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Synthesis, characterization and catalytic studies of aluminium complexes containing sulfonamido–oxazolinate or –pyrazolinate ligands

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ABSTRACT

A series of sulfonamido–oxazolinate ligand precursors, **HNSO$_2$Ph^{H}Oxa**, **HNSO$_2$Ph^{Me}Oxa**, **HNSO$_2$Ph-^{TriMe}Oxa**, or sulfonamido–pyrazolinate ligand precursors, **HNSO$_2$Ph^{H}Pz^H**, **HNSO$_2$Ph^{Me}Pz^H**, **HNSO$_2$Ph-^{TriMe}Pz^H**, **HNSO$_2$Ph^{F}Pz^H**, **HNSO$_2$Ph^{H}Pz^{Me}**, **HNSO$_2$Ph^{Me}Pz^{Me}**, **HNSO$_2$Ph^{TriMe}Pz^{Me}**, have been prepared. Treatment of ligand precursors, HNSO$_2$Ph^{A}Oxa or HNSO$_2$Ph^{A}Pz^B, with 1.1 equiv. of AlMe$_3$ in THF affords aluminium sulfonamido–oxazolinate dimethyl complexes, (NSO$_2$Ph^{A}Oxa)AlMe$_2$ [A = H (**1**); A = Me (**2**); A = TriMe, (**3**)], or aluminium sulfonamido–pyrazolinate dimethyl complexes, (NSO$_2$Ph^{A}Pz^B)AlMe$_2$ [A = H, B = H (**4**); A = Me, B = H (**5**); A = TriMe, B = H (**6**); A = F, B = H (**7**); A = H, B = Me (**8**); A = Me, B = Me (**9**); A = TriMe, B = Me (**10**)]. The aluminium bis(sulfonamido–pyrazolinate) methyl complex **5′** was isolated from recrystallization of **5** as minor product. The molecular structures of compounds **2**, **5′** and **8** were determined by single-crystal X-ray diffraction techniques. Their catalytic activities towards the ring opening polymerization of ε-caprolactone in the presence of benzyl alcohol are also under investigation.

1. Introduction

Aliphatic polyesters, prepared from various lactones and/or lactides, having the thermoplastic, biocompatible and biodegradable properties make them to be the leading candidates in biomedical and pharmaceutical industries [1–5]. The major synthesized method employed in industry to prepare these polyesters has been the ring opening polymerization (ROP) using well-defined metal complexes with auxiliary ligands. There is a number of excellent initiators/catalysts have been examined for the ROP during the past decade [6–14]. The main challenge in elaborating catalytic systems effective for ROP is the development of novel efficient metal catalysts to produce the polymers bearing the properties of precisely molecular weight, narrow polydispersity index (PDI), efficient rate and high enantio- or regio-selectivity under mild conditions. Among these studies, the metal complexes supported by sulfonate [15,16] or sulfonamido [18–23] anionic multidentate ligands have been a focus of interest, mainly due to their good catalytic activities for ROP of cyclic esters. The magnesium complexes bearing sulfonate phenolate ligands have been prepared and displayed efficient catalytic activities for ROP of ε-caprolactone, L-lactide or trimethyl carbonate by the Lin's and Ko's groups [15,16]. However, the reactivity of magnesium bis-adduct complexes derived from bis-phenolate ligands show only moderate activity in the ROP of L-lactide in the presence of additional alcohols [17]. The Lin's group also reported the aluminium complexes containing sulfonamido/Schiff base ligand are efficient initiators for ROP of L-lactide in well-controlled fashion [19]. The Mountford's group reported that the metal complexes such as titanium [20], zirconium [20], aluminium [21] or indium [22], bearing tetradentate bis(sulfonamide)amino ligands also showed the well-controlled ROP of *rac*-lactide. Recently, some Group 1 metal complexes bearing cyclohexyl-backboned bis-sulfonamido ligand displayed the modest stereo-selectivity and well-controlled fashion for ROP of *rac*-lactide under lower temperature condition were reported by Lin's group [23].

In our previous reports, some zinc [24,25], aluminium [25] or magnesium [26] anilido–oxazolinate complexes, or aluminium anilido–pyrazolinate complexes [28] have shown their catalytic activities toward the ROP of ε-caprolactone or L-lactide. In view of the potential application of metal sulfonate or sulfonamido complexes in ROP, we are interested in exploring the catalytic behaviour of the metal complexes bearing related sulfonamido ligands derived from our previous works. On the other respect, the steric or

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electronic sulfonamides in general are attractive synthetic targets due to their relatively easy and simple preparation from the corresponding sulfonyl chlorides and related amines or anilines under mild conditions. Although aluminium complexes containing anionic multidentate ligands, such as β-diketiminates [29], anilido-iminates [30,31], amidinates [32,33] or phosphino-iminates [34,35], have been reported their catalytic activities for ROP of cyclic esters recently. However only few examples of aluminium complexes containing sulfonamido groups have been applied in ROP as initiators/catalysts [18,19,21]. Herein we report the synthesis and structures of aluminium complexes containing sulfonamido–oxazolinate or –pyrazolinate ligands. Their catalytic activities toward the ring opening polymerization of ε-caprolactone in the presence of benzyl alcohol are also examined.

2. Results and discussion

2.1. Preparations of sulfonamide ligand precursors

A series of sulfonamido–oxazolinate or –pyrazolinate ligand precursors [$HNSO_2Ph^ROxa$, Ph^R = phenyl (R = H), tolyl (R = Me) or mesityl (R = TriMe), $HNSO_2Ph^RPz^H$, Ph^R = phenyl (R = H), tolyl (R = Me), mesityl (R = TriMe) or 4-fluorophenyl (R = F) and $HNSO_2Ph^RPz^{Me}$, Ph^R = phenyl (R = H), tolyl (R = Me) or mesityl (R = TriMe)] were prepared by the reactions of 2-(4,4-dimethyl-4,5-dihydrooxazo-2-yl)-phenylamine, 1-(2-aminophenyl)pyrazole or 1-(3,5-dimethyl-2-aminophenyl)pyrazole with 1.1 molar equivalent of the corresponding substituted benzenesulfonyl chlorides and triethylamine in dichloromethane at room temperature, as shown in (Scheme 1). These ligand precursors were easily purified by column chromatography and afforded the satisfied yields. The N–H signals on ^1H NMR spectra for these ligand precursors were observed at the range of 12.29–12.56 ppm for oxazolinate sulfonamides and 8.68–10.10 ppm for pyrazolinate–sulfonamides. Since the NH of sulfonamides have been still reacted with excess sulfonyl chlorides in the presence of base to form bis-sulfonamides, the bis-pyrazole-sulfonamide by-product $N(SO_2Ph^R)_2Pz^H$ [Ph^R = phenyl (R = H), tolyl (R = Me) or 4-fluorophenyl (R = F)] could also be observed and collected with 7–17% isolated yields upon preparing the target compounds of $HNSO_2Ph^RPz^H$ [Ph^R = phenyl (R = H), tolyl (R = Me) or 4-fluorophenyl (R = F)], as shown in (Scheme S1). All of these sulfonamido ligand precursors and some bis-sulfonamides

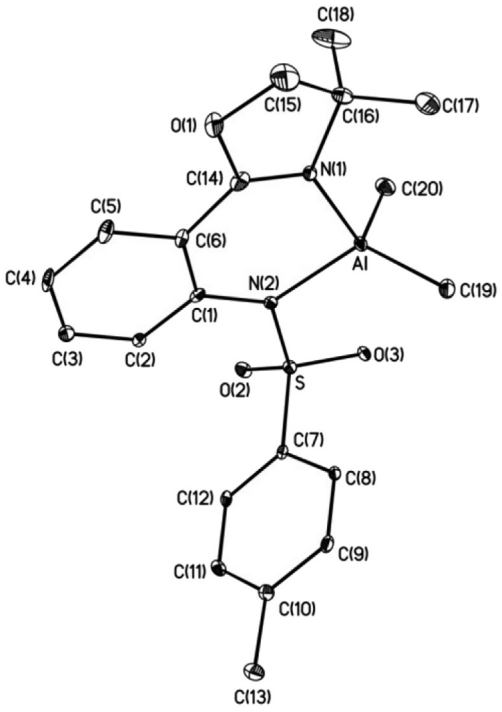
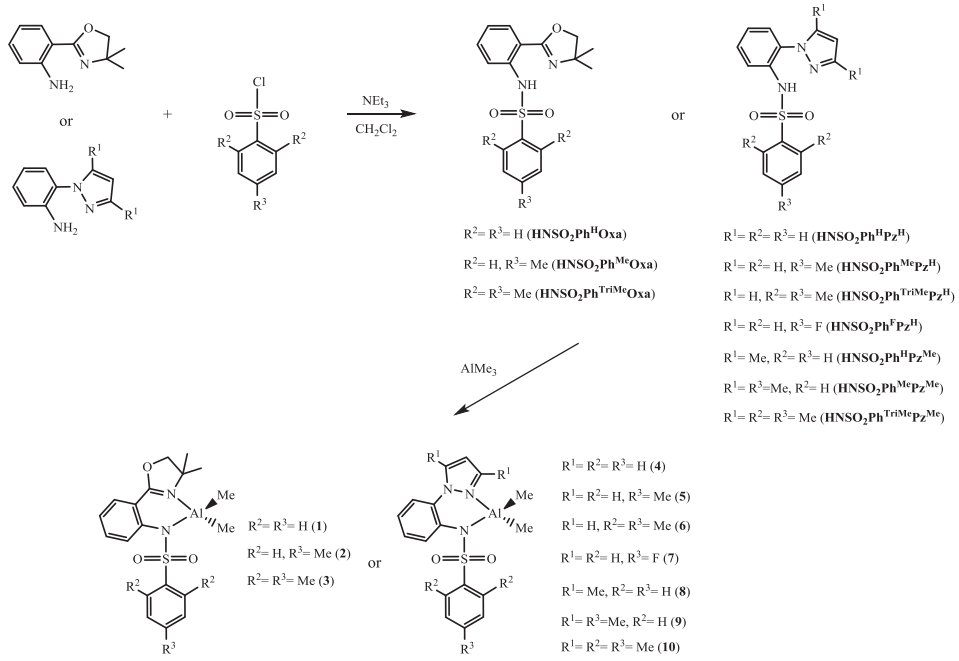


Fig. 1. Molecular structure of one of the crystallographically independent molecules of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al–N(1), 1.961(3); Al–N(2), 1.948(3); Al–C(19), 1.961(4); Al–C(20), 1.955(4); S–O(2), 1.435(3); S–O(3), 1.439(3); S–N(2), 1.635(3); S–C(7), 1.763(4); N(1)–C(14), 1.292(5); N(2)–C(1), 1.416(5); C(1)–C(6), 1.411(5); C(6)–C(14), 1.452(5); N(1)–Al–N(2), 90.69(13); C(19)–Al–C(20), 116.63(19); N(2)–Al–C(19), 117.22(15); N(2)–Al–C(20), 115.55(17); N(1)–Al–C(19), 105.29(16); N(1)–Al–C(20), 106.59(16); O(2)–S–O(3), 117.86(16); N(2)–S–C(7), 107.40(16).



Scheme 1. Preparation of ligand precursors and complexes **1**–**10**.