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Alkali metal complexes of tridentate amine-bis(phenolate) ligands and their *rac*-lactide ROP activity

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ABSTRACT

Three complexes were prepared using lithium, sodium and potassium reagents and an amine-(bis) phenol proligand. The proligand, benzylamino-*N*,*N*-bis(2-methylene-4-methyl-6-*tert*-butylphenol) (abbreviated H_2[**L**]), was reacted with *n*-butyllithium to give the lithium complex, Li_2[**L**] (**1**), and NaH or KH to give the sodium, Na_2[**L**] (**2**), and potassium, K_2[**L**] (**3**), complexes, respectively. The compounds were also found to contain varying numbers of coordinated THF molecules. These complexes were characterized using ^{1}H, ^{13}C, and ^{7}Li NMR (for the lithium complex), MALDI-TOF MS, elemental analysis and FT-IR. The potassium complex (**3**) was characterized in the solid state and exhibits η^6 K-arene bonds as well as η^1-bonding of the K ion to the *ipso*-carbons of the phenolate fragments. The reactivity of **1**–**3** towards the ring-opening polymerization of *rac*-lactide to form polylactide (PLA) was explored.

1. Introduction

Aminophenolates are versatile ligands that have been widely studied for use in metal-catalyzed polymerization, including the ring opening polymerization (ROP) of ε-caprolactone and lactide [1]. Numerous derivatives of this ligand class have been used with main group and d-block metals, including lithium [2–12], magnesium [13–19], calcium [20], zinc [14,21–29], aluminium [30–32], zirconium [33,34] and titanium [35], as well as the rare-earths [36,37]. Many of these complexes have been reported to be excellent initiators for ROP and the s-block metal complexes are attractive because of their generally low toxicity and low cost.

Lithium compounds are excellent candidates in the search for efficient, stable, cheap and nontoxic catalysts. As well as their potential catalytic activity, lithium amino-bis(phenolate) compounds have also been shown to display interesting structural behaviour depending on the steric and geometric properties of the ligand or the solvent used [2–12].

Previous reports described dimeric, tetranuclear lithium complexes of tetradentate diamine-bis(phenolate) ligands [8,11,12,38]. When the phenolate groups possessed bulky *tert*-butyl groups in the *ortho* position to the phenoxy site, ladder-like conformations were adopted in the solid-state [8,11,38]. Cubanoid Li_4O_4 cores were obtained for tetradentate ligands lacking substituents in the *ortho* position [12]. Motifs such as these are commonly observed in lithium chemistry [39–41]. When monoanionic diamino-phenolate ligands were employed, trimetallic Li_3O_3 "pin-wheels" have been observed [4].

Complexes of alkali metals involving aryloxide and alkoxide ligands have been shown to produce interesting aggregates [42–46]. Alkali metal bis(phenolate) complexes exhibit various structural motifs with the most common formations being rings, ladders or cubanoids. Subtle changes in the ligand or solvent can cause significant differences in the structures of otherwise similar metal adducts. For example, we previously showed that the tripodal $[Me_2NCH_2CH_2N(CH_2\text{-}2,4\text{-}t\text{-}Bu_2C_6H_2O)_2]^{2-}$ and linear (so-called salan) $[CH_2NMe(CH_2-2,4-t-Bu_2C_6H_2O)]_2^{2-}$ ligands, which are constitutional isomers, generated lithium complexes in the presence of 1,4-dioxane that exhibited solvent-bridged polymeric and dimeric structures, respectively, in the solid-state [9]. The larger potassium ion-containing complexes also exhibit π-bonding interactions with the arene rings of phenolate groups in ligands such as mono- and bis(phenolates), bis(phenolate)-phosphines and calixarenes [46–56].

We sought to investigate the influence of the alkali metal on the structural properties of amine-bis(phenolate) complexes, as well as the effect on ROP of *rac*-lactide. Following our reports on the structures of amino-bis(phenolate)-tetrahydrofuranyl lithium complexes, which were used as precursors for the synthesis of transition metal compounds [38], and benzylamino-bis(phenolate)

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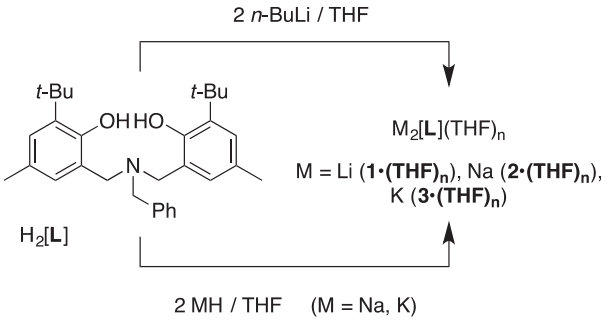

Scheme 1. Synthesis of the THF adducts of complexes **1**–**3**.

lithium complexes, which were used as catalysts for ROP of *rac*-lactide, ε-caprolactone and β-butyrolactone [2], we decided to prepare Li, Na and K complexes of benzylamino-*N*,*N*-bis(2-methylene-4-methyl-6-*tert*-butylphenolate) (abbreviated [**L**]) and their activity for ROP of *rac*-lactide. Herein we report the spectroscopic properties of these compounds, the structure of a potassium amine-bis(phenolate) complex, and the catalytic activity of these group 1 compounds in ring-opening polymerization of *rac*-lactide.

2. Results and discussion

2.1. Synthesis and characterization of alkali-metal amine-(bis) phenolate complexes

Reactions of H_2[**L**] with 2 equiv of *n*-BuLi or an excess of NaH or KH in THF gave Li_2[**L**](THF)$_n$ (**1**·(THF)$_n$), Na_2[**L**](THF)$_n$ (**2**·(THF)$_n$), and K_2[**L**](THF)$_n$ (**3**·(THF)$_n$), as shown in Scheme 1. The three complexes were characterized using MALDI-TOF MS, elemental analysis, FT-IR, ^{1}H, ^{13}C{^{1}H} NMR, as well as ^{7}Li{^{1}H} NMR for **1**. As observed for our previously reported lithium amine-bis(phenolate) complexes [2], the ^{1}H NMR spectra of complexes **1**–**3** were broad in D_6-benzene at room temperature, whereas spectra obtained in D_5-pyridine were sharper and readily assignable. In this coordinating solvent, we have previously shown that pyridine adducts of the formula Li_2[**L**](Py)$_2$ were formed [2] and it is expected that similar behaviour occurs with **1**–**3** in this strongly coordinating solvent. In all complexes, ^{1}H and ^{13}C NMR showed the presence of residual THF from the amorphous powders. Similarly, the elemental analysis indicated 2 equiv of THF per Li_2[**L**] unit in **1**, 1 equiv of THF per Na_2[**L**] unit in **2** and 3 equiv per K_2[**L**] unit in **3**. The ^{7}Li NMR spectrum of **1** in D_5-pyridine shows two peaks, as expected, at 4.27 and 3.78 ppm. This is comparable to the chemical shifts observed for the related tridentate and tetradentate lithium amine-bis(phenolate) complexes [2].

Based on spectroscopic and combustion analysis data, the structure of **1** is expected to be a ladder-like bis-μ-O dimer (Fig. 1, top), similar to that found for the related lithium-benzylamino-*N*,*N*-bis(2-methylene-4,6-di-*tert*-amylphenolate) compound (abbreviated [$Li_2[O_2N]^{AmAmBn}$(THF)]$_2$) [2] and other amine-bis(phenolate) complexes [8,11,38]. Structures of sodium complexes of amine-bis(phenolate) complexes have not, to our knowledge, been reported. A sodium diamine-bis(phenolate) complex, however, has been structurally characterized and exhibits a tetranuclear distorted cubane structure [11].

Complex **3** is poorly soluble in most non-coordinating solvents (*e.g.* toluene, heptane and benzene), however, the compound could be dissolved in toluene by adding a small amount of THF to the mixture. The solid-state structure of **3**·(THF)$_n$ was obtained and is shown in Fig. 2. Crystallographic parameters are given in Table 1. The complex crystallizes as a tetrametallic species with two

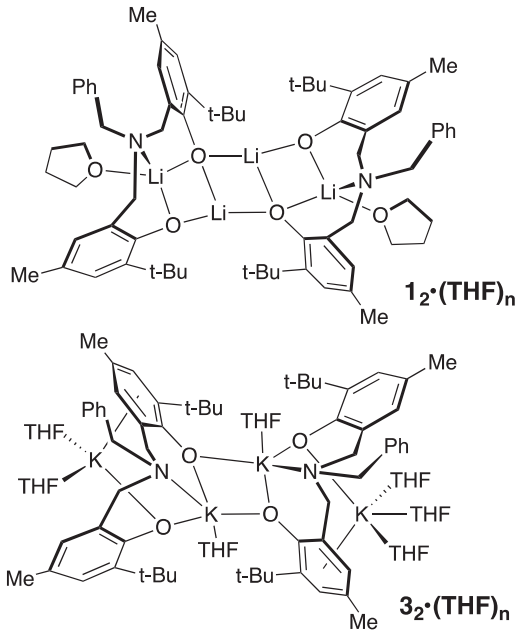

Fig. 1. (Top) Representation of the anticipated structure of lithium complex **1**$_2$·(THF)$_n$ (where $n = 2$) based on previously observed analogues. (Bottom) The crystallographically authenticated potassium complex **3**$_2$·(THF)$_n$ where $n = 7$.

formula units of K_2[**L**] and an asymmetric arrangement of THF molecules bonded to the potassium centres resulting in a formula described as **3**$_2$·(THF)$_n$. A simplified illustration of the bonding in **3**$_2$·(THF)$_n$ is shown in Fig. 1 (bottom). This contrasts with the bonding observed in the previously reported Li analogues, which possess three and four-coordinate lithium atoms and described as **1**$_2$·(THF)$_n$ [2,38]. Two potassium atoms (K(2) and K(3)) form a rhomboid structure with two bridging phenolate oxygen donors, O(2) and O(4). Atoms K(2) and K(3) are each five-coordinate and bonded to the amine nitrogen atom and other oxygen donor of the tridentate ligand, as well as a THF molecule. A K(2)–K(3) interatomic distance of 3.754 Å is observed, which is within the typical range observed for four-membered K–O–K–O rhomboid motifs [57]. K(2) and K(3) also exhibit η^1-interactions with the *ipso* carbons bonded to the phenolate oxygen atoms. The K(2)–C(1) distance of 3.177(4) Å and the K(3)–C(32) distance of 3.186(4) Å are within the ranges observed for similar interactions of this type in potassium phenolate complexes [49,54,58–60].

The other two potassium atoms (K(1) and K(4)) are strongly σ-bonded to the phenolate oxygen atoms O(1) and O(3), respectively. Their coordination spheres also comprise η^6-coordination to the neighbouring arene rings. The η^6-K–C_{aryl} bond distances span the range 3.100(4) Å for K(4)–C(43) to 3.365(4) Å for K(1)–C(14) (average K(1)–C_{arene} = 3.235 Å, average K(4)–C_{arene} = 3.150 Å) and compare well to the 3.1–3.9 Å range of η^6-K–C_{aryl} bond distances reported in the literature [61–66]. The K–C_{arene} distances are of similar length to the η^1-interactions exhibited by K(2) and K(3). The K(1)–C_{cent} distance of 2.915 Å and K(4)–C_{cent} distance of 2.820 Å are comparable to those observed in a potassium bis(phenolate) complex (where K–C_{cent} = 2.842 Å) [47] and a potassium complex of a *cyclo*-amino-ether-phenolate ligand having a K–C_{cent} distance of 2.907 Å [61], but mildly longer than that found in a potassium bis(phenolate) phosphine complex (where K–C_{cent} = 2.808 Å) [46].

2.2. Ring-opening polymerization of rac-lactide

Compounds **1**·(THF)$_n$, **2**·(THF)$_n$, and **3**·(THF)$_n$ were investigated for their catalytic potential in the ring-opening polymerization of