CHAPTER 2

Materials and Methods

2.1 Chemicals

Reagent grade chemicals were used for all the reactions. The sources of the chemicals are given below:

Sodium thiosulfate, potassium dihydrogen phosphate, potassium hydrogen phosphate, petroleum ether (boiling range 60–80 °C), ethanol, hydrogen peroxide, ethyl acetate, acetone, acetonitrile, methanol, potassium permanganate (RANKEM); styrene, sodium hydroxide, sulfuric acid, glacial acetic acid, potassium dichromate, diethyl ether, iodine (E. Merck, India); chitosan (medium molecular weight, deacetylated degree 85%, viscosity 200-800 cps), sodium acetate anhydrous, potassium iodide, sodium bicarbonate, silica gel (60-120 mesh), boric acid (SRL); L-valine, L-asparagine, maltol (3-hydroxy-2-methyl-4-pyrone), deferiprone (3-hydroxy-1,2-dimethylpyridin-4-one), cyclohexene, cyclooctene, DL-limonene, 4-chlorophenyl methyl sulfide**,** 4-bromophenyl methyl sulfide, 2-(phenylthio)ethanol [TCI Chemicals (India) Pvt. Ltd.]; *p*-nitrophenyl phosphate (*p*-NPP), acid phosphatase from wheat thylakoid membrane (ACP), norbornene, chloromethylated poly(styrene-divinylbenzene) (2.5 mmol g^{-1} Cl^- loading, 2% DVB) (Merrifield resin-**MR**), poly(sodium methacrylate) (M_w= 4000), glycine, pyridine, niobium(V) oxide, methyl phenyl sulfide, methyl *p*-tolylsulfide, dimethyl sulfide, dibutylsulfide, diphenylsulfide, phenylvinyl sulfide, diphenyl sulfide, dihexyl sulfide, allyl phenyl sulfide and 5-hydroxy-2-methylfufural (HMF) were purchased from Sigma-Aldrich Chemical Company, Milwaukee, USA. Before functionalization, the **MR** was pre-treated with aqueous dioxane (50:50 (v/v)) followed by washing with methanol and dried under vacuum at 90 °C for 8 h. The precursor for the synthesis of pNb complexes, $Na_3[Nb(O_2)_4]\cdot 13H_2O$ (**TpNb**), was prepared based on previously reported methods [1]. Solutions were prepared under distilled and deionized water.

2.2 Elemental analysis

2.2.1 Niobium

The amount of niobium in the synthesized compounds was determined by Energy Dispersive X-Ray (EDX) analysis, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) as well as Atomic Absorption Spectroscopy (AAS).

2.2.2 Peroxide [2-5]

2.2.2.1 Permanganometry [2]

A peroxidoniobium compound with an accurately weighed amount was dissolved in a freshly prepared 7 N sulfuric acid solution containing 4 g of boric acid. Boric acid forms perboric acid and prevents active oxygen loss from the solution. The resulting solution was titrated with a standard potassium permanganate solution.

$$1\ \text{mL of 1N}\ KMnO_4 = 0.01701\ \text{g of}\ H_2O_2$$

This method is appropriate for the estimation of peroxide content in peroxidoniobium(V) compounds.

2.2.2.2 Iodometry [3,4]

To a freshly prepared solution of 2 N sulfuric acid containing potassium iodide (~1 g in 100 mL) and 0.5 g of sodium bicarbonate, a precisely weighed amount of peroxido-Nb compound was added. The mixture was kept still for *ca.* 15 min in the dark in a CO_2 atmosphere. The amount of released iodine was titrated against standard sodium thiosulfate solution. A few drops (1-5 mL) of 1% starch solution was added afterwards near the final point, and the solution was then turned a deep purple colour. The solution was titrated until it became colourless, and the final reading was observed. Thus, the total amount of peroxide present in the compound can be determined by this method.

$$1\ \text{mL of 1N}\ Na_2S_2O_3 = 0.01701\ \text{g of}\ H_2O_2$$

2.2.2.3 By standard Ce(IV) solution [5]

An accurately weighed amount of peroxidoniobate was dissolved in a 0.7 N sulfuric acid solution containing an excess of boric acid. The estimation of the peroxide percentage in the compound was conducted by titrating with standard Ce(IV) sulfate solution.

2.2.3 Carbon, hydrogen and nitrogen

The percentage of carbon, hydrogen and nitrogen in the compounds was calculated by Perkin Elmer 2400 series II CHN elemental analyzer at the Department of Chemical Sciences, Tezpur University.

EDX analysis was also carried out to determine the C and N contents.

2.2.4 Chlorine

The amount of chlorine in the complexes was determined by EDX analysis.

2.2.5 Sodium

The sodium amount in the compounds was determined by EDX and ICP-OES analyses.

2.3 Physical and spectroscopic measurements

2.3.1 pH measurement

E. Merck Universal indicator pH 0-14 paper and an Orion VERSARSTAR pH meter were used to measure the pH of the reaction solutions.

2.3.2 Electronic spectra

The diffuse reflectance electron absorption spectra of the solid compounds were collected in a Hitachi U-3400 spectrophotometer provided with the diffuse reflectance accessories, and $BaSO_4$ was the standard.

The UV-Vis absorption spectra in solution were recorded in an Agilent Cary100 Bio UV-Vis spectrophotometer equipped with a Peltier-controlled constant temperature cell, using cuvettes of 1 cm of path length.

2.3.3 Infrared (IR) and Raman spectra

The IR spectra of the compounds in KBr pellet forms were generated in the 4000-400 cm^{-1} range by a Perkin-Elmer spectrum 100 FTIR spectrophotometer.

An EZRaman-N (Enwaveoptronics) equipped with a diode laser of 350 mW maximum power of laser output and 785 nm of excitation wavelength was used to record the Raman spectra of the complexes. The measurement parameters were: 10 s of exposure time, 5 accumulation, 10% of output power and 1.44 cm^{-1} per pixel resolution.

2.3.4 Surface morphology analysis by Scanning Electron Microscope (SEM)

A JEOL JSM6390LV scanning electron micrograph attached with an energy-dispersive X-ray detector with a scanning range of 10–50 μm was utilized to conduct the

SEM and EDX analysis. The images were captured at a magnification of 20 kV, and the data were generated in the INCA software.

Gemini 500 field emission scanning electron microscope (FESEM) was used for higher-resolution imaging. This system is equipped with a LaB6 field emitting electron gun and three types of detectors, *viz*., InLens, secondary electron (SE2) and energy selective backscattered-detectors (ESB). Samples are mounted firmly on the stainless-steel stub using C-tape.

2.3.5 Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectrometry was carried out in a Thermo iCE 3000 series Atomic absorption spectrophotometer (model analyst 200).

2.3.6 Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

ICP-OES analysis of the compounds was performed with an Avio 220 Max Perkin Elmer inductively coupled plasma-optical emission spectrometer.

2.3.7 Powder X-ray diffraction (PXRD)

The PXRD patterns were generated in the 2θ range of 10–70° at 10° min^{-1} scanning rate with Cu Kα (k = 0.154 nm) radiation using a Rigaku X-ray diffractometer (Miniflax, UK).

2.3.8 X-ray photoelectron spectroscopy (XPS)

The XPS analysis was performed on an X-ray photo spectrometer of a Thermo Fisher Scientific Instrument with an Al Kα monochromatic X-ray source and 12 kV and 2×10^{-9} mbar of the operating voltage of the base pressure maintained in the analyzing chamber.

2.3.9 Surface area analysis

The surface area was measured by nitrogen adsorption/desorption measurements based on the Brunauer–Emmett–Teller (BET) method [6] at 77.3 K on a standard module NOVA 1000E, Quantachrome Instruments. The pore size and pore volumes were measured by the use of the Barrett–Joyner–Halenda (BJH) model [7] using a NOVA 1000E, Quantachrome Instruments.

2.3.10 ^{1}H NMR spectra

^{1}H NMR spectra were recorded on JEOL JNM-ECS400 or Bruker AVANCE NEO, 400 NanoBay 400 MHz FT-NMR spectrophotometer using deuterated solvents. The chemical shifts are referenced with respect to TMS = δ 0 ppm. The values are given in ppm. To represent the singlet, doublet, multiplet and broad absorption signals, s, d, m and br abbreviations are used, respectively.

2.3.11 ^{13}C NMR spectra

The solid-state ^{13}C NMR analysis was performed with the CP-MAS technique (cross-polarization, magic-angle-spinning) using JEOL JNM-ECX400II or JEOL JNM-ECZ400R/S1 spectrometer. Spectra were recorded at a ^{13}C frequency of 100.5 MHz (field strength of 9.38 T); CP/MAS sequence was used with the following parameters as the number of scans: 1024-2048, relaxation delay: 5 s, MAS frequency: 10 kHz and contact time: 5 ms.

The solution state ^{13}C NMR spectra of the compounds were recorded with JEOL JNM-ECS400 or Bruker AVANCE NEO, 400 NanoBay 400 MHz FT-NMR spectrometer at a carbon frequency of 100.61 MHz, number of scans 1024-20000, 1.38 s of acquisition time in D_2O, methanol-d_4 or $CDCl_3$ as solvents.

2.3.12 ^{93}Nb NMR spectra

^{93}Nb NMR spectra were recorded on JEOL JNM-ECS400 with a niobium frequency of 97.85 MHz, 32,768 X-resolution points, 1024 scans, 83 ms of acquisition time and 90° pulse length. The ^{93}Nb NMR chemical shifts were referenced to an external saturated solution of $NbCl_5$ in CD_3CN.

2.3.13 GC/GC-MS analysis

GC/GC-MS analysis was carried out in a PerkinElmer Clarus680 GC/600C MS instrument fitted with a 60.0 m × 250 μm column using He as the carrier gas.

2.3.14 High performance liquid chromatography (HPLC)

HPLC analysis was carried out on a Thermo-Scientific Dionex Ultimate 3000 HPLC system equipped with a UV detector.

2.3.15 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was conducted on a SHIMADZU TGA-50 system at a 10 °C min^{-1} heating rate under an N_2 atmosphere by using an aluminium pan.

2.3.16 Melting point determination

Melting points were measured in open capillary tubes using a Büchi Melting Point B-540 apparatus.

2.3.17 Magnetic susceptibility

Gouy method [4] was used for the magnetic susceptibility measurements, and Hg[Co(NCS)] was used as the calibrant (EMU 50 Magnetometer).

References

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