

## Synthesis and Characterization of Niobium and Tantalum Complexes with Bidentate Ligand and its use in Ring Opening Polymerization of $\epsilon$ -Caprolactone

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Reaction of two equivalents of the bidentate 2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH]<sub>2</sub> with one equivalent of niobium pentachloride gave the complex Nb{2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>}<sub>2</sub> (**1**). Similar use of two equivalents of the same ligand with one equivalents tantalum pentachloride afforded Ta{2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>}<sub>2</sub> (**2**). The molecular structure of complexes **1** and **2** have been characterized by IR and <sup>1</sup>H NMR. Both complexes were investigated as catalysts for polymerization of cyclic esters ( $\epsilon$ -caprolactone) with no solvent at various time at 110 °C. In all cases the polymer produced was of high yield percent.

**Keywords:** Niobium(V), Tantalum(V), Phenolate,  $\epsilon$ -Caprolactone, Ring opening polymerization.

### INTRODUCTION

Biodegradable polymeric material produced *via* ring opening polymerization (ROP) of  $\epsilon$ -caprolactone continues to catch much attention by reason of a wide range of applications [1,2]. A variety of catalysts have been used as initiators for ring opening polymerization and coordination chemistry shows a significant role in this process, the use of niobium and tantalum compounds received more attention due to no toxicity related with these metals. According to the literature a few papers published on these metals complexes as catalysts toward polymerization of lactide, lactone or ethylene [3-6]. The use of Schiff base ligation has received more interest because of easy to prepare [7] and versatile applications of Schiff base and their complexes as biological activity, antifungal properties, anticancer properties, application in modern technologies, application in synthesis and chemical analysis [8-13].

In this paper, two complexes of niobium and tantalum were synthesized, characterized and their catalytic behaviour was investigated. As compared with one equivalent of 2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH]<sub>2</sub> prepared by Redshaw *et al.* [14] and Müller *et al.* [15], we have found that by employing two equivalent of 2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH]<sub>2</sub> ligand can be beneficial in term of control of polymerization.

### EXPERIMENTAL

Dried environment was carried out throughout the experiment. Solvents were dried before use. Infrared spectra were recorded

using Nicolet Avatar 360 FTIR spectrometer. <sup>1</sup>H NMR were recorded at 400 MHz in a (VXR 400 S) spectrometer.

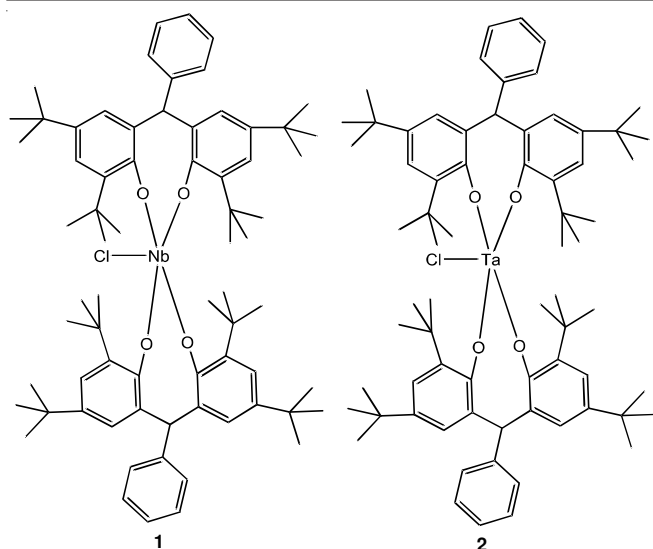
**Synthesis of Nb{2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>}<sub>2</sub> complex (**1**):** A toluene solution of 20 mL of 2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH]<sub>2</sub> (1 g, 1.99 mmol) and NbCl<sub>5</sub> (1.12 g, 0.99 mmol) was dissolved in 10 mL toluene and mixed with ligand solution. The mixture was refluxed for 6 h followed by the removal of volatiles and extracted the solid into acetonitrile (20 mL) to give red coloured solid complex **1**.

**Synthesis of Ta{2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>}<sub>2</sub> complex (**2**):** By following same procedure as described for synthesis of complex **1**, the complex **2** was synthesized by the reaction of TaCl<sub>5</sub> (1.21 g, 0.99 mmol) with 20 mL of 2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH]<sub>2</sub> (1.00 g, 1.99 mmol) to give pink coloured solid complex **2**.

**Ring opening polymerization:** Complex **1** or **2** (0.30 g, 266.46  $\mu$ mol),  $\epsilon$ -caprolactone (6.08 mL, 52.39 mmol) and alcohol (0.01 mL, 118.3  $\mu$ mol) mixed together in absence of solvent and the system was placed in an oil bath at 100 °C. After 1 h, the mixture quenched by added methanol (250 mL).

### RESULTS AND DISCUSSION

The compound 2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH]<sub>2</sub> was prepared according to reported procedure [4,14]. Reaction of ligand with toluene solution of niobium pentachloride (2:1) ratio and tantalum pentachloride (2:1) ratio has resulted in the formation of Nb{2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>}<sub>2</sub> (**1**) complex and Ta{2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>}<sub>2</sub> (**2**) complexes.



Structure of Nb{2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>}<sub>2</sub> (**1**) and Ta{2,2'-PhCH[4,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>}<sub>2</sub> (**2**)

**Infrared spectra:** The IR spectra of both complexes presented a characteristic absorption single at 2900 cm<sup>-1</sup> belonging to *t*-butyl group while peaks at 3200-3100 cm<sup>-1</sup> shifted to shorter wave length indicated that coordination has happened through -OH group.

**<sup>1</sup>H NMR spectra:** The <sup>1</sup>H NMR spectra of complexes was performed in CDCl<sub>3</sub> at room temperature. The spectrum of complex **1** revealed the signals at 1.27 (s, 36H, *t*-Bu), 1.30 (s, 36H, *t*-Bu), 3.77 (s, 1H, CH-bridge) and 6.67-7.51 (m, 18H, Ar-H) (Fig. 1). For complex **2**, <sup>1</sup>H NMR spectrum showed the signals at 1.29 (s, 18H, *t*-Bu), 1.42 (s, 18H, *t*-Bu), 4.43 (s, 1H, CH bridge) and 7.15-7.43 (m, 18H, Ar-H) (Fig. 2).

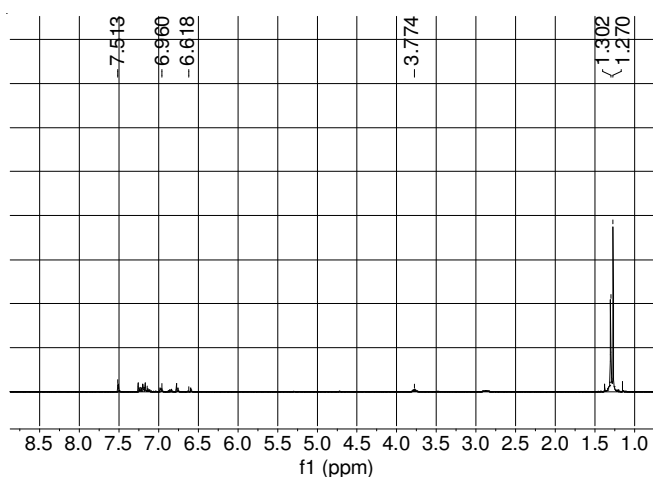


Fig. 1. <sup>1</sup>H NMR spectrum of complex **1**

**Ring opening polymerization of  $\epsilon$ -caprolactone:** The ability of synthesized complexes toward the ring opening polymerization of  $\epsilon$ -caprolactone were assessed (Scheme-I). Polymerization of  $\epsilon$ -caprolactone by complexes **1** and **2** which includes the phenoxide group were noted to be active (Table-1). The polymer molecular weight (*M<sub>n</sub>*) obtained by Ta catalyst is much lower as compared to Nb catalyst [16].

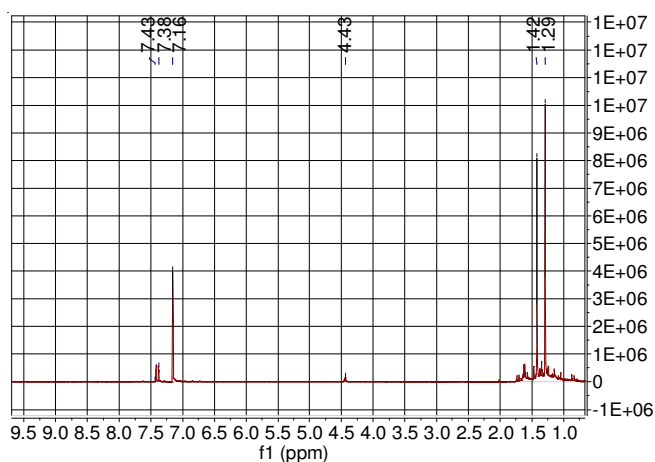
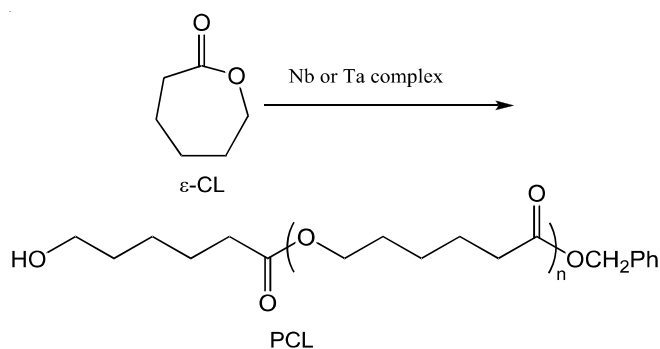


Fig. 2. <sup>1</sup>H NMR spectrum of complex **2**



Scheme-I: Ring opening polymerization of  $\epsilon$ -CL

TABLE-1  
POLYMERIZATION OF  $\epsilon$ -CAPROLACTONE  
USING COMPOUNDS **1** AND **2**<sup>a</sup>

Catalyst	Yield (%)	Time (min)	<i>M<sub>n</sub></i> <sup>b</sup>	PDI <sup>c</sup>
Nb complex	81	30	12900	1.10
Ta complex	77	40	6500	1.29

<sup>a</sup>Conditions: 0.0123 mol of complexes; 1.0 M  $\epsilon$ -CL in toluene. CL: [cat] : BnOH = 200:1:1. <sup>b</sup>from GPC.

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