes have also been developed in recent years. The binuclear homo-metallic pNb complexes like $(gu)_5[Nb_2(O_2)_4(tart)(Htart)] \cdot 6H_2O \cdot H_2O_2$ (**Fig. 1.7**) with tartaric acid [126], and $(gu)_3[Nb_2(O_2)_4(dtpaO_3)] \cdot 3H_2O$ and $(gu)_3[Nb_2(O_2)_4(HtthaO_4)] \cdot 2H_2O$ with *N*-oxidized poly-aminocarboxylic acids [128], along with their respective hetero-metallic complexes, $(gu)_5[NbTa(O_2)_4(tart)(Htart)] \cdot 4H_2O$ [126], $(gu)_3[NbTa(O_2)_4(dtpaO_3)] \cdot 5/2H_2O$ and $(gu)_3[NbTa(O_2)_4(HtthaO_4)] \cdot 2H_2O$ [136] have been reported. The spectral patterns and thermal behaviour of the binuclear complexes do not significantly differ from that of similar mononuclear complexes [12]. Additionally, thermogravimetric analysis and mass spectrometry provided valuable pieces of information about the heteronuclearity of the hetero-metallic pNb complexes [12]. In the complex anion, $[Nb_2(O_2)_4(tart)(Htart)]^{5-}$ (**Fig. 1.7**), the tartrate groups act as tetradentate ligands and connect the two diperoxidoniobium(V) centres *via* bridging thereby completed the eight-fold coordination around each Nb(V) [126].
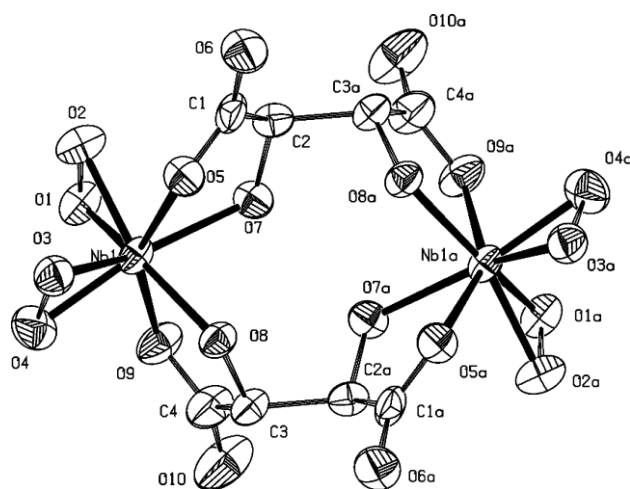


**Fig. 1.7** ORTEP representation of the bimetallic molecular anion, $[Nb_2(O_2)_4(tart)(Htart)]^{5-}$ with 50% ellipsoid probability [126].

In addition, organometallic chloro-peroxidoniobium complexes have also been synthesized with substituted cyclopentadienyl ligands such as $(R-Cp)_2Nb(O_2)Cl$ with R=H [139] or $CH_3$ [141] where two $\eta^5$-Cp rings and a side-on $\eta^2$-peroxido group are coordinated to niobium completing an 18 electron configuration and nine-fold coordination number. The peroxido derivatives were synthesized from the corresponding dichloro compounds, $(R-Cp)_2Nb^{IV}Cl_2$, by treating with $H_2O_2$ under a $CH_2Cl_2$ medium. Colletti and Halterman

described the successful synthesis of bis($\eta^5$-indenyl)chloroniobium(V) peroxide complex from the respective niobocene(IV) dichloride and hydrogen peroxide under an inert atmosphere [142]. Thereafter, Rakhmanov *et al.* prepared a series of four sandwich organometallic pNb complexes with substituted indenes as co-ligands by following a similar synthetic procedure (**Scheme 1.4**) [143].
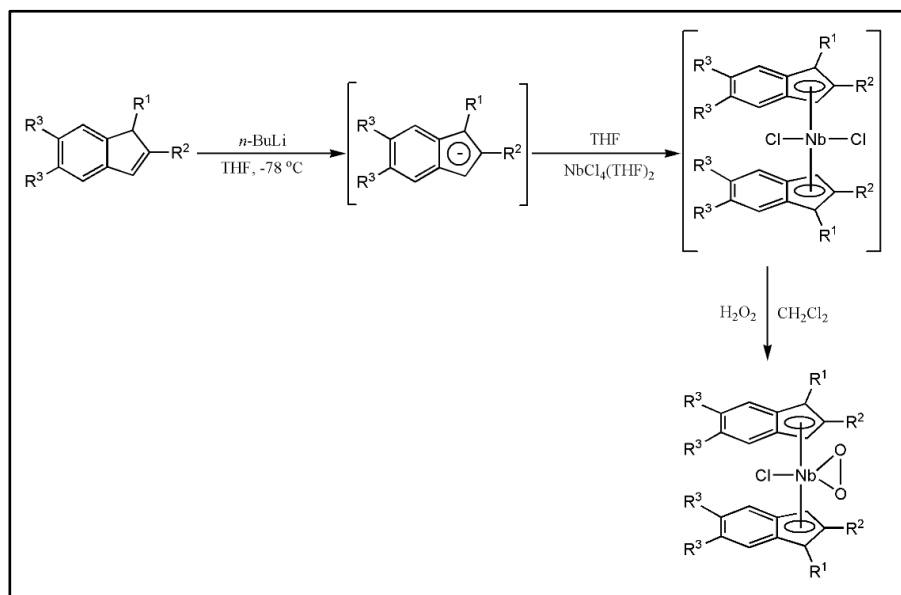


**Scheme 1.4** Synthesis of indenyl peroxidoniobium complexes [143].

## 1.2.3.2 Applications of peroxidoniobium (pNb) compounds

As revealed by a perusal of the literature, the applications of peroxidoniobium compounds, have so far been focused mainly on two exclusive areas: (i) as ideal water-soluble precursors to obtain Nb-based oxide materials *via* wet chemical solution routes and (ii) as catalysts for organic oxidation reactions [12].

In this context, it is somewhat surprising that although Nb belongs to the same periodic group as V and notwithstanding the favourable bio-relevant features possessed by Nb and some of its compounds, very few studies have been devoted to exploring the biochemical potential of peroxido compounds of niobium [4,13,14]. Whereas, despite the toxicity and stability issues associated with peroxido derivatives of V, these systems continue to receive tremendous importance as clinically relevant potent insulin mimics [11,16,92,94,95,98,99,117] and anticancer agents [93-97].

Among the limited studies available, Maniatakou *et al.* [14] reported the insulin-like activity of pNb complexes like $(gu)_3[Nb(O_2)_4]$ and $(gu)_2[Nb(O_2)_3(quin\text{-}2\text{-}c)]\cdot H_2O$

(**Fig. 1.8 A**). These complexes effectively inhibited the *in vitro* free fatty acid (FFA) release from the rat adipocytes in a concentration-dependent manner. On the other hand, Thomadaki and group [13] reported the anticancer activity of a triperoxidoniobium complex containing ascorbate anion as co-ligand (**Fig. 1.8 B**). Compared to ascorbic acid, the compound exerted enhanced antiproliferative activity on human leukemia cells [13]. Recently Pereira-Maia *et al.* [4] have reported a new class of peroxidoniobium containing polyoxoniobates, which were found to be potential anticancer agents for photodynamic therapy. Furthermore, previous work from our group have introduced mononuclear heteroleptic pNb complexes with biogenic co-ligands (**Fig. 1.8 C**), as well as a macromolecular pNb complex (**Fig. 1.8 D**) as strong inhibitors of acid phosphatase [144,145].

Nevertheless, there still remains a paucity of information regarding the pharmacological potential of discreet synthetic peroxidoniobium compounds or their effect on the activity of different enzyme functions. Currently, studies on the inhibition of various enzymes by metal complexes have emerged as a significant area of research in the context of acquiring an insight into the mechanism of action of different inorganic drug materials [146,147].
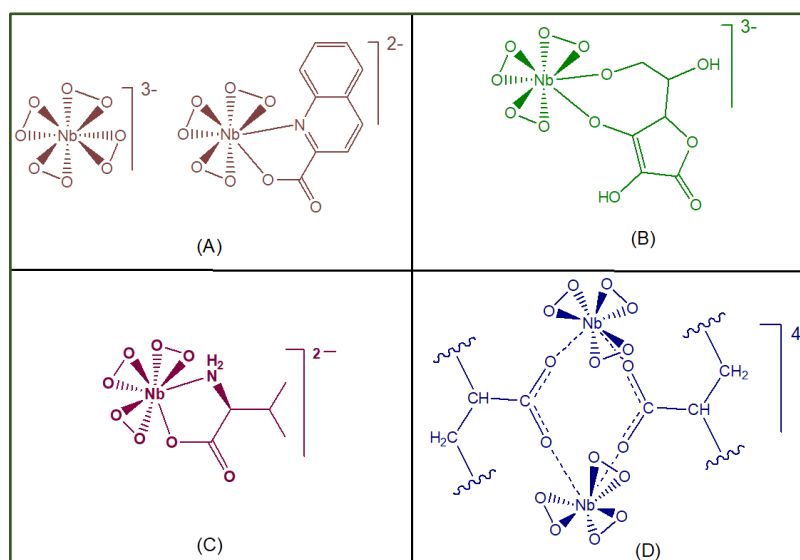


**Fig. 1.8** The peroxidoniobium complexes tested for their (A) insulin-like activity: $[Nb(O_2)_4]^{3-}$ and $[Nb(O_2)_3(quin-2-c)]^{2-}$ [quin-2-c = quinoline-2-carboxylate ion] [14], (B) anticancer activity: $[Nb(Asc)(O_2)_3]^{3-}$ [Asc = ascorbate anion] [13], (C) acid phosphatase inhibition: $[Nb(O_2)_3(val)(H_2O)]^{2-}$ [val = valinato] [144] and (D) $[Nb_2(O_2)_6(carboxylate)_2]$-PA [PA = poly(sodium acrylate)] [145].

## 1.2.3.2.1 Application as molecular precursors to obtain Nb-oxide materials

One of the most well-established and industrially important attributes of peroxidoniobium compounds is their ability to serve as water-soluble molecular precursors for preparing oxide materials [12]. The "ceramic method" is the conventional way for the preparation of oxide materials which involve the solid-state reactions between the binary oxides requiring heat treatments classically beyond 1000 ℃ [126]. With the ever-growing importance of greener chemical approaches, there is increasing attention on 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 [148-150].

A simple, efficient, low cost and eco-compatible synthetic methodology to prepare nano-sized $K_{0.5}Na_{0.5}NbO_3$ powders from pure aqueous precursor solutions was successfully demonstrated by Stavber *et al.* [148] (**Scheme 1.5**). They used precursors based on the niobium(V)-peroxido-citrate and niobium(V)-peroxido-glycine intermediates to afford stable $Nb^{5+}$ ions in water and establish compositional homogeneity and the fine particle size of the nano-powders [148].
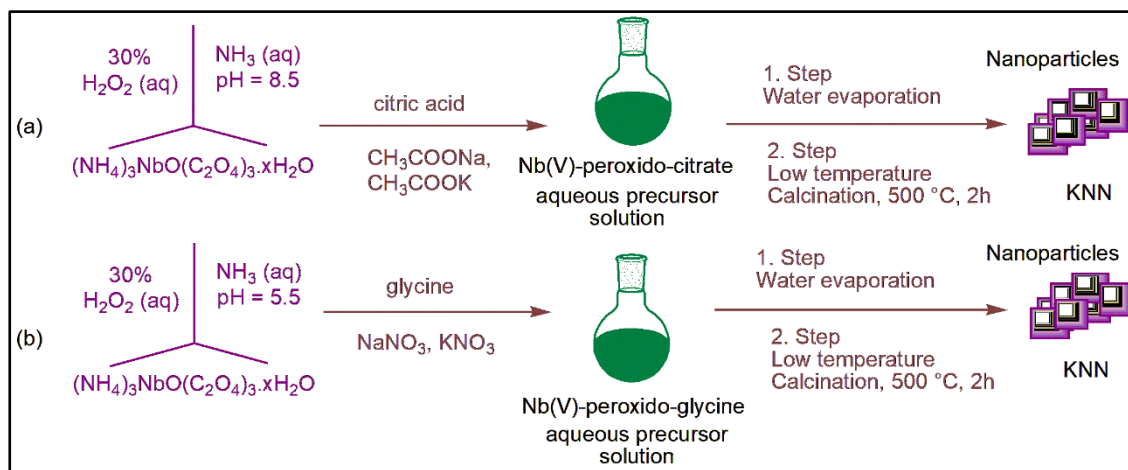


**Scheme 1.5** An illustration of the green synthetic approach for preparation of KNN powders from aqueous solutions through a) niobium(V)-peroxido-citrate b) niobium(V)-peroxido-glycine precursors [148].

Multimetallic Nb and Ta-based oxides have attracted considerable interest in many fields due to their attractive physical properties [1-3,25,29,50,151,152]. Using pre-isolated water-soluble EDTA complexes as molecular precursors, under reasonably mild

conditions, Bayot and Devillers [149] developed multimetallic oxides of the general formula $(Ta_xNb_{1-x})_2O_5$, $Ta_xNb_{1-x}VO_5$ and $BiTa_xNb_{1-x}O_4$ $(0 < x < 1)$ with specific morphology and textural properties. Report from the same laboratory demonstrated that water-soluble homo and hetero bimetallic peroxido complexes of niobium and tantalum with high-denticity poly-aminocarboxylate ligands have been implemented as molecular precursors for Nb-Ta mixed oxides [126]. They also discussed the ability of peroxido-carboxylato complexes of the general formula $(NH_4)_3[NbO(ox)_3]\cdot H_2O$ as valuable precursors to attain Nb-Mo oxide phases supported on silica by combining with analogous Mo(VI) complexes, $(NH_4)_2[MoO_3(ox)]\cdot H_2O$ [153]. Using the triperoxidoniobate complex, $Na[Nb(O_2)_3]\cdot 2H_2O$ as a precursor molecule, Dey *et al.* synthesized pure crystalline $NaNbO_3$ by simple calcination of the triperoxidoniobate compound in air at reduced temperature of 400-500 ºC [154]. Narendar *et al.* synthesized a peroxido-citrato-niobium complex and reported it as a novel aqueous precursor of niobium oxide [102].

### 1.2.3.2.2 Application in catalysis

A plethora of industrially significant selective oxidation processes, such as oxidation of olefins [60,71,155-159], alcohols [57,160-163], thioethers [164-166], amines [44,167,168] etc., have been documented to be catalyzed by *in situ* generated pNb species in presence of a variety of oxidants, *viz.*, hydrogen peroxide, *tert*-butyl hydroperoxide (TBHP) or urea-hydrogen peroxide. **Fig. 1.9** depicts the selective oxidation of various organic and inorganic substrates catalyzed by different peroxido-Nb systems.
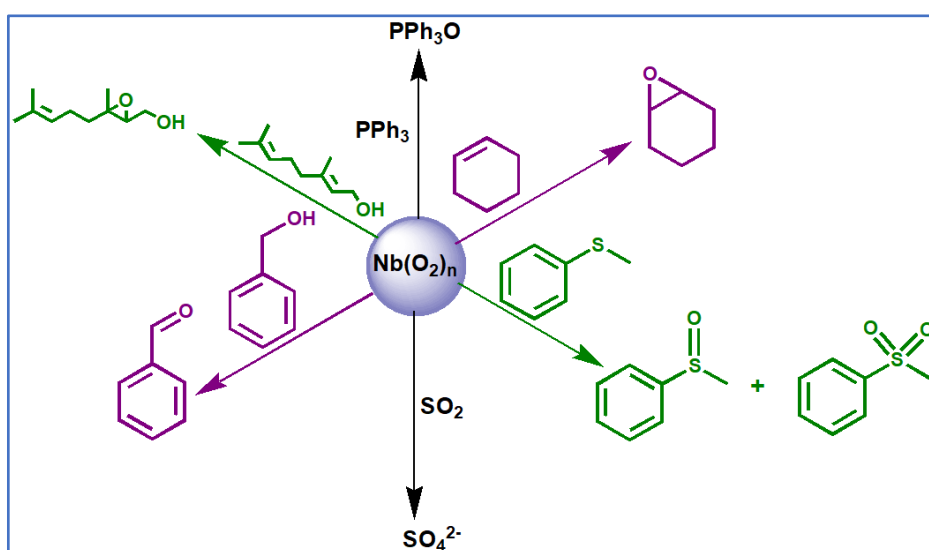


**Fig. 1.9** Selective oxidations of organic compounds by peroxido-Nb systems in the presence of hydrogen peroxide [58,141,161,169,170].

The tetraperoxidoniobate species, $Na_3[Nb(O_2)_4]\cdot13H_2O$ was utilized as a homogeneous catalyst in the liquid-phase epoxidation of cyclohexene with $H_2O_2$ and provided good epoxide selectivity of 73% though with moderate activity [100]. Schiff bases incorporated diperoxidoniobium complexes in the presence of TBHP served as active catalysts in the oxidation of secondary alcohols (15-52% conversion) and epoxidation of cyclohexene with moderate selectivity [132]. As reported by Tarafder [133], diperoxido complexes with the general formula, $[Nb(O_2)_2L]$ (L = hqn) are reactive to both inorganic and organic substrates and stoichiometrically oxidize phosphines to their respective oxides as well as olefins to epoxides. Our research group has earlier introduced a set of triperoxido-Nb complexes with biogenic co-ligands [**Fig. 1.10**] as highly effective catalysts in the oxidation of a variety of aromatic and aliphatic sulfides to the corresponding sulfoxide and sulfones with $H_2O_2$ in aqueous medium [171].
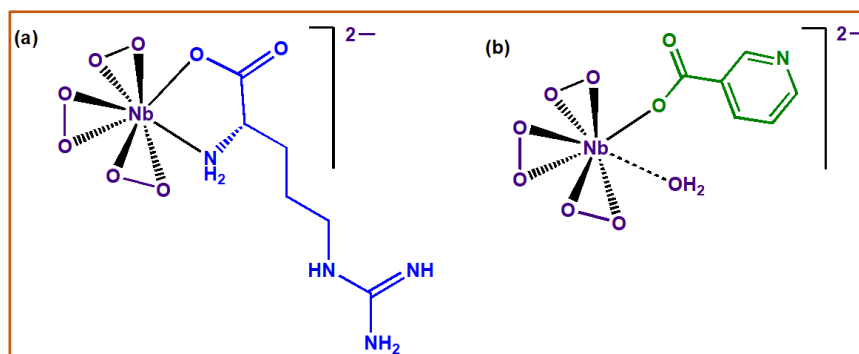


**Fig. 1.10** Structures of the peroxidoniobium catalysts in sulfide oxidation reaction: (a) $Na_2[Nb(O_2)_3(arg)]\cdot2H_2O$ [arg = arginate] and (b) $Na_2[Nb(O_2)_3(nic)(H_2O)]\cdot H_2O$ [nic = nicotinate] [171].

Kholdeeva *et al.* reported series of Nb-monosubstituted Lindqvist-type polyoxometalates (POMs) [42,62,172], including a protonated peroxido complex, $(Bu_4N)_2[HNb(O_2)W_5O_{18}]$ ($HNb(O_2)W_5$ [which interconverts with the other Nb-POMs] (**Scheme 1.6**), and studied their catalytic performances in oxidation of olefins and thioethers with hydrogen peroxide. As shown in **Scheme 1.6**, based on the DFT calculations, the protonated peroxido species "$HNb(O_2)$" was in equilibrium with a hydroperoxido intermediate "$Nb(\eta^2\text{-}OOH)$", the species responsible for the faster epoxidation of the substrate [62] compared to the unprotonated peroxido complex $(Bu_4N)_3[Nb(O_2)W_5O_{18}]$. DFT calculations also indicated that protonation was crucial to generate the active species and increasing the electrophilicity of peroxido-PONs [62,172].

However, in case of sulfide oxidation, additional protonation of the peroxido-complexes was not necessary as sulfides are more nucleophilic in comparison to olefins [172].
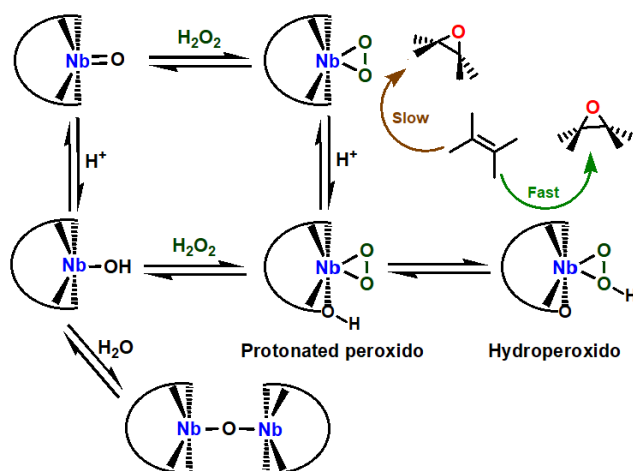


**Scheme 1.6** Interconversion between the different forms of Nb-POMs in presence of aqueous $H_2O_2$ and formation of the active hydroperoxido species [42,62].

Peroxidoniobate functionalized ionic liquids (ILs) developed by Chen *et al.* [58] efficiently catalyzed epoxidation of a range of allylic alcohols. They also proposed the hydrogen bonding mechanism for the oxidation process based on DFT calculations, in which OOH in $[Nb(O-O)_2(OOH)_2]^-$ acts as the active group to oxidize the C=C bond of allylic alcohols while the peroxido group (O-O) can effectively adsorb the substrate through H-bond interaction (**Scheme 1.7**) [58]. Same research group has reported a series of nano-sized ionic liquid stabilized Nb-oxoclusters (**Fig. 1.11**) prepared by the condensation of peroxy-niobic acid, which displayed remarkably high catalytic activity
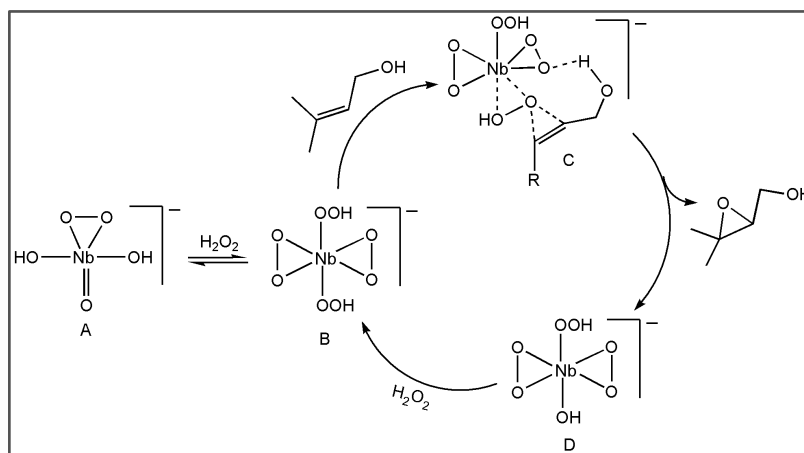


**Scheme 1.7** Proposed mechanism for epoxidation of allylic alcohols with $H_2O_2$ catalyzed by the monomeric peroxidoniobate anion of IL [58].

in sulfoxidation reaction [173]. Subsequently, they have developed a new class of Nb-oxoclusters, stabilized by the coordination of Nb sites with F atoms of organic fluoride salts and proposed the active involvement of $Nb(\eta^2\text{-}O_2)$ species in allylic alcohol epoxidation (**Scheme 1.8**) [174]. The fluoride atom favoured the epoxidation reaction by forming H-bond with the -OH group of allylic alcohols as shown in **Scheme 1.8** [174]. Furthermore, organic carboxylic acids such as lactic acid, glycolic acid or malic acid-coordinated monomeric peroxidoniobate-based ionic liquids have been developed as active and recyclable olefin epoxidation catalysts and afforded the desired epoxide *via* formation of the three-membered ring transition state between the substrate and the peroxido group (**Scheme 1.7**) as reported by Ma *et al.* [169]. Very recently, Ding and group reported a specific ionic liquid, designed *via* the supramolecular complexation between 18-crown-6 (CE) and ammonium peroxidoniobate and further coordination with glycolic acid, acted as an efficient and recoverable catalyst for the $H_2O_2$-induced epoxidation of a range of olefins and allylic alcohols under mild conditions [175].
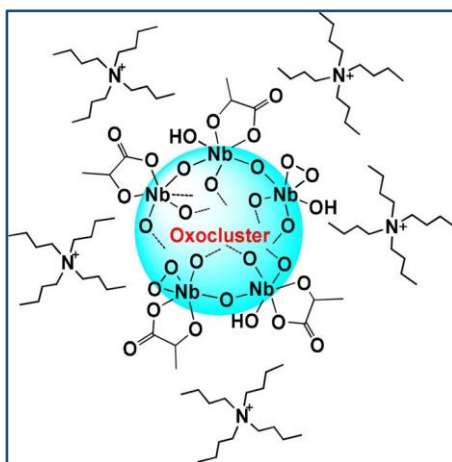


**Fig. 1.11** The ionic liquid [TBA][LA]-stabilized Nb oxocluster [173].

It is worth noting that organometallic peroxido complexes of the type, (R-Cp)$_2$Nb(O$_2$)Cl (R = H or CH$_3$) have been demonstrated to be capable of oxidizing a diverse range of substrates, including triphenylphosphine (**Eq. 1.1**), sulfur dioxide (**Eq. 1.2**) and cyclohexene *via* transferring oxygen atom(s) from their peroxido group to the substrates [141]. On the other hand, Colletti *et al.* performed enantioselective catalytic epoxidation of unfunctionalized alkyl and aryl olefins using niobocene peroxide complexes [142].

$$(\text{R-Cp})_2\text{Nb(O}_2)\text{Cl} + \text{PPh}_3 \quad \rightarrow \quad (\text{R-Cp})_2\text{NbOCl} + \text{PPh}_3\text{O} \qquad \textbf{(1.1)}$$

$$(\text{R-Cp})_2\text{Nb(O}_2)\text{Cl} + \text{SO}_2 \quad \rightarrow \quad (\text{R-Cp})_2\text{Nb(SO}_4)\text{Cl} \qquad \textbf{(1.2)}$$
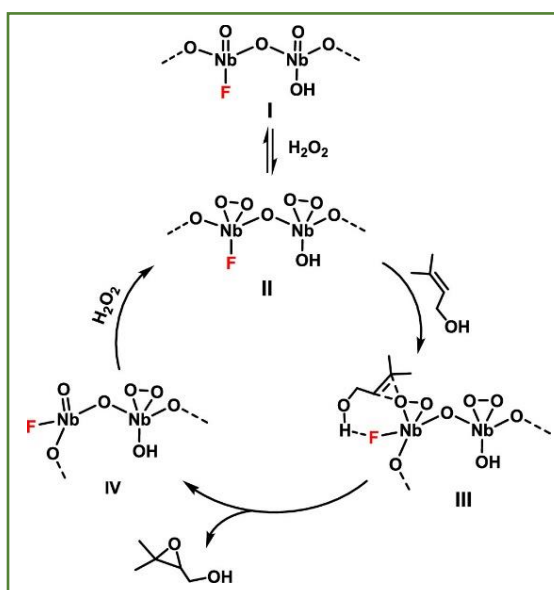
**Scheme 1.8** Proposed mechanism for epoxidation of allylic alcohols with $H_2O_2$ catalyzed by Nb-oxocluster complex [174].

Peroxido compounds, generated in a solution of $NbCl_5$ and $H_2O_2$ in the presence of ligands like 2,2-bipyridine or phosphonic acid, when employed in oxidation of benzylic alcohol using a phase-transfer catalyst ($Bu_4NOH$), under biphasic conditions afforded benzaldehyde as major product in excellent yield [161]. Egami *et al.* [162] successfully implemented *in situ* formed Nb(salan) [salan = *N,N*'-bis(*o*-hydroxybenzyl)-1,2-diaminoethane (SaleanH$_4$)] complex in the highly enantioselective asymmetric epoxidation of allylic alcohol with a urea-hydrogen peroxide adduct in an aqueous medium. The epoxidation reaction proceeded *via* the formation of a hepta-coordinated (allylalkoxo)(peroxido) metal intermediate (a) formed by pre-coordination of allylic alcohols with the metal ion (**Scheme 1.9**) [162]. The catalyst was ineffective in the epoxidation of a simple olefin such as 1,2-dihydronaphthalene [162].
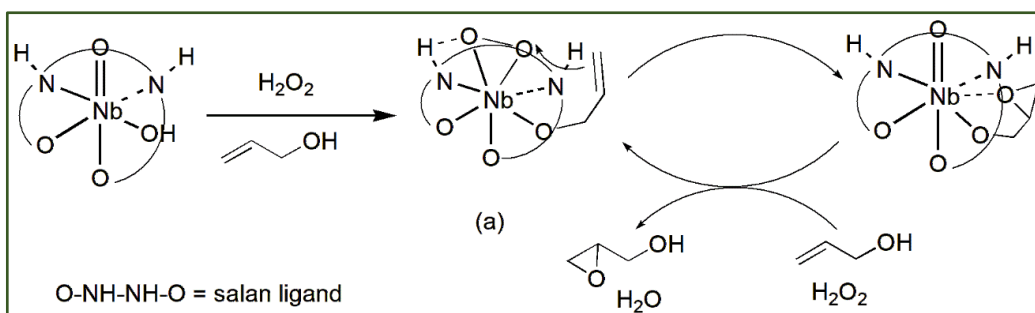


**Scheme 1.9** Plausible mechanism for the epoxidation using pre-treated Nb(salan)(O*i*Pr)$_3$ as a catalyst [162].

Silva *et al.* reported a highly reactive heterogeneous catalyst based on the immobilization of peroxido-niobium over iron oxide, formed *in situ* by treating Nb-doped iron oxide composites with $H_2O_2$ [176]. The innovative materials were observed to possess remarkable activity in the liquid phase oxidation of organic dye and could successfully be regenerated for up to six catalytic cycles [176].

Apart from the peroxidoniobium based homogeneous and heterogeneous catalytic systems, a large number of promising supported Nb and Ta oxide-based catalysts have been developed in recent years for catalytic oxidation of a vast range of organic substrates using different oxidizing agents [39,59-61,69-72,177-184]. Majority of the heterogeneous Nb-based oxidation catalysts supported on porous siliceous oxide or other metal oxide supports (MCM-41 and SBA-15), are, however, known to be associated with certain limitations in terms of their activity/selectivity profile as well as regeneration [39,59,61,69,70,181-184]. The advancement in liquid phase olefin epoxidation over niobium and tungsten-based nanostructured catalysts has been comprehensively reviewed by Yan *et al*. recently [39]. It has been noted that notwithstanding the considerable progress in improving the activity of Nb and W nanostructured catalysts, poor selectivity and stability of such systems are still major issues to address [39,182,185,186]. Thus, developing more productive catalyst systems to support organic oxidations under mild conditions still remains an important goal as well as a notable challenge in designing Nb-based solid catalysts.

In this context, it is pertinent to highlight that, despite increasing demand for the application of polymer-supported catalysts in the production of bulk organic substances [187-189], the development of solid niobium-based oxidation catalysts supported on organic polymers seems to have received scant attention.

### 1.2.4 Polymer immobilized metal complexes – general aspects

Chemistry of metal-containing macromolecules constitutes an active discipline of material science [190]. With the inherent ability of metals to adopt various oxidation states, coordination numbers and geometries, it can be appreciated that incorporating a metal or metal complex into a polymer matrix can lead to the development of functional materials possessing unique attributes, with potential applications in a wide range of areas, including hydrometallurgy [191], engineering [191-193], cosmetics [194], bio-medicines [195-197], supramolecular chemistry [198], environmental applications [199-201] as well as organic

synthesis and catalysis [202-205]. Haag and Whitehurst [206] introduced the first example of a metal-incorporated organic polymer, sulfonated polystyrene-supported Pt(II) complexes in the year 1969.

In addition to carbon, a polymer network mainly comprises of five other elements: nitrogen, oxygen, sulfur, silicon and phosphorus [207]. Based on the diverse combinations of those elements, polymers can be categorized into- (i) organic polymers with only carbons in the backbone (e.g. polyacetylenes, polystyrene), (ii) inorganic polymers without any C-atoms in the main chain (e.g. polyphosphacenes, polysiloxanes), and (iii) semi-organic polymers with at least one other element along with carbons (e.g. polythiophenes, polypyrrole) [207].

A variety of arrangements of the aforementioned polymers with metals or metal complexes can be obtained by adopting different synthetic approaches such as encapsulation, ion exchange, adsorption, gel immobilization, coordinate/covalent bond formation [187,208] etc. The supporting processes have been described by using different terminologies like anchoring, attachment, immobilization, or "heterogenization of homogeneous complexes" [187].

According to the definition of "metallopolymers", such systems are required to possess metal centres either as an integral part of the leading polymer network or as an attachment to the polymer as a pendant side chain [209]. The classification of metal-containing polymers proposed by Ciardelli *et al.* [210], based on their interaction type, is shown in **Fig. 1.12**.

**Macromolecular Metal Complex** (**Type I**)**:** In such complexes**,** as depicted in **Fig. 1.12**, metal ions/complexes are attached to the polymer chain or surface through (a) electrostatic, (b) coordination or (c) covalent interaction.

**Metal or Ligand Macromolecular Complex** (**Type II**)**:** In this group of metallopolymers, either metal complexes form part of the polymer backbone *via* covalent linkage or metal-ligand coordination forms part of the polymer main chain. In both type I and II metal polymers, the close coupling between metal and the polymer network enables the metal centers to enhance the material properties.

**Macromolecule Incorporated Metal Complexes** (**Type III**)**:** In such compounds, metals are inserted into the polymer by physical interactions. The release of negative free

energy due to the polymer chelate effect thermodynamically drives the formation of such materials.

Grafting and (co)polymerization are the two well-established primary procedures employed for synthesizing metal-containing polymers. Grafting is defined as the attachment of the transition metal ion or complex to the polymer backbone after the completion of the polymerization process [211]. On the other hand, in (co)polymerization, the metal complex itself acts as a monomer incorporated into the polymer network [211]. Additionally, diverse processes such as polycondensation, chain growth condensation polymerization, ring-opening polymerization, electropolymerization, as well as living ionic and controlled radical polymerization have been utilized by chemists to obtain the desired metallopolymers [209].
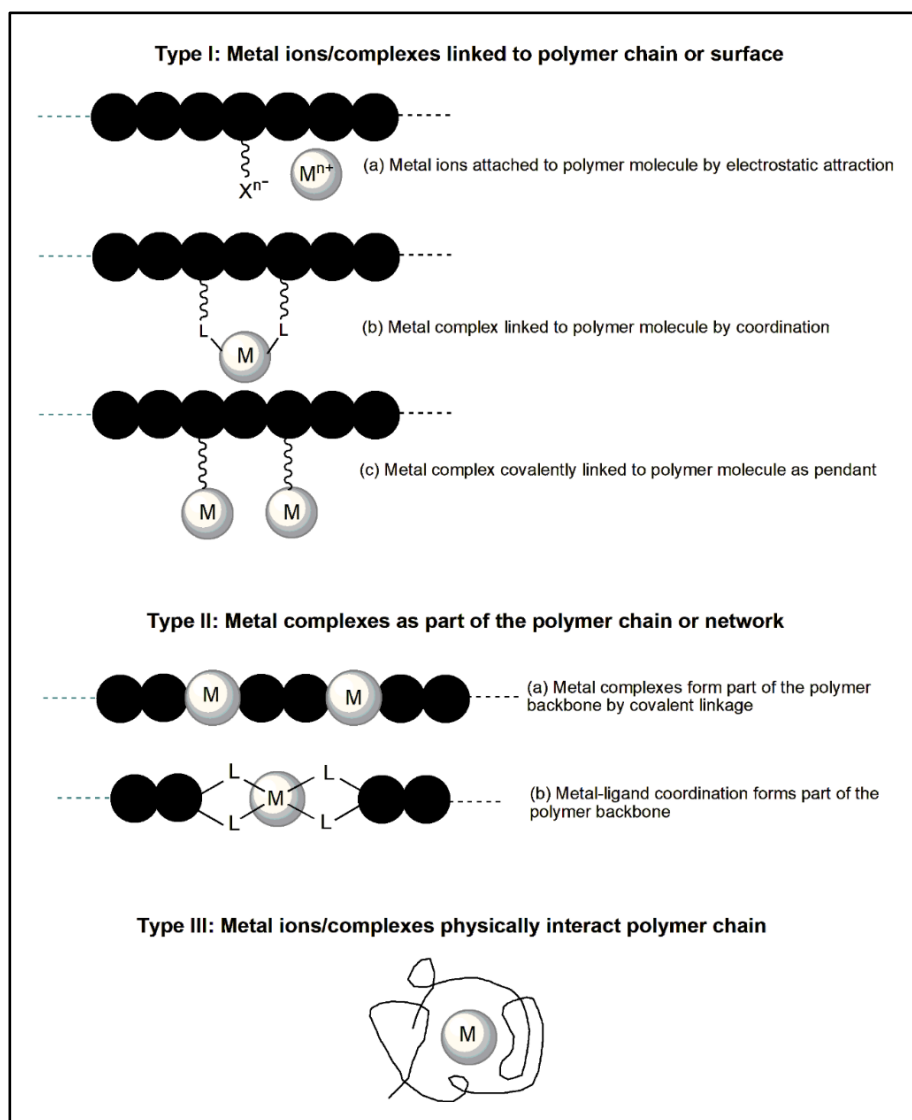


**Fig. 1.12** Different approaches for the formation of metal-containing polymers [211].

A variety of synthetic as well as natural polymers have been utilized for anchoring different metal complexes [189]. Incorporating a definite metal ion into a specific macromolecular matrix leads to the development of materials with specific properties like activity, selectivity, high performance and stability due to the inherent steric effect and the special environment provided by the polymer ligand [190,207,212]. Hence, there are enormous possibilities to prepare metal-polymer complexes with varied applications by altering the polymeric network, metal ion and the nature of the ligand. In light of these, the present thesis discusses the preparation and significance of different metal-containing polymers in two particularly relevant domains, *viz.*, catalysis and biological application.

**1.2.4.1 Catalytic application of polymer-supported metal complexes**

The ever-increasing ecological consciousness in recent years and the resulting emphasis on developing eco-compatible synthesis procedures have evoked a renewed interest in generating metallopolymer catalysts for industrially significant chemical transformations that furnish high stability as well as activity/selectivity [213-216]. In fact, polymer-immobilized catalysts also referred to as "heterogenized homogeneous catalysts", usually combine the advantageous characteristics of homogeneous, heterogeneous and enzymatic catalysts, augmenting their catalytic efficiencies [213-219]. Such systems often provide the benefits of easy removal from the reaction mixture and reusability that improves the overall productivity and cost-efficiency of reactions while diminishing their environmental impact, eventually contributing to the sustainability of the processes [213-219]. Consequently, both soluble and insoluble polymeric matrices have been investigated as catalyst support [189,203,212-220]. Recently, Nasrollahzadeh and his group have comprehensively reviewed the current developments in the manufacture and catalytic activity of various multi-dimensional polymer-supported cobalt- and ruthenium-complexes/NPs in different oxidation reactions using $H_2O_2$, $O_2$ or TBHP as oxidizing agents [221,222].

Several factors are associated with the catalytic activities of immobilized catalysts, such as the nature and distribution of the metal ions on the support, the type of attachment between the catalytic sites and the support, the density of the catalytic sites, and their locations on the polymer matrix, and the physicochemical properties of polymer backbone [212]. In addition, the level of cross-linking in the polymer network also influences the attributes of the polymer-metal complexes [189,215]. Linear polymers are often soluble in

organic solvents, whereas increasing cross-links reduces the solubility of the polymer support [212]. Therefore, homogeneous polymer-metal complexes can be converted to heterogeneous ones and *vice versa*, which is a noteworthy aspect of such systems [189].

Natural polymers such as cellulose, chitin and chitosan (**Fig. 1.13**) have gained enormous importance as potential green supports to meet the requirements for new-generation catalysts [223-228]. High thermal stability and durability, high metal dispersion, non-toxicity, biocompatibility and biodegradability, versatility, and insolubility in organic solvents are some of the unique and attractive features of biopolymers [224,229-232]. Among the members of polysaccharides, cellulose is the most abundant naturally occurring bio-macromolecule [233,234]. Due to the very high content of functionalizable hydroxyl groups, cellulose can easily bind to various metal ions and be applied as soluble or insoluble support [235].
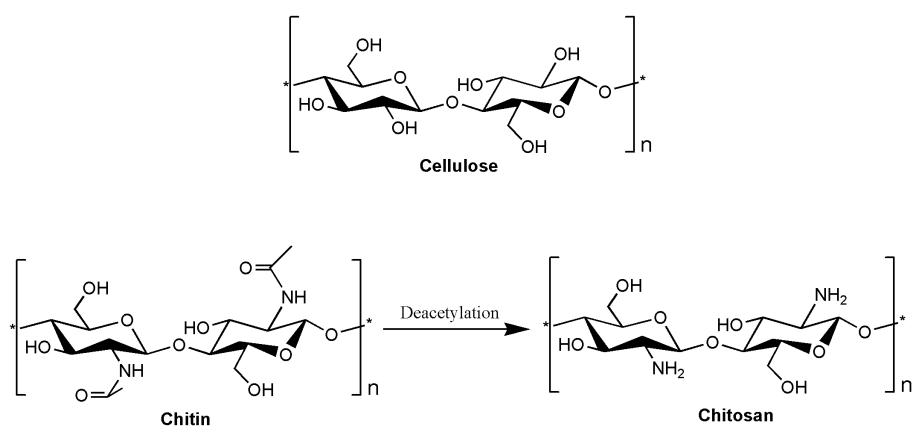
**Fig. 1.13** Structural representation of cellulose, chitin and chitosan [236].

Quignard *et al.* first reported the application of cellulose as catalyst support [237]. They immobilized the water-soluble catalytic precursor $Pd(OAc)_2/5$ TPPTS on cellulose and investigated the efficiency in the Trost Tsuji allylic alkylation reaction [237]. Apart from that, various cellulose-supported metal systems have emerged as successful heterogeneous and recyclable catalysts for a wide range of organic transformations such as coupling reactions [225,234,238], selective oxidation of alcohol [238-241] and sulfides [240,241] as well as reduction of nitroarenes, [239] etc. The nanohybrid catalyst obtained by depositing gold on cellulose nanocrystals displayed much better stability and catalytic activity than unsupported Au-nanoparticles and other Au-containing catalysts in reducing 4-nitrophenol as reported by Wu *et al.* [242].

Chitosan is the deacetylated derivative of chitin (**Fig. 1.13**), which is composed of β-(1–4)-linkages of 2-amino-2-deoxy-D-glucose repeating units [232,243,244]. Chitosan attracted the interest of researchers for many years as support for heterogeneous catalysts due to its greater flexibility than chitin [224]. Besides catalysis, recent studies on the applicability of chitosan/chitosan derivatives have been conducted extensively in bio-medicine, bio-engineering, chemical industry, and environmental protection [224,230-232,243-246]. The presence of reactive functional groups – hydroxyl, amino, or acetylamino group enables chitosan to afford a variety of chemical modifications and forming of valuable derivatives [247], as depicted in **Fig. 1.14**. Metal-chitosan complexes are catalytically useful in a vast range of reactions, including condensation [229,248], polymerization [249], hydration [250], hydroxylation [251], coupling reactions [252-254], water splitting reactions [255,256], oxidation and reduction [224] etc. Pispisa and Chiessi first reported the oxidation by a chitosan-based catalyst where immobilized $Fe^{III}$ and $Cu^{II}$ complexes were employed in the oxidation of catecholamines, and the reaction proceeded through intramolecular electron transfer within a binary adduct under an alkaline solution [224,257]. In addition, a recent review by Molnár [224] revealed that several chitosan-supported complexes have been shown to effectively catalyze the oxidation of a variety of substrates like cyclohexane, ethyl benzene, alcohol, toluene etc.
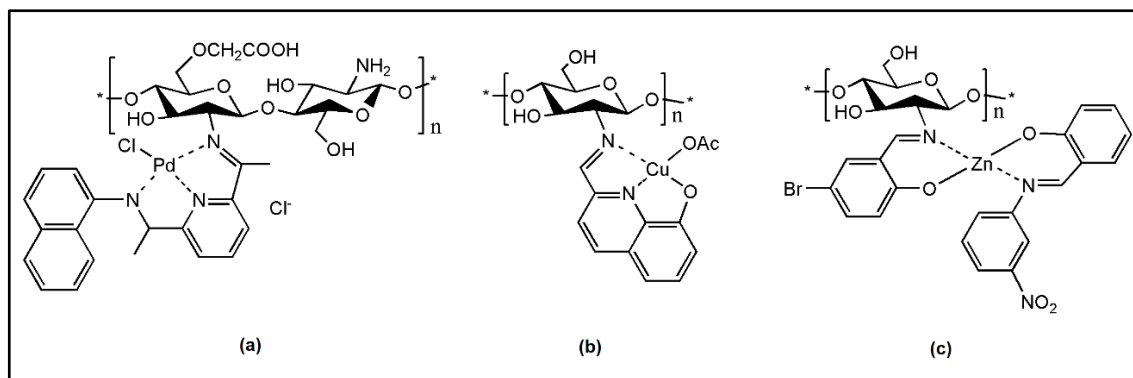


**Fig. 1.14** Examples of different metal complexes immobilized on modified chitosan support. Compound (a) [258], (b) [259] and (c) [224].

Lately, Shen *et al.* [260] reported a heterogeneous silica-supported chitosan@vanadium catalyst (**Fig. 1.15**), which attained asymmetric oxidation of sulfides to sulfoxide with high yield (63-95%) and moderate enantioselectivities. The efficiency of the developed methodology was demonstrated by the successful synthesis of the marketed drug Nexium with a high yield (92%) and enantiomeric excess (68%) [260]. Research

groups of Veisi and Fakhri have reported the oxidation of sulfides to the corresponding sulfoxides by magnetically separable $Fe_3O_4$@chitosan-based vanadium [261] and copper [262] catalysts. Moreover, various chitosan-based noble metal-based catalysts were developed for the epoxidation of alkenes [263-265]. Recently, a catalyst bearing magnetite-chitosan core-shell-type nanocomposite with Mo-Schiff base has been reported for olefin epoxidation reaction [266].
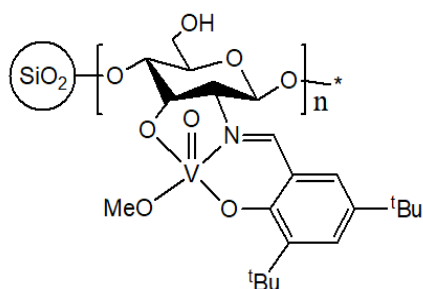
**Fig. 1.15** Silica-supported chitosan@vanadium catalyst reported by Shen *et al.* [260].

Chloromethylated polystyrene cross-linked with divinyl benzene (PS-DVB) or Merrifield resin (MR), the most widely used macromolecular support for catalyst immobilization, was pioneered by Merrifield during his early work in solid-phase peptide synthesis [267]. As evident from several exhaustive reviews on supported solid catalysts [267-270], MR with a basic structure of the type shown in **Fig. 1.16**, is still acknowledged as one of the most attractive polymeric solid supports for catalyst immobilization. Apart from being cost-effective and readily available, polystyrene-based supports display multiple favourable features like non-toxicity, non-volatility, chemical inertness, mechanical robustness, ease of functionalization, and compatibility under a wide range of reaction conditions [267-270].
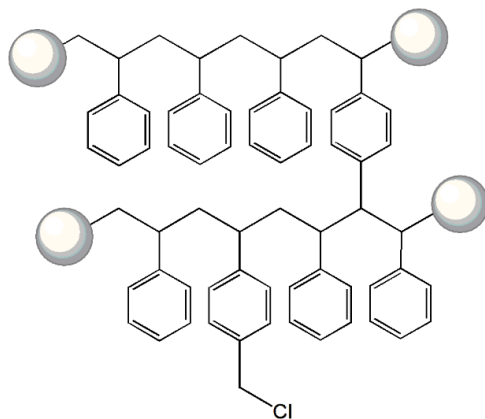
**Fig. 1.16** Structure of Merrifield resin [217]. The ball represents the polymer main chain.

Three main synthetic procedures are generally made use of for immobilization of a homogeneous catalyst on solid polymer support: (a) entrapment, where a preformed catalyst is enveloped within a polystyrene network, (b) ion-pairing where cations or anions are bound to complementary resin sites, and (c) covalent binding [187,208].

Functionalization of MR with different functional ligands *via* the aromatic ring provided the potential sites for metal anchoring [219]. Various types and percentages of cross-linkers are usually incorporated into the PS resin on the basis of requirement. Polystyrene resins can afford a reasonably large number of post-functionalization processes and accommodate different types of cross-linking agents due to their excellent swelling properties, constituent potential anchoring sites, and high loading capacity [212]. **Fig. 1.17** illustrates some examples of reported polymer-functionalized ligands developed by post-modification of Merrifield resin.
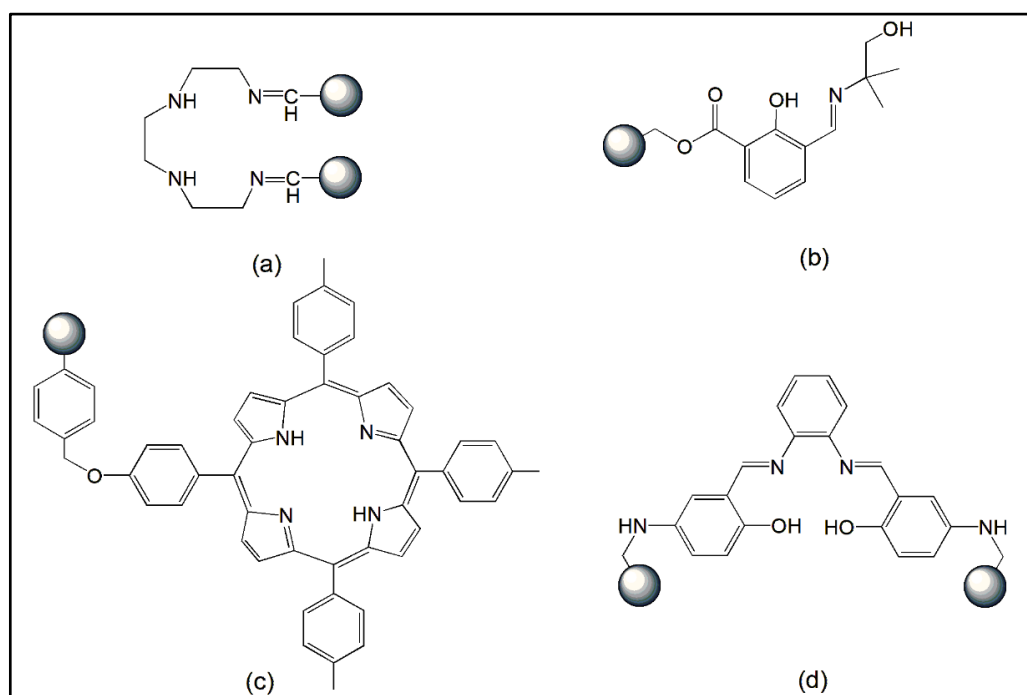


**Fig. 1.17** Examples of some polymer anchored ligands obtained by the reaction of PS-CH$_2$Cl with different organic compound. (a) [271], (b) [272], (c) [273] and (d) [274].

The utility of functionalized polystyrene-supported metal systems for a number of catalytic transformations have been adequately highlighted in the literature [212-215,219,222]. Sreekumar *et al*. discussed the development of a wide variety of polystyrene-bound Cr-based oxidants to oxidize primary and secondary alcohols [275]. Boruah *et al*. prepared a dioxo-Mo(VI) complex supported on Schiff-base functionalized

Merrifield resin (MR-SB-Mo) and employed for the solventless selective oxidation of different alcohols [276]. PS-supported manganese porphyrin complexes were described as high-yielding and easily recoverable epoxidation catalysts for various alkenes [277,278], including inactivated substrates such as cyclooctene as well as cyclohexene [278]. One of the first successful syntheses of PS-supported Jacobsen's Mn(salen) complex was reported by Salvadori, which catalyzed asymmetric epoxidation of styrene [279]. Latterly, Ti(IV)-based complexes of cross-linked swellable polystyrene with ethyl-(4-vinylbenzyl)-L-tartrate, and ethyl-(2R,3R)-2,3-dihydroxy-4-oxido-5-(4-vinylphenyl) pentaneate, were reported to be highly active catalysts (conversion and enantioselectivity up to 99%) for Sharpless epoxidation of cinnamyl alcohols [280]. A pair of 4-azidomethyl substituted polystyrene-supported chiral *N*-salicylidene oxidovanadium(V) *tert*-leucinates were developed by click chemistry as depicted in **Scheme 1.10**, which promoted the aerobic asymmetric oxidation of α-hydroxy (thio)esters and amides with nearly 99% of enantioselectivities [281].
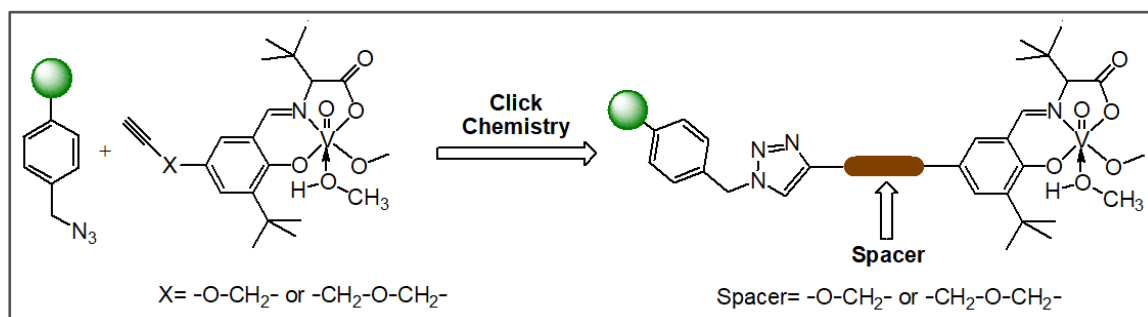


**Scheme 1.10** Synthesis of 4-azidomethyl substituted PS-supported chiral vanadyl catalysts by click chemistry [281].

Jang [282] has demonstrated the preparation of a palladium-based Merrifield resin-derived catalyst (**Scheme 1.11**), which facilitated the Suzuki coupling reaction of organoboranes with a good isolated yield of 78-96%. In addition to that, several polystyrene-based complexes mainly supported on palladium have been developed as stable, robust and reusable catalysts to conduct various coupling reactions, *viz.*, Sonogashira coupling, Heck-Matsuda cross-coupling, Suzuki-Miyaura coupling reactions [283-285]. It is worth noting that, under solvent-free conditions, PS-supported *N*-phenylpiperazine–Cu(II) complex served as an efficient and versatile catalyst with excellent recyclability for the selective three-component coupling reaction with ketone–amine–alkyne to give the corresponding propargylamines [286].
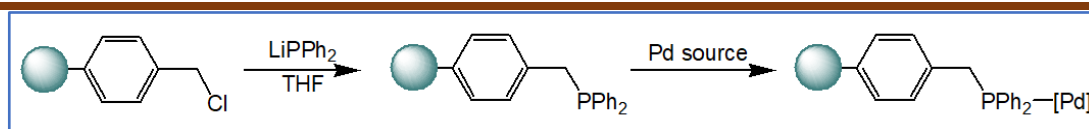
**Scheme 1.11** Synthesis of MR-supported Pd catalyst reported by Jang [282].

Ruthenium-based PS-bound complexes were well established as catalysts for olefin metathesis reactions [287-289]. Nguyen *et al.* [287] developed a series of PS-supported Ru-vinyl-carbene catalysts based on soluble $Cl_2(PR_3)_2Ru=CH-CH=CPh_2$ complexes to produce living polymers in solution. The catalysts were reported to assist the metathesis of acyclic olefins as well as ring-opening metathesis polymerization of cyclic olefins [288,289]. Merrifield resin-supported Co(II)-porphyrin developed by Gao and co-workers [290], could catalyze the oxidation of 5-hydroxymethylfurfural (HMF) into 2,5-furandicarboxylic acid (FDCA) with HMF conversion of 95% and FDCA yield of 90% at 100 °C. Moreover, Maurya and group synthesized a number of PS-supported V(V), Mo(VI), and W(VI) compounds which catalyzed the oxidation of phenol, styrene, sulfide and bromide [291,295].

Several research groups have documented the functionalization of polystyrene-divinylbenzene with bifunctional N, O-donor amino acid ligands [270,296-299]. Petit *et al.* reported the first instance of attachment of various optically active α-amino acids (proline, threonine, phenylalanine, etc.) onto cross-linked polystyrene resin and their subsequent complexation with Cu(II) [300]. However, their catalytic potential was not determined [300]. As revealed by Valodkar *et al.,* Pd(II) [296] as well as Ru(III) [301] immobilized on L-valine functionalized cross-linked poly(styrene-divinylbenzene) resin were able to hydrogenate various substrates such as 1-octene, acetophenone, cyclohexene, and nitrobenzene with high selectivity under mild conditions and epoxidize styrene, norbornene, cyclohexene, and cyclooctene using TBHP, respectively. Moreover, polystyrene-supported amino acid catalysts, *viz.*, PS-threonine, -tyrosine, -hydroproline and -serine have been reported by Qi *et al.* with high chemical and thermal stability, which behaved as efficient catalysts for the $CO_2$ fixation reaction [297].

In addition to the above-mentioned macromolecular supports, various other polymers such as polyacrylate, polyvinyl, poly(2-oxazoline), polyether, poly(ethylene glycol), dendrimers, and silicon polymers, etc., have also been implemented as support for various catalytic applications [187,189,190,208,210-213,268]. A list of different

combinations of metal and polymer support and their catalytic applications is displayed in **Table 1.3**.

It is relevant here to mention that during the past few years, researchers from our group have developed a number of supported $d^0$ transition metal-based homogeneous and heterogeneous catalyst systems by exploiting a range of macromolecular supports such as water-soluble polymers [302-309], biopolymers [310,311], in addition to insoluble cross-linked polymer resins [299,312]. These structurally defined immobilized peroxidometallates proved to be excellent catalysts in a variety of selective organic oxidations with $H_2O_2$, an ideal non-polluting and cost-effective oxidant, under environmentally acceptable reaction conditions [299,306-309,312]. Each of these catalysts was observed to be structurally robust, recyclable and water-tolerant. Moreover, macromolecular peroxidometallates anchored to linear water-soluble polymers (WSP), synthesized in our laboratory, exhibited unique bio-relevant features [302-305,309].

## 1.2.5 Water-soluble polymers (WSPs) as metal supports – significance in catalysis and biology

Synthetic water-soluble polymers represent a class of non-toxic and biocompatible macromolecular support, which has been finding extensive applications in diverse research domains, including in drug delivery systems, catalytic and separation processes, as well as in environmental applications as heavy metal removers [313-315]. The ease of product synthesis and characterization offered by such supports as a result of their advantage of homogeneity is one of the key aspects of a soluble polymer-supported reagent [203,316]. Recent advances in the field of water-soluble polymers have led to the development of innovative polymer-based drug delivery systems, as polymers are often comprised of several unique features such as flexibility, variety in terms of conformation and properties, functionalization ability, as well as the possibility of smart response to environmental stimuli [314,317,318]. Unlike, monomeric species, these polymers are devoid of inconvenient properties such as lability, volatility, toxicity, and odour [319]. Thus, it is easy to comprehend the significance of coupling drug molecules, including low molecular weight metal complexes, to soluble macromolecular carriers as these systems are likely to overcome drawbacks like toxic side effects by enhancing drug absorption and extending their duration of action [197,318,337].

**Table 1.3** The summary of different combinations of metal complexes and macro-ligands, as well as catalyzed reactions

| Polymer support | Functional group | $MX_n$ | Catalyzed reaction | Ref. |
|---|---|---|---|---|
| Phosphinated CSDVB | -PPh$_2$ | RhCl(PPh$_3$) Rh(CO)$_2$(PPh$_3$)$_2$ | Hydrogenation | [189] |
| | | PdCl$_2$(PPh$_3$) RuCl$_2$(CO)$_2$(PPh$_3$)$_3$ | Hydroformylation | |
| | | RhHCO(PPh$_3$)$_3$ [COdRhCl]$_2$ | Deuterium/hydrogen exchange | |
| | | Cocl$_2$(PPh$_3$) | Isomerization | |
| | | Mo(CO)$_2$(PPh)$_2$ | Oligomerization | |
| | | Fe(CO)$_4$PPh$_3$ | Cyclooligomerization | |
| PPESK | -- | [PW$_9$O$_{34}$]$^{9-}$ | Benzyl alcohol Oxidation | [320] |
| PA | -- | Ni(napht) | PhA hydrogenation | [189] |
| PMMA | -COOCH$_3$ | Pd$^0$ | Nitro compound hydrogenation | [189] |
| PS-BBP | -- | PdCl$_2$ | Suzuki coupling | [321] |
| Porphyrin based POP | -- | Fe(III) | HMF oxidation | [322] |
| TPA based POP | -- | Phosphomolybdate | Olefin oxidation | [323] |
| PAN | -C≡N | M(AcAc)$_2$ (M=Mn,Co) | Ethyl benzene Isopropyl benzene oxidation | [189] |
| PE-gr-PAAc | -COOH | Co(AcAc) | Cyclohexene oxidation | [189] |
| PEI | -NH | Rh$^{3+}$ | Formation of H$_2$ from H$_2$O | [189] |

*Continued…*

| Polymer support | Functional group | $MX_n$ | Catalyzed reaction | Ref. |
|---|---|---|---|---|
| PE-gr-P4VP | Py | $PdCl_2(PhCN_2)$ | *p*-Nitrochlorobenzene hydrogenation | [189] |
| PEG | -- | Pd nanoparticle | Heck cross-coupling | [324] |
| PEI/SiO$_2$ | NH | $Pd^0$ | nitrobenzene | [189] |
| P-HPHZ | -- | Fe(III)/ Cu(II)/ Zn(II) | phenol and cyclohexene Oxidation | [325] |
| Poly(2-vinylpyridine-co-styrene) | -- | $Fe^{3+}$, $Co^{2+}$, phthalocyanines | $H_2O_2$ oxidation | [189] |
| PS-naph | -- | Oxidovanadium(IV) | Aromatic alkane and alkene oxidation | [326] |
| PNB with aryloxide ligand | -OH | Titanocene | Ethylene polymerization | [327] |
| c-PMA$_n$ | -- | V | Olefin oxidation | [328] |
| PEG supported tartarates | -- | Ti(O-i-Pr)$_4$ | Prochiral sulfide Oxidation | [329] |
| Ethanolamine modified PAN | -- | PdCl$_2$ | Suzuki coupling | [330] |
| PAACA | -- | $[PV_xW_{12-x}O_{40}]^{(3+x)-}$ | Sulfide oxidation | [331] |
| PS-An | -NH$_2$, -COOH | Oxidovanadium(IV) | Oxidative bromination | [332] |
| PS-DVB | -- | CpNbCl$_4$, CpTaCl$_4$, (PhCH$_2$)NbCl$_4$, (PhCH$_2$)TaCl$_4$ | Olefin hydrogenation, isomerization, ethylene dimerization | [333] |
| HCPs-PPh$_3$ | -- | Au(I) | Hydration of alkyne | [334] |
| Schiff base-COP | -- | Ag | Nitroaromatics reduction | [335] |
| Graphene modified-POP | -- | Phosphotungstic acid | Alkylation desulfurization | [336] |
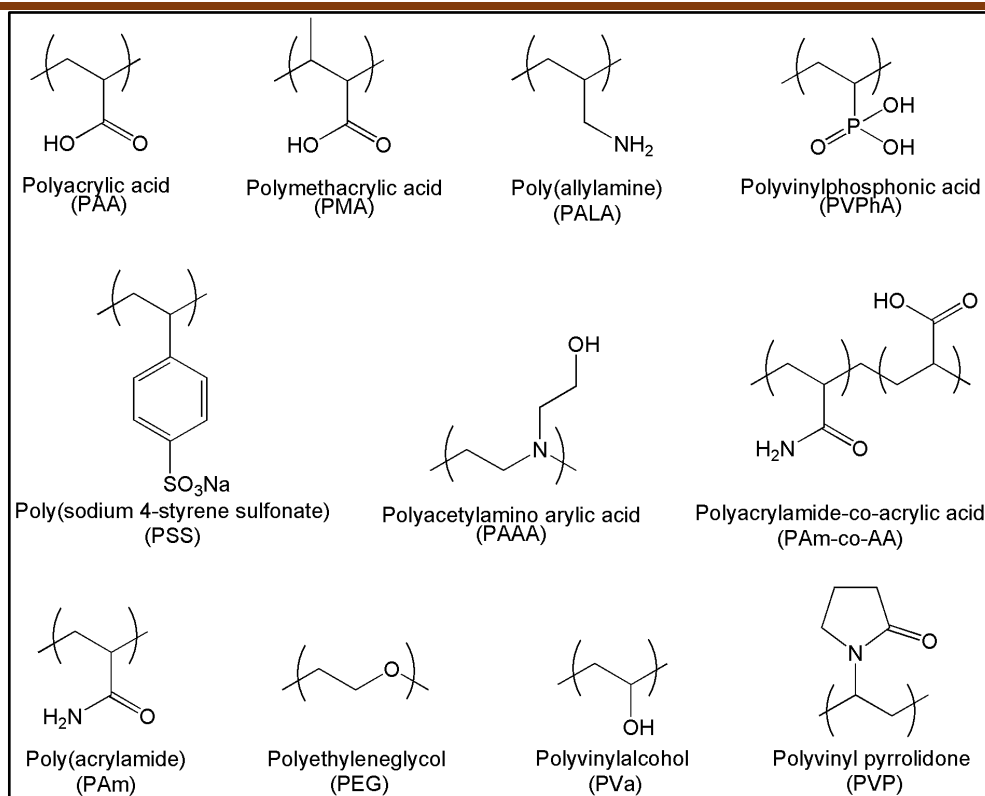
**Fig. 1.18** Some water-soluble polymers used for metal ion interaction [314,316].

In **Fig. 1.18,** examples of selected water-soluble polymers containing different functional groups which are commonly used as support to incorporate metal ions are presented. These macromolecular ligands usually comprise hydroxyl, amine, amide, carboxylic acid, amino acid, ether, and pyridine functional groups as common coordinating sites [315,338]. They can form complexes with other high or low-molecular-weight species in an aqueous solution. WSP can be a homo- or co-polymer, where with a suitable choice of the co-monomer, properties like the solubility, sorption capacity of metals, and selectivity can be controlled or boosted [201,315]. Polyethylene glycol, polyvinyl alcohol, polyacrylic acid, polyacrylamide, and polyvinyl pyrrolidine are examples of common synthetic water-soluble polymers preferred for metal anchoring [203,313,314,316].

**1.2.5.1 Catalytic application of soluble polymer anchored metal complexes**

The application of WSP for the recovery of catalysts and ligands in synthetic procedures for peptide and oligopeptide preparation was established by Merrifield as well as Letsinger and Wagner in the 1960's [339,340]. Such discoveries revolutionized the industrial and academic research toward developing immobilized or heterogenized homogeneous catalyst systems. The use of a soluble polymer as an alternative to a cross-

linked, insoluble polymeric resin for supporting a chiral ligand was first reported by Bayer and Schurig in 1976 [341]. A linear polystyrene-bound version of DIOP [4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxidolane] ligand was allowed to react with $HRh(CO)(PPh_3)_3$, and the resulting polymer-bound Rh complex was used for the hydroformylation of styrene [341]. Significant progress in soluble polymer support occurred when Han and Janda reported immobilized chiral catalysts for asymmetric dihydroxylation of olefins in 1996 [342]. Besides, the efficacy of soluble polymers as supports for catalysts in different organic transformations such as Heck reaction, hydrogenation, oxidation, etc. as well as tools in liquid/liquid separation of the polymer-bound species has been thoroughly discussed by Bergbreiter *et al.* [343-348].

Despite the several merits of insoluble supports, certain limitations such as unequal access to the reaction, solvation issues, nonlinear kinetic behaviour, and difficulties in transferring chemical reactions to the solid phase in chemical processes etc., are often encountered with respect to these heterogeneous matrices [316]. The strategies that employ soluble polymers are likely to combine the advantages of homogeneous solution chemistry, such as high reactivity, lack of dispersion, and easy analysis, with the accessible separation property of the heterogeneous methods [203,212]. Another benefit of using such polymer support is that solution state spectroscopy can make monitoring the chemical reaction that occurs on such polymers possible [349,350]. Notwithstanding these advantages, the concept of using WSP as supporting material in catalysis received relatively lesser attention mainly because of their recovery and recycling in catalysis were presumed to be cumbersome [203,309,346]. In practice, however, various methodologies have been implemented based on the properties of soluble supports to accomplish product isolation from the reaction mixture [203,316]. Solvent-induced precipitation is one such method where a homogeneous polymer solution is diluted employing a suitable solvent that prompts precipitation of the support, subsequently filtration to separate the polymer [203,316,346]. Apart from this approach, dialysis, crystallization, or centrifugation are other techniques for isolating the polymer from reaction media [203,316]. Thus, the green catalytic concept of "recovery and recycling" is ideally satisfied by soluble polymer-supported catalysts.

Among the popularly known soluble polymers, the differently functionalized poly(ethylene glycol) (PEG) has been widely used as a support material in organic synthesis. PEG can serve as a cost-beneficial, environmental-friendly reaction medium

with tuneable physicochemical properties [351,352]. A catalyst can acquire a range of advantageous features by functionalizing with PEG, including solubility and easy separation from the reaction medium [203,353]. Various ligands have been used to functionalize PEG over the years, such as phosphine, dipyridyl, salen, cinchona alkaloid, porphyrin, tartrate ester, and BINOL, etc., to improve catalysts' stability and recyclability [203,316,342,354-358]. Variously functionalized PEGs have been used in variety of catalytic processes such as hydrogenation [354], asymmetric dihydroxylation reaction [342], C-C bond formation reaction [359,360], hydroformylation [355], Wacker oxidation [356,361], hydroxylation of aromatic compounds [357], epoxidation [316,358] as well as phase transfer reactions [316,362]. Liu *et al.* [359] have established the utility of three *in situ* generated Pd-catalyst with PEG-functionalized imidazolium salts for the aqueous phase Suzuki reaction. Again, salicylaldoxime functionalized PEG-bridged dicationic ionic liquid ligands could facilitate the Pd-mediated Suzuki Miyaura reaction with good yield [360]. Very recently, Ballmann and co-workers have reported three amphiphilic Au(I) complexes based on PEG ubiquinol succinate (PQS)-bound *N*-heterocyclic carbene (NHC) (**Fig. 1.19**) as active micellar catalysts which prompted cyclization reactions of acetylenic or allenic substrates in water [363].
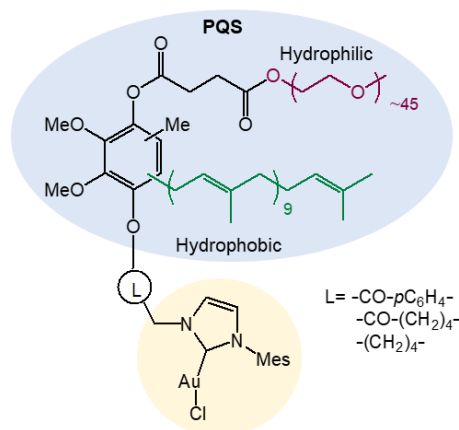


**Fig. 1.19** General structure of the three PQS-bound NHC−Au(I) complexes [363].

Lu and Toy reviewed the catalytic potential of various soluble polymers in the year 2009 [364]. Polycarboxylic acid and its derivatives are often utilized to prepare soluble polymer-based catalysts [365-367]. Poly(acrylic acid), as well as optically active phosphine-modified polyacrylamide supported-Rh(II) complexes, were reported to be highly active hydrogenation catalysts [368,369]. In addition, linear polymers, such as poly(vinylpyrrolidine), polyacrylonitrile, polyethyleneamine, and poly(ethylene

diaminoacetic acid) with different metals have been applied as hydrogenation catalysts as reported by Bayer and Schuman in the literature [370]. Very recently, Basak *et al.* [371] put forth the developments in designing and activity of stimuli-responsive metal-containing polymers. Macromolecular *N*-(isopropylacrylamide) is a fascinating thermo-responsive polymer whose application in organic synthesis was broadly investigated by Bergbreiter [344]. Zhang *et al.* immobilized an Mn-salen complex on this "smart" polymer and studied for asymmetric olefin epoxidation [372]. Ru complex of a pH-responsive polymer synthesized by copolymerization of dimethyl aminopropyl acrylamide and N-*p*-styrenesulfonyl-1,2-diphenylethylenediamine could effectively enable asymmetric transfer hydrogenation of ketones [373].

**1.2.5.2 Biological applications of soluble macro complexes**

Metal-containing soluble polymers often display tunable physical properties along with diverse redox properties as well as varied organic chemistry which enhance their suitability as promising systems for various biological applications [195-197]. A variety of soluble macromolecules and their derivatives, *viz.*, poly(ethylene glycol), poly(ethyleneimine), poly (vinyl alcohol), polyvinyl pyrrolidine, poly(acrylamide), poly(aspartamide), phosphazene, poly(methacrylic acid) have been utilized in pharmaceutical applications [197,313,314,374].

Soluble metallopolymer complexes can serve as biomimetic models as they can conduct multi-center activation of substrates in a manner similar to metal enzymes [375]. The macromolecular metal complexes were reported to be acting as models for various metalloproteins as well as metalloenzymes, namely vitamin B12, hemoglobin, myoglobin, cytochrome P450, peroxidase, catalase, proteolytic and other enzymes [187,189]. Recently, Kubota and co-workers [376] developed a carboxymethylpoly(1-vinylimidazole)-based Mn-porphyrin system as an active artificial center of catalase, and it is reported to be the first water-soluble polymer-bound Mn-porphyrin as an artificial catalase model that is active at physiological pH. Besides that, soluble polymer immobilized polymers also find their use as biosensors, photodynamic therapy agents, biocide, and in bioimaging as well as radiotherapy [197,377].

Bonding of potential drug molecules to soluble polymer matrices offers several advantages, such as improved drug pharmacokinetics, programmed drug release profile, facilitation of the preferred uptake by the targeted cell, and reduced toxicity to the healthy

organs [378,379]. Besides these, applying WSP can solubilize the hydrophobic drugs allowing their intravenous administration [380]. Over the last few decades, a large number of macromolecules have been used in designing therapeutic formulations and other biomedical applications [314,317,374,381,382]. Yan *et al.* reviewed the biomedical relevance of a variety of metal-containing polymeric complexes [197]. Drug conjugation with polymer carriers is the most common route for metal-based polymeric drugs, particularly Pt-drugs [383], as depicted in **Fig. 1.20**. This concept was introduced by Neuse *et al.*, which significantly lowered the drug dosage, thus reducing the side effects caused by the high dose of pure drug [197,384]. Additionally, the physical encapsulation of Ru complexes in photothermic biocompatible polymers, like polyaniline or melanin derivatives, has been another potential delivery system for combined photothermal and chemo-therapy [385].
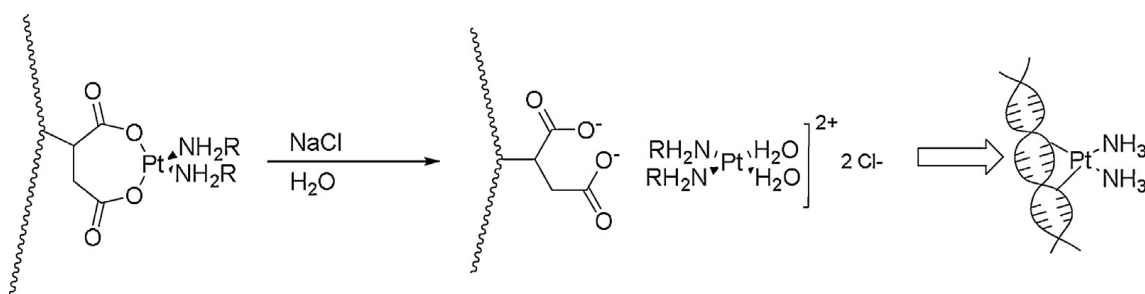


**Fig. 1.20** Polymer-platinum conjugation through leaving ligands, here bidentate carboxylato groups [383].

Most metallopolymers, especially transition metal-encapsulated polymers, reveal promising antimicrobial and antiviral properties [197]. Metal-polymers are active contenders against various bacterial strains, including drug-resistant ones [197]. Polymeric Schiff base ligands supported on different metals exhibited good antibacterial activity along with significant antifungal activity [386]. Rivas and his co-workers introduced water-soluble Ag(I) based polymeric complexes with biocidal properties against Gram-positive and Gram-negative bacteria [380].

Previous research from our group has shown that peroxidovandate species immobilized on WSP can effectively inhibit the growth of lung carcinoma cells (A549) [387]. Poly(methacrylate) incorporated peroxidovanadium (pV) compound also exhibited antibacterial activity against Gram-negative *E. coli* and Gram-positive *S. aureus* bacteria [388]. Moreover, it has been demonstrated for the first time that polymer-anchored peroxido compounds of Groups V and VI can induce strong inhibitory effects on the activity of phosphohydrolase enzymes [302,303,305]. In a recent work, it has been

observed that poly(acrylate) bound V and Nb peroxido derivatives could serve as potent inhibitors of calcineurin, a serine/threonine phosphatase [304]. Thus, by developing a series of water-soluble peroxido complexes and exploring their catalytic and biochemical properties [302-309], studies from our laboratory have established the possibility of obtaining stable, well-defined macromolecular complexes by anchoring metal peroxido species to suitable WSPs.

In line with the scope highlighted above, in the present research programme, we have endeavoured to establish facile synthetic routes to new mixed ligand oxido- and peroxido-niobium complexes, including macromolecular peroxidoniobates supported on soluble as well as insoluble polymer matrices. The work is mainly focused on pursuing the following primary objectives: (i) to develop new homogeneous and heterogeneous peroxidoniobium-based catalysts for organic oxidation which would be selective, robust and recyclable (ii) to establish eco-compatible protocols for selective organic oxidative transformations using $H_2O_2$ as an oxygen source, which can perform efficiently under organic-solvent-free condition or in the aqueous medium, and (iii) to generate water soluble compounds of Nb(V) with biologically significant characteristics. An important goal of the work is to investigate the activity of oxido- and pNb complexes as enzyme inhibitors.

Chapters **3** to **6** of the thesis present interpretative accounts of the findings of our investigations on the abovementioned features of peroxidoniobium 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 the relevant bibliography. The new results presented in chapters 3-6 have already been published.

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