



## SYNTHESIS, SPECTROSCOPIC STUDIES AND REACTIVITY OF MONOCHLOROTETRAKIS (2-/4-ISOPROPYLPHENOXO) NIOBIUM (V) COMPLEXES

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### ABSTRACT

Complexes of composition  $[\text{NbCl}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2)_4]$  (1) and  $[\text{NbCl}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2)_4]$  (2) have been synthesized in quantitative yields by the reaction of niobium pentachloride with four equivalents of 2- and 4-isopropylphenols in carbon tetrachloride and characterized by elemental analyses, molar conductance, molecular weight determination, IR, <sup>1</sup>H and <sup>13</sup>C NMR and mass spectral studies. From these studies, a dimeric structure bridging through isopropylphenoxo group for the complexes has been inferred. The X-ray diffraction pattern of complexes has suggested amorphous nature of 1 and that of 2 as polycrystalline. The reactions of 1 and 2 with sodium alkoxides, NaOR (OR = OMe, OEt, OBut) yielded mixed alkoxo-phenoxo complexes of composition  $[\text{Nb}(\text{OR})(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2)_4]$  and  $[\text{Nb}(\text{OR})(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2)_4]$  authenticated by physicochemical, IR and <sup>1</sup>H NMR spectral studies.

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### INTRODUCTION

Literature survey reveals that there has been an enormous research interest over the years in the synthesis and characterization of metal alkoxides and metal aryloxides not only due to their rich structural chemistry but also due to the wide applications of these compounds as polymerization catalysts, surfactants and molecular precursors in the synthesis of advanced technological materials based on simple and complex metal oxides. The current interest in using metal oxides in optoelectronics, high-T superconductors and ceramics has led to a resurgence of interest in the chemistry of these compounds. The phenoxides of main group elements, transition metals, lanthanides and actinides are well documented.<sup>1</sup> Of transition metals, the chemistry of niobium has been a fascinating area of study owing to its applications in material science.<sup>2-9</sup> The niobium alkoxides<sup>10-17</sup> and aryloxides<sup>18-22</sup> have been the subject of numerous studies because of their versatile structural features<sup>23</sup> and potential catalytic properties.<sup>24-26</sup> Recently, niobium based ethylene polymerization procatalysts bearing the chelating di and triphenolate ligands have been reported<sup>27</sup>. The development of niobium complexes as catalysts for highly stereoselective ring opening of meso-epoxides and meso-aziridines has also been described.<sup>13</sup> Compared to alkoxide ion, phenoxide ion lends itself to a systematic investigation of steric and electronic effects arising from substituents in the benzene ring.

The substituted phenols containing substituents such as t-butyl, phenyl, isopropyl, methyl, methoxy, chloro, nitro groups at 2, 4 and 6- positions for complexation find frequent mention in literature. In particular, ortho substituted phenols represent an important class of ligands, as this ring position has the largest effect on the steric "cone" around each metal ion and may undergo chelation to the metal centre. A large variety of aryl/alkyl group substitution patterns include the widely used 2,6-dimethyl, di-iso-propyl and diphenylphenols. Although, isopropylalcohol and 2,6-isopropylphenolas ligands have been well-studied for the synthesis of niobium alkoxide and aryloxide complexes, yet to our knowledge the bonding properties of 2- and 4-isopropylphenols (Fig. 1) have not been explored towards the preparation of niobium(V) derivatives. As a part of our continuing interest on niobium aryloxides<sup>28-30</sup> and an extension of a previous paper where we have studied the coordination behaviour of  $[\text{NbCl}_4(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2)_4]$  complexes, the present work describes the synthesis and characterization of monochlorotetrakis(2-/4-isopropylphenoxo) complexes of composition  $[\text{NbCl}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2)_4]$  (1) and  $[\text{NbCl}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2)_4]$  (2) as a means of providing better understanding of the coordinating phenolic ligands. The reactivity of 1 and 2 towards NaOR (OR = OMe, OEt, OBu<sup>t</sup>) has been investigated and the resulting complexes have been characterized.

### Experimental

### MATERIALS AND PHYSICAL MEASUREMENTS

NbCl<sub>5</sub> (Fluka) was used without further purification and its purity was checked by chlorine analysis. 2-Isopropylphenol

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(Merck b.pt. 210 °C) was purified by vacuum distillation and 4-isopropylphenol was recrystallized from benzene (m.pt. 59 °C). Solvents were made anhydrous before use by standard methods. The niobium content in complexes was estimated as Nb<sub>2</sub>O<sub>5</sub> after decomposing the complexes with a mixture of conc. H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> followed by heating at 650-700 °C. Chlorine was determined by Volhard's method. Micro-analysis for carbon and hydrogen were performed on Eager 300 NCH System Elemental Analyzer. The molar conductances (10<sup>-3</sup> M solutions) of complexes in nitrobenzene were obtained at 25±0.1 °C on an Elico conductivity bridge (type CM-82T). The molecular weights were determined cryoscopically in benzene (0.0015-0.0020 M) using a Beckmann thermometer. IR spectra of complexes were recorded as (KBr pellets) on Nicolet-5700 FTIR spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on BRUKER AVANCE II 400 spectrometer using CDCl<sub>3</sub> as solvent. The mass spectra of complexes were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. The samples dissolved in chloroform were introduced into the ESI source through a syringe pump at the rate of 5 µl per min. The ESI capillary was set at 3.5 kV and the cone voltage was 40 V. The spectra were collected in 6 scans and print outs were averaged spectra of 6-8 scans. X-ray diffraction pattern of **1** and **2** complexes in powdered form were recorded on Philips PW 3071 X'PERT-PRO X-ray diffractometer (XRD) in 5-70° 2θ range and 0.017 step sizes in continuous scanning mode at 25 °C using Cu-Kα radiation. Phillips X'Pert software was used to obtain precise value of parameters. The molecular modelling calculations using Hyper-Chem 7.5 (student version) were performed to visualize the probable geometry acquired by complexes applying MM<sup>+</sup> force field with Polka-Ribiere algorithm and RMS gradient 0.01 kcal/mole. The molecular dynamic simulation was done upto 1000K (relaxations time 1 ps).

#### Preparation of Metal Complexes

##### [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2/4)<sub>4</sub>]

To a suspension of niobium pentachloride (3.0 g, 0.011 mol / 2.5 g, 0.009 mol) in CCl<sub>4</sub> (25 ml) were added four equivalents of 2-isopropylphenol (6.06 ml, 0.044 mol) and 4-isopropylphenol (5.04 g, 0.037 mol) in the same solvent (25 ml) in separate experiments. The mixing of the reactants resulted in an immediate colour change from yellow to dark orange with the evolution of HCl gas. The reaction mixture was initially stirred for 3-4 h and was then refluxed till the evolution of hydrogen chloride gas ceased, which ensured the completion of the reaction. No separation of any solid was observed during the course of the reaction in the solution mixture. It was filtered and excess solvent was then removed by distillation. The resultant concentrated solution was then evaporated under vacuum. The concentrate was treated with petroleum ether (40-60 °C range) and was dried under vacuum when maroon and yellow solids with 2.4 g, 80% / 2.20 g, 88% yield respectively were obtained. Anal.Calcd.for [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub>] (**1**) (%): C, 6.58; H, 5.31; Cl, 64.62; Nb, 13.91. Found: C, 6.55; H, 5.30; Cl, 64.60; Nb, 13.90. Λ<sub>m</sub>(PhNO<sub>2</sub>): 0.44 Scm<sup>2</sup>mol<sup>-1</sup>. Anal.Calcd.for [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub>] (**2**) (%): C, 6.58; H, 5.31; Cl, 63.62; Nb, 13.91. Found: C, 6.56; H, 5.32; Cl, 64.61; Nb, 13.92. Λ<sub>m</sub>(PhNO<sub>2</sub>): 0.76 Scm<sup>2</sup>mol<sup>-1</sup>. MolwtCalcd: 672.5, Found: 675.

#### Synthesis of sodium alkoxides (OR = OMe, OEt and OBu<sup>t</sup>)

Sodium methoxide, ethoxide and tert-butoxide have been synthesized by reported methods.<sup>31,32</sup>

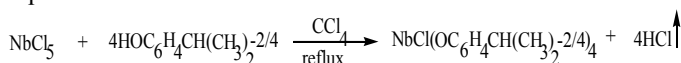
##### Reactions of [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2/4)<sub>4</sub>](**1,2**) with Sodium alkoxides NaOR (OR = OMe, OEt and OBu<sup>t</sup>)

In a typical reaction, to a solution of **1** and **2** (0.5 g, 0.00074 mol) in benzene was added methanolic solution of a slight excess than 1:1 molar ratio of sodium methoxide (0.5 g, 0.0093 mol) in separate experiments. The mixing of reactants did not result in any change of colour of the solution. The reaction mixture was then refluxed for 6-7 h in order to ensure the completion of the reaction during which a marked colour change was observed. It was filtered to remove the solid formed (sodium chloride), during the course of the reaction. The filtrate was concentrated under vacuum. The solid thus obtained was treated with petroleum ether (40-60 °C range) and was dried under vacuum.

The reactions with solution of sodium tert-butoxide in t-butyl alcohol were carried out employing similar procedure. In case of reactions of parent complexes with ethanolic solution of sodium ethoxide, the addition of acetonitrile resulted in the formation of mixed-ligand complexes as solids. Anal.Calcd.for [Nb(OCH<sub>3</sub>)(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub>] (%): C, 66.87; H, 7.08; Nb, 14.00. Found: C, 66.85; H, 7.05; Nb, 14.01. Λ<sub>m</sub>(PhNO<sub>2</sub>): 0.41 Scm<sup>2</sup>mol<sup>-1</sup>. Anal.Calcd.for [Nb(OCH<sub>3</sub>CH<sub>2</sub>)(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub>] (%): C, 67.26; H, 7.23; Nb, 13.72. Found: C, 67.27; H, 7.20; Nb, 13.73. Λ<sub>m</sub>(PhNO<sub>2</sub>): 0.39 Scm<sup>2</sup>mol<sup>-1</sup>. Anal.Calcd.for [Nb(OBu<sup>t</sup>)(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub>] (%): C, 67.99; H, 7.51; Nb, 13.17. Found: C, 67.97; H, 7.50; Nb, 13.15. Λ<sub>m</sub>(PhNO<sub>2</sub>): 0.36 Scm<sup>2</sup>mol<sup>-1</sup>. Anal.Calcd.for [Nb(OCH<sub>3</sub>CH<sub>2</sub>)(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub>] (%): C, 67.26; H, 7.23; Nb, 13.72. Found: C, 67.24; H, 7.21; Nb, 13.71. Λ<sub>m</sub>(PhNO<sub>2</sub>): 0.68 Scm<sup>2</sup>mol<sup>-1</sup>.

## RESULTS AND DISCUSSION

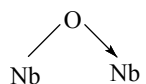
The formation of niobium(V) complexes of composition [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2/4)<sub>4</sub>] is represented according to the equation



The analytical data of complexes are in good agreement with their stoichiometric formulations. The complexes are moisture sensitive, brown to orange solids and are sparingly soluble in CHCl<sub>3</sub>, C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>. The molar conductance values of the complexes in nitrobenzene indicated these to be non-electrolytes.<sup>33</sup> The cryoscopic molecular weight determination of complexes in benzene suggested their dimeric nature in this solvent.

**FT-IR spectra:** In order to ascertain the formation of complexes, the IR spectra of complexes were compared with that of respective free 2- and 4-isopropylphenols. The band occurring at 3431 cm<sup>-1</sup> in 2-isopropylphenol and at 3313 cm<sup>-1</sup> in 4-isopropylphenol was absent in complexes indicating thereby the deprotonation of the phenolic proton upon complexation. The important and intense bands due to ν(C-O) mode are known to occur in 1260-1180, 1300-1200 and 1410-1310 cm<sup>-1</sup> regions in free phenols.<sup>34,35</sup> The bands appeared in 1364-1236 cm<sup>-1</sup> and 1362-1221 cm<sup>-1</sup> regions in 2- and 4-isopropylphenols respectively have been assigned to ν(C-O) mode. The bands occurring in 1339-1237 cm<sup>-1</sup> and 1382-1238 cm<sup>-1</sup> regions in respective complexes are diagnostic of

Nb←OAr II bonding. The appearance of bands in 590-580 cm<sup>-1</sup> and 550-520 cm<sup>-1</sup> regions assigned to ν(Nb–O) and



Nb mode characteristic of dimeric compounds is in agreement with previous reports on niobium alkoxides and phenoxides.<sup>36</sup> The medium to sharp absorption bands appeared at 357 and 359 cm<sup>-1</sup> in **1** and **2** respectively may be assigned to ν(Nb–Cl) mode.<sup>37</sup>

**<sup>1</sup>H NMR spectra;** The ligand-to-metal bonding in new niobium(V) complexes is further supported by <sup>1</sup>H NMR spectra. The complexes did not display signal due to phenolic –OH proton occurring at δ 5.42 ppm and at δ 4.91 ppm in respective 2- and 4-isopropylphenols suggesting thereby the deprotonation upon complexation. The uncoordinated 2-isopropylphenol exhibited two doublets centered at δ 6.85 and δ 7.37 ppm due to H – 6 and H – 3 respectively and two triplets at δ 7.08 and δ 7.20 ppm due to H – 5 and H – 4 respectively. The resonances due to methine and methyl substituents appeared as heptet and doublet at δ 3.39 and δ 1.42 ppm respectively. The 4-isopropylphenol displayed respective signals due to ortho (H – 2 and H – 6) and meta (H – 3 and H – 5) aromatic ring protons and aliphatic methine and methyl protons at δ 6.75, δ 7.23 and at δ 3.20 and δ 1.24 respectively.

Complex of composition [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub>] showed two distinct doublets centered at δ 6.77 ppm and δ 7.13 ppm due to aromatic protons at position 3 and 6 respectively and two triplets at δ 6.94 and δ 6.78 ppm due to aromatic protons at position 5 and 4 respectively. The [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub>] exhibited signals due to ortho (H – 2 and H – 6) and meta (H – 3 and H – 5) aromatic protons in δ 6.78-7.13 ppm range. The downfield shifts observed in aromatic ring proton resonances may be ascribed to the deshielding of these protons due to transfer of electron density from aromatic nucleus to the metal atom as (ArO ↔ Nb)<sup>36,37</sup>. The proton resonances due to methine and methyl groups remained almost unaltered upon complexation (Table 1). The integration of protons supported the formation of complexes (Fig. 2 and 3).

isopropylphenoxy group. The other carbon resonances showed a moderate shift upon complexation viz C-2 in (**1**) and C-4 in (**2**) shifted upfield by δ 0.69 and δ 2.37 ppm (Fig. 4 and 5) relative to free phenols. An upfield shift by δ 1.08 and δ 1.41 ppm due to methine carbon was observed in **1** and **2** respectively (Table 2).

**Mass spectra.** The [ES] mass spectra of NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub> (**1**) and NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub> (**2**) did not display any molecular ion peak at m/z 668 (Table 3). The higher values of fragment ions than molecular mass suggested the dimeric nature of the complexes. The fragment ion appeared at m/z 1207 in complex (**1**) corresponding to [2M-3Pr<sup>i</sup>]<sup>+</sup> indicated primary decomposition by the removal of three isopropyl groups. The base peak at 217/218 corresponded to [Nb<sub>2</sub>O<sub>2</sub>]<sup>+</sup>. The fragments ions at m/z 1169, 988, 804, 670, 655, 602/603, 591, 523, 417, 273, 185, 155, 122 corresponded to [2M-3Pr<sup>i</sup>-Cl-2H]<sup>+</sup>, [Nb<sub>2</sub>(OArPr<sup>i</sup>-2)<sub>5</sub>(OAr)Cl-H]<sup>+</sup>, [NbCl(OArPr<sup>i</sup>-2)<sub>4</sub>]<sup>+</sup> + [(HOArPr<sup>i</sup>-2)]<sup>+</sup>, [M+2H]<sup>+</sup>, [Nb<sub>2</sub>Cl(OArPr<sup>i</sup>-2)<sub>3</sub>+ 2Me]<sup>+</sup>, [M-Cl-2Me]<sup>+</sup>, [NbCl(OArPr<sup>i</sup>-2)<sub>4</sub>-Cl-Pr<sup>i</sup>+H]<sup>+</sup>, [Nb<sub>2</sub>O<sub>2</sub>Cl(OArPr<sup>i</sup>)<sub>2</sub>]<sup>+</sup>, [Nb<sub>2</sub>(OArPr<sup>i</sup>-2)(OAr)+3H]<sup>+</sup>, [(HOArPr<sup>i</sup>-2)<sub>2</sub>+H]<sup>+</sup>, [Nb(OC<sub>6</sub>H<sub>5</sub>-H)]<sup>+</sup>, [NbO<sub>2</sub>+2Me]<sup>+</sup> and [Nb+2Me-H]<sup>+</sup> respectively. In complex (**2**), the fragment ion appeared at m/z 1293 and m/z 1173 corresponding to [2M-Pr<sup>i</sup>]<sup>+</sup> and [2M-3Pr<sup>i</sup>-Cl]<sup>+</sup> indicated primary decomposition by one isopropyl group and secondly three isopropyl groups accompanied by chloride ion respectively. The base peak at 551 corresponded to [Nb<sub>2</sub>OCl(OArPr<sup>i</sup>)<sub>2</sub>+Pr<sup>i</sup>+H]<sup>+</sup>. The fragments ions at 507, 217, 155, 122 corresponded to [Nb<sub>2</sub>OCl(OArPr<sup>i</sup>)<sub>2</sub>]<sup>+</sup>, [Nb<sub>2</sub>O<sub>2</sub>]<sup>+</sup>, [NbO<sub>2</sub>+2Me]<sup>+</sup> and [Nb+2Me-H]<sup>+</sup>.

Based upon physico-chemical and spectroscopic studies coupled with molecular modelling calculations, a dimeric structure bridging through iso-propylphenoxy groups exhibiting an octahedral environment around niobium has, tentatively been proposed for niobium(V) complexes (Fig. 6 and 7).

**Table 1** <sup>1</sup>H-NMR data of Niobium(V) complexes (ppm).

Complex	Isopropyl substituent			Aromatic phenolic ring protons			Aliphatic protons	
	-(CH <sub>3</sub> ) <sub>2</sub>	-CH	H-3	H-4	H-5	H-6	-OCH <sub>2</sub> -	-CH <sub>2</sub> -
NbCl(OC <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> ) <sub>2</sub> -2) <sub>4</sub>	1.20-1.22	3.25-3.37	6.76-6.78(d)	6.80-6.83(t)	6.96-6.99(t)	7.12-7.14(d)	----	----
Nb(OCH <sub>3</sub> )(OC <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> ) <sub>2</sub> -2) <sub>4</sub>	1.15-1.17	3.36-3.55	6.72-6.74(d,d)	6.75-6.80(d,t)	6.92-6.96(d,t)	7.08-7.10(d,d)	3.3	----
Nb(OCH <sub>2</sub> CH <sub>3</sub> )(OC <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> ) <sub>2</sub> -2) <sub>4</sub>	1.06-1.22	3.47-3.51	6.70-6.72(d,d)	6.74-6.78(d,t)	6.91-6.94(d,t)	7.08-7.10(d,d)	3.44-3.46	1.22
Nb(OBu <sup>t</sup> )(OC <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> ) <sub>2</sub> -2) <sub>4</sub>	1.10-1.18	3.19-3.28	6.70-6.72(d,d)	6.74-6.78(d,t)	6.91-6.95(d,t)	7.06-7.08(d,d)	----	1.25
NbCl(OC <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> ) <sub>2</sub> -4) <sub>4</sub>	1.23-1.27	2.83-2.92	7.11-7.13(d)	7.27-7.28(d)	6.77-6.78(d)	6.78-6.80(d)	----	----
Nb(OCH <sub>2</sub> CH <sub>3</sub> )(OC <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> ) <sub>2</sub> -4) <sub>4</sub>	1.11-1.13	2.52-2.73	7.12-7.14(d)	7.22-7.24(d)	6.63-6.65(d)	6.92-6.94(d)	2.75-2.77	1.19-1.20

**Table 2** <sup>13</sup>C-NMR data of isopropylphenols and niobium(V) complexes (ppm)

Complex	Aromatic phenolic ring carbons						Substituent (Isopropyl carbons)	
	C-1	C-2	C-3	C-4	C-5	C-6	-CH	-(CH <sub>3</sub> ) <sub>2</sub>
HOArPr <sup>i</sup> -2	153.14	135.21	127.20	121.60	126.99	115.94	27.45	23.12
NbCl(OArPr <sup>i</sup> -2) <sub>4</sub>	153.91	134.43	125.85	118.95	125.56	114.77	26.39	22.24
HOArPr <sup>i</sup> -4	154.50	115.40	127.70	141.30	127.70	115.40	31.70	24.40
NbCl(OArPr <sup>i</sup> -4) <sub>4</sub>	155.49	115.29	127.18	139.07	127.18	115.29	33.11	24.54

**<sup>13</sup>C NMR spectra:** The <sup>13</sup>C NMR spectra of [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub>] (**1**) and [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub>] (**2**) showed signals at δ 153.91 ppm and δ 155.49 ppm respectively shifted downfield by δ 0.77 ppm and δ 0.99 ppm in respective complexes relative to this signal occurring at δ 153.14 and δ 154.50 ppm in 2- and 4-isopropylphenol respectively. The observed downfield shifts are indicative of stronger bonding of 4-isopropylphenoxy group than 2-

**X-ray Diffraction Studies:** X-ray diffraction patterns of [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub>] (**1**) and [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub>] (**2**) have been obtained in order to investigate their nature (amorphous or crystalline). The [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub>] (**1**) has recorded two reflections of 2θ at 24° and 50° indicative of its amorphous nature (Fig. 8). The XRD pattern of [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub>] (**2**) however, revealed both high and low intense peaks (Fig. 9). Indexing of XRD peaks was

done from  $\sin^2\theta$  values. The indices hkl indicated its polycrystalline nature (Table 4).

**Table 3** Selected positive-ion electrospray mass spectral data of niobium(V) complexes

NbCl(OArPr <sup>i</sup> -2) <sub>4</sub> [M]	m/z	Int%	NbCl(OArPr <sup>i</sup> -4) <sub>4</sub> [M]	m/z	Int%
[2M-3Pr <sup>i</sup> ] <sup>+</sup>	1207	3	[2M-Pr <sup>i</sup> ] <sup>+</sup>	1293	16
[2M-3Pr <sup>i</sup> -Cl-2H] <sup>+</sup>	1169	5	[2M-3Pr <sup>i</sup> -Cl] <sup>+</sup>	1171	12
[Nb <sub>2</sub> (OArPr <sup>i</sup> -2) <sub>5</sub> (OAr)Cl-H] <sup>+</sup>	988	28	[Nb <sub>2</sub> (OArPr <sup>i</sup> -2) <sub>5</sub> (OAr)-H] <sup>+</sup>	952	36
[NbCl(OArPr <sup>i</sup> -2) <sub>4</sub> + (HOArPr <sup>i</sup> -2)] <sup>+</sup>	804	17	[Nb <sub>2</sub> Cl <sub>2</sub> (OArPr <sup>i</sup> -2) <sub>4</sub> ] <sup>+</sup>	797	28
[M+2H] <sup>+</sup>	670	91	[NbCl(OArPr <sup>i</sup> -2) <sub>4</sub> + Me+H] <sup>+</sup>	699	14
[Nb <sub>2</sub> Cl(OArPr <sup>i</sup> -2) <sub>3</sub> + 2Me] <sup>+</sup>	655	14	[NbOCl(OArPr <sup>i</sup> -2) <sub>4</sub> ] <sup>+</sup>	684	56
[M-Cl-2Me] <sup>+</sup>	602/603	93	[Nb <sub>2</sub> (OArPr <sup>i</sup> -2) <sub>3</sub> Cl-H] <sup>+</sup>	625	87
[NbCl(OArPr <sup>i</sup> -2) <sub>4</sub> -Cl-Pr <sup>i</sup> +H] <sup>+</sup>	591	42	[Nb <sub>2</sub> OCl(OArPr <sup>i</sup> ) <sub>2</sub> +Pr <sup>i</sup> +H] <sup>+</sup>	551(B. P.)	100
[Nb <sub>2</sub> O <sub>2</sub> Cl(OArPr <sup>i</sup> ) <sub>2</sub> ] <sup>+</sup>	523	23	[Nb <sub>2</sub> OCl(OArPr <sup>i</sup> ) <sub>2</sub> ] <sup>+</sup>	507	23
[Nb <sub>2</sub> (OArPr <sup>i</sup> -2)(OAr)+3H] <sup>+</sup>	417	32	[Nb <sub>2</sub> O <sub>2</sub> ] <sup>+</sup>	217/218	34
[(HOArPr <sup>i</sup> -2) <sub>2</sub> +H] <sup>+</sup>	273	9	[NbO <sub>2</sub> +2Me] <sup>+</sup>	155	13
[Nb <sub>2</sub> O <sub>2</sub> ] <sup>+</sup>	217/218 (B. P.)	100	[Nb+2Me-H] <sup>+</sup>	122	27
[Nb(OC <sub>6</sub> H <sub>5</sub> )-H] <sup>+</sup>	185	29			
[NbO <sub>2</sub> +2Me] <sup>+</sup>	155	6			
[Nb+2Me-H] <sup>+</sup>	122	8			

**Table 4** Indexing of the Reflections and the Determination of the Lattice Parameter of [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub>]

Sin <sup>2</sup> θ	N = sin <sup>2</sup> θ/comm. fa.	hkl	Quadratic forms of Miller Indices	a = ½λ√N/sin <sup>2</sup> θ	Error function ½(cos <sup>2</sup> θ/sinθ + cos <sup>2</sup> θ/θ)
0.002574	1	(100)	Sc and Hexagonal	15.18	9.99
0.020584	8	(220)	Sc, Fcc, Bcc, Diamond and Hexagonal	15.18	3.47
0.00656	3	(111)	Sc, Fcc, Diamond and Hexagonal	16.47	6.24
0.03856	15	----	Hexagonal	15.18	2.49
0.00569	2	(110)	Sc and Hexagonal	14.44	6.70
0.02180	9	(221)	Sc and Hexagonal	15.65	3.37
0.032572	13	(320)	Sc and Hexagonal	15.38	2.73

Where Sc = Simple cubic, Fcc = Face centered cubic, Bcc = Body centered cubic

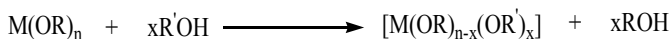
**Crystallite Size:** The crystalline size of NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub> has been calculated using Scherrer equation:

$$\text{Crystalline size} = \frac{k\lambda}{\beta \cos\theta}$$

where k is the constant of proportionality (Scherrer constant) and depends on how the line width is determined and value of k is generally taken as 0.9, λ represents the wavelength of the X rays and has a value of 1.54 Å, θ is the half of the angle (2θ) of diffraction and β is the value of broadening of line at Full Width Half Maximum (FWHM) in radians. The average crystalline size has been found to be 8.62 nm.

**Reactions of [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub>] (1) and [NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub>] (2) with Sodium alkoxides NaOR (OR = OMe, OEt and OBu<sup>t</sup>)**

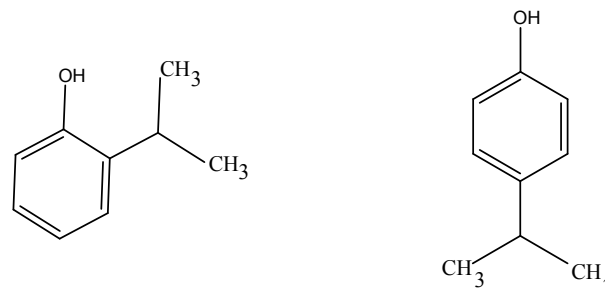
Metal alkoxides are known to react with a variety of primary, secondary and tertiary alcohols as well as with phenols in accordance with the reaction:



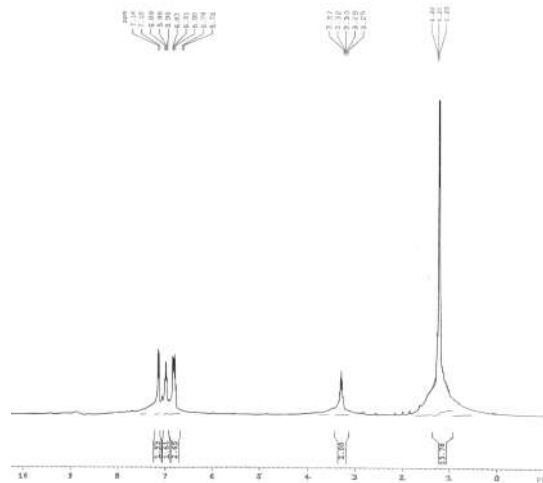
The displaced alcohols in these reactions are removed by fractional distillation or as an azeotrope by adding a suitable solvent.<sup>38</sup> Although, the formation of mixed alkoxo and alkoxo-phenoxo metal complexes by the alcohol-alcohol and alcohol-phenol interchange method continues to be the subject of numerous studies still, the reports relating to the reactions of alcohols with metal phenoxides are rather limited.

Complexes of composition NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub> (1) and NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub> (2) react with sodium alkoxides NaOR (OR = OMe, OEt and OBu<sup>t</sup>) by replacing chloride ion with alkoxo group affording the formation of mixed alkoxo-phenoxo niobium(V) complexes in consonance with their analytical data. The complexes are moisture

sensitive solids but are quite stable in dry air. The complexes are soluble in benzene, nitrobenzene and chloroform. The molar conductance values of the millimolar solutions of the complexes in nitrobenzene showed their non-electrolytic nature.



**Fig 1** Structure of 2- and 4-Isopropylphenol



**Fig 2** <sup>1</sup>H NMR spectra of NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub>

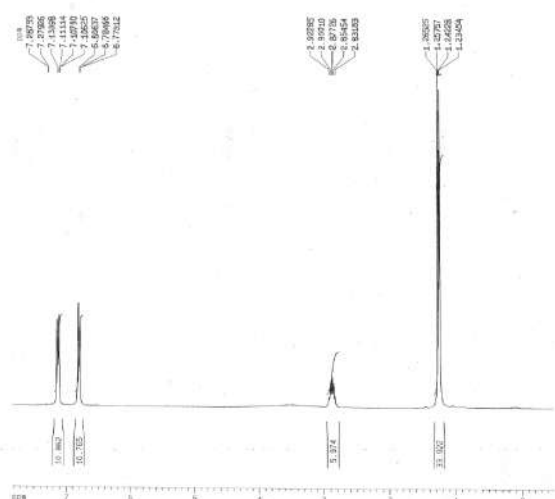


Fig 3 <sup>1</sup>H NMR spectra of NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub>

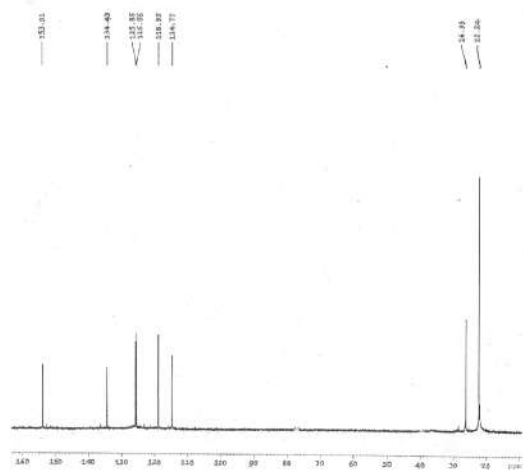


Fig 4 <sup>13</sup>C NMR spectra of NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub>

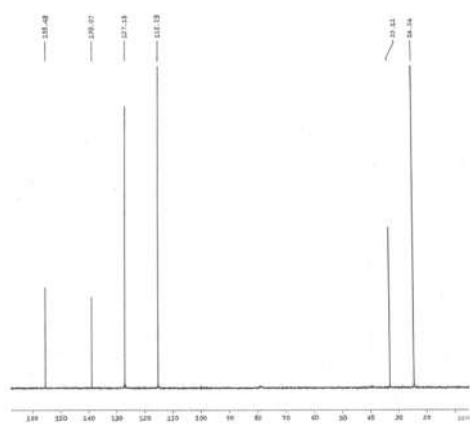
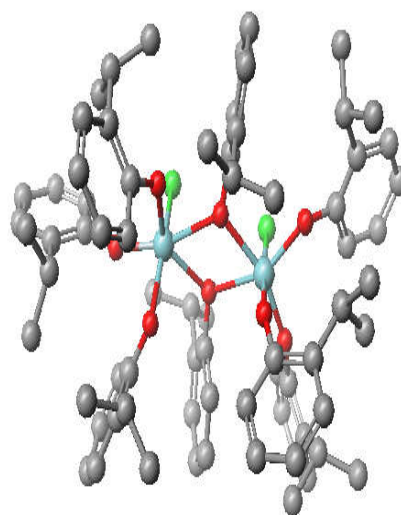
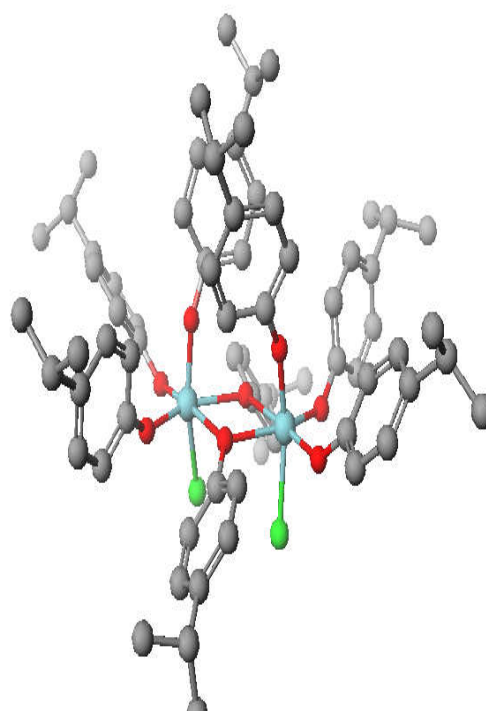


Fig 5 <sup>13</sup>C NMR spectra of NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub>



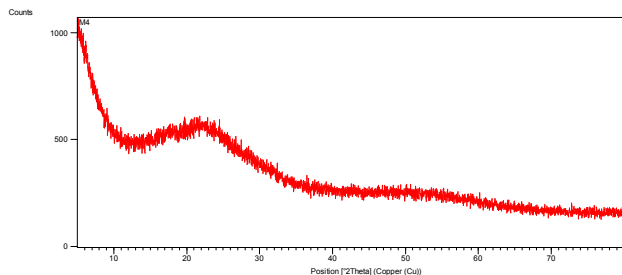
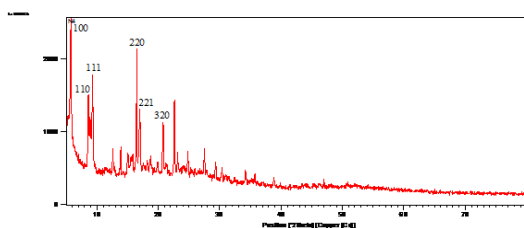
- niobium
- oxygen
- carbon
- chlorine

Fig 6 Molecular structure of NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-2)<sub>4</sub>



- niobium
- oxygen
- carbon
- chlorine

Fig 7 Molecular structure of NbCl(OC<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>-4)<sub>4</sub>


 Fig 8 XRD pattern of  $\text{NbCl}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2-2)_4$ 

 Fig 9 XRD pattern of  $\text{NbCl}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2-4)_4$ 

**FT-IR spectra:** The characteristic vibrational modes of the coordinated alkoxy groups are known to occur in  $1150-1000\text{ cm}^{-1}$  region in metal alkoxides. Also, the number and band positions are related to the terminal and bridged alkoxy groups.<sup>39</sup> The  $\nu(\text{CO})$  mode has been reported to usually shift to higher frequencies upon complexation and a splitting of band in the presence of bridged and terminal alkoxy groups may occur. A careful and close examination of IR spectra of mixed-ligand complexes showed the occurrence of absorptions bands in  $1189-1010\text{ cm}^{-1}$  region attributed to  $\nu(\text{CO})$  mode of terminal alkoxy groups. It is quite noteworthy that, quite a large number of absorptions bands have been observed in C–O stretching region for complexes containing an ethoxide ion over methoxide ion in line with previous reports.<sup>40,41</sup> The absorption bands characteristic of alkoxy groups at  $\sim 2900\text{ cm}^{-1}$  and  $\sim 1450\text{ cm}^{-1}$  due to  $\nu(\text{CH})$  and  $\nu(\text{C-H})$  modes have also been observed in complexes. The absorption bands due to phenoxo group were found to undergo slight change in band positions and intensity. The occurrence of absorption bands at  $540\text{ cm}^{-1}$  due to  $\nu(\text{Nb-O})$  mode only suggested the rupture of bridging isopropylphenoxy groups in parent complexes. The absence of bands due to  $\nu(\text{Nb-Cl})$  mode in parent complexes confirmed the substitution of chloride ion by alkoxide ions in mixed-ligand complexes.

**<sup>1</sup>H-NMR Spectra.** The incorporation of alkoxy (OR = OMe, OEt, OBU<sup>t</sup>) groups in new mixed-ligand alkoxy-isopropyl phenoxoniobium(V) complexes is further supported by the <sup>1</sup>H-NMR spectra. Although complexes displayed complex <sup>1</sup>H-NMR pattern because of the probable overlapping of signals due to protons of isopropyl group substituent at aromatic ring and those of methoxy, ethoxy and t-butoxy groups yet it has been possible to assign the peaks and confirm the formation of alkoxy-isopropylphenoxy complexes. Complex of composition  $[\text{Nb}(\text{OMe})(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2-2)_4]$  showed a distinct signal at  $\delta$  3.30 ppm assignable to Nb(OMe) group. It is worth mentioning here that in case of  $[\text{NbCl}_4(\text{OMe})\text{MeCN}]$ , this resonance is reported to occur at  $\delta$  3.90 ppm<sup>42</sup>. In case of  $[\text{Nb}(\text{OC}_2\text{H}_5)(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2-2/4)_4]$ , the signals due to methyl and methine groups appeared as triplet and quartet in  $\delta$  3.42 –

3.46 ppm and  $\delta$  1.20 – 1.22 ppm range respectively. In  $[\text{Nb}(\text{OBU}^t)(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2-2)_4]$  a distinct signal due to t-butoxy group appeared at  $\delta$  1.25 ppm (Table 1). In addition to these signals, resonances corresponding to isopropyl substituent and phenolic protons were also observed in the expected region, though slightly shifted relative to parent complexes.

## CONCLUSIONS

The spectroscopic studies of newly synthesized niobium(V) complexes of composition  $[\text{NbCl}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2-2)_4]$  (1) and  $[\text{NbCl}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2-4)_4]$  (2) suggested dimeric structure involving bridging through 2-/4-isopropylphenoxy groups. X-ray diffraction studies showed their amorphous and polycrystalline nature respectively. The reactions of  $[\text{NbCl}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2-2)_4]$  and  $[\text{NbCl}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2-4)_4]$  with sodium alkoxides, NaOR (OR = OMe, OEt, OBU<sup>t</sup>) yielded mixed alkoxy-isopropylphenoxy complexes authenticated by physicochemical, IR and <sup>1</sup>H NMR spectral studies.

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