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Research paper

# Tetranuclear complexes of group 12 and 13 supported on a polynucleating ligand and activity studies in the ROP of *rac*-lactide



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| ARTICLE INFO                                                                                                    | A B S T R A C T                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |
|-----------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Keywords:<br>Al, Ga, and Zn complexes<br>Polynucleating ligands<br>Polylactide<br>rac-Lactide<br>Polymerization | A polynucleating ligand (L-H <sub>4</sub> ) containing four <b>N</b> , <b>O</b> bidentate sites was cleanly metallated by four equivalents of AlMe <sub>3</sub> , GaMe <sub>3</sub> and ZnEt <sub>2</sub> resulting in tetranuclear complexes $L(MMe_2)_4$ (M = Al (1), Ga (2)) and $L(ZnEt (CH_3CN)_{0.5})_4$ (3). The Al complex shows the best catalytic activity for the ring-opening polymerization (ROP) of <i>rac</i> -lactide ( <i>rac</i> -LA) in the present family of tetranuclear compounds. Polymerization studies indicate the lack of cooperativity between metal centers in the ROP of <i>rac</i> -LA, despite having a ligand platform which binds to four metal centers. |

# 1. Introduction

Polymerization of rac-lactide (rac-LA) has been extensively studied due to its potential use as biodegradable, biocompatible, renewable polymer [1]. Polylactide (PLA) can be used in sutures and packaging materials, and eventually might replace the polymers obtained from non-renewable fossil sources. PLA can be efficiently obtained by ring opening polymerization (ROP) of rac-LA utilizing diverse catalysts, many of them are based on Al(III) complexes of tetradentate Schiff base ligands [2,3]. Particularly, salen-type Al complexes have been successfully used as initiators to obtain isotactic PLA with narrow molecular weight distributions [4-6]. Systematic investigations showed that the role of the substituents in the phenoxide donor and the backbone linker of the salen ligand have significant influence over the polymerization. Sterically demanding ortho-phenoxy substituents and larger and flexible backbone linkers increase the isotacticity of the resulting polymer, while electron-withdrawing groups increase the polymerization rate [7,8]. Related Al complexes of salicylaldiminato bidentate N,O ligands are also explored as alternatives to Al-salen complexes in the ROP of rac-LA, as the former have less coordinatively saturated metal centers [9]. Interestingly, salen-Al dinuclear complexes show cooperative effects between the metallic centers leading to an increase in the activity in comparison with the analogous mononuclear complex, although in some cases lower  $P_m$  values are observed [10]. Several other Al dinuclear complexes have also shown cooperativity effects in

the ROP of *rac*-LA [11–15]. Recent studies with trinuclear salen-Al complexes show very high activity and isoselectivity [16]. Additional studies include copolymerization of L-LA and  $\varepsilon$ -caprolactone by salen-Al dinuclear complexes [17]. Several reports include Al<sub>4</sub> aggregates with some Al centers bound (Al<sub>bound</sub>) to the polynucleating ligand while the remaining interact with substituents from Al<sub>bound</sub> forming adducts, although the aggregates are structurally interesting, reactivity studies on ROP of *rac*-LA were not performed [18–20]. To the best of our knowledge, the formation of tetranuclear Al complexes on a single polydentate ligand platform with each Al center coordinated to an individual bidentate site has not been investigated. Herein, we report on related tetranuclear Al, Ga, and Zn complexes supported on a ligand with four bidentate *N*,*O* sites and their catalytic activity in the ROP of *rac*-LA.

# 2. Experimental

# 2.1. General methods

All manipulations involving air-sensitive substances were carried out in an inert-atmosphere glovebox or using standard Schlenk techniques under argon or dinitrogen. All solvents were dried using an MBraun-SPS system. Commercially available reagents were used without further purification, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was synthesized according to the literature [21]. The <sup>1</sup>H and <sup>13</sup>C NMR

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spectra were recorded on a Varian Mercury-400 MHz (400 MHz for <sup>1</sup>H and 100.58 MHz for <sup>13</sup>C) spectrometer in CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> at room temperature (293 K). <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were determined by reference to residual solvent signals. Melting points were measured in a Mel Temp II device using sealed capillaries. Mass spectra (EI or FAB<sup>+</sup>-MS) were obtained using a JEOL magnetic sector spectrometer JMS700. Infrared spectra were recorded in KBr pellets using a Nicolet 6700 Analytical FT-IR spectrometer. Molecular weight and molecular weight distributions of PLA polymers were determined by GPC chromatography on a Waters 2695 ALLIANCE Separation Module equipped with two HSP gel columns (HR 4E molecular weight range from 50 to  $1 \times 10^5$  and HR 5E from  $2 \times 10^3$  to  $4 \times 10^6$ ) in series and a RI Waters 2414 detector. THF was used as eluent at 35 °C with a flow rate of 1.0 mL/min. Ten linear polystyrene standards of narrow dispersity were used for GPC calibration curves.

# 2.2. X-ray diffraction

Yellow rhombic crystals of Zn complex 3 suitable for X-ray diffraction measurements were taken directly from solution under argon atmosphere, coated with mineral oil, mounted on a glass fiber and measured at 100 K. X-ray intensity data were collected using the software CrysAlisPro [22] on a four-circle SuperNova, Dual EosS2 CCD diffractometer with monochromatic Cu-K $\alpha$  radiation ( $\lambda = 1.54184$  Å). Cell refinement, data reduction, incident beam, decay and absorption corrections were carried out with the use of the program CrysAlisPro [22]. Using Olex 2 [23], the structure was solved by direct methods with the program SHELXT and refined by full-matrix least-squares techniques with SHELXL [24-26]. All hydrogen atoms were generated in calculated positions and constrained with the use of a riding model. The final model involved anisotropic displacement parameters for all non-hydrogen atoms. CCDC 1837655 contain the supplementary crystallographic data for compound 3. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; or e-mail: deposit@ ccdc.cam.uk.

#### 2.3. Synthesis

#### 2.3.1. L-H<sub>4</sub>

L-H<sub>4</sub> was obtained via a Schiff base condensation reaction [21]. N,N,N',N'-Tetrakis(3-aminopropyl)-1,4-butadiene (DAB-Am4, 1.6 mL, 0.005 mol) was dissolved in 20 mL of ethanol and added dropwise to a suspension of 3,5-di-tert-butyl-2-hydroxybenzaldehyde (4.6 g, 0.02 mol) in 30 mL of ethanol. The reaction mixture was stirred at room temperature for 4 h, then filtered, the cake was rinsed with 30 mL of water and the filtrate was extracted with 40 mL of CH<sub>2</sub>Cl<sub>2</sub> three times. The organic phases were combined and dried over Na<sub>2</sub>SO<sub>4</sub> for 1 h and after filtration the volatiles were removed under dynamic vacuum resulting in a yellow solid (5.5 g, yield = 93%, MW: 1181.83). m.p.: 54 °C. <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  13.95 (b, 4H, –OH), 8.35 (s, 4H, CH= N), 7.37 (d, 4H, Ph-H), 7.07 (d, 4H, Ph-H), 3.60 (t, 8H, =N-CH<sub>2</sub>-), 2.53 (t, 8H, -CH2-N), 2.43 (s, 4H, N-CH2-), 1.83 (t, 8H, -CH2-CH2-CH2-), 1.45 (s, 36H, -C(CH<sub>3</sub>)<sub>3</sub>), 1.43 (s, 4H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.30 (s, 36H,  $-C(CH_3)_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  165.94 (C=N), 158.35 (C-OH, Ph), 139.97 (C-C(CH<sub>3</sub>)<sub>3</sub>, Ph), 136.77 (C-C(CH<sub>3</sub>)<sub>3</sub>, Ph), 126.79 (C-H, Ph), 125.81 (C-H, Ph), 118.01 (C-C=N, Ph), 57.68 (= N-C), 54.22 (-N-C), 51.60 (-CH<sub>2</sub>-CH<sub>2</sub>-N-), 35.17 (-C(CH<sub>3</sub>)<sub>3</sub> <sup>t</sup>Bu), 34.25 (-C(CH<sub>3</sub>)<sub>3</sub> <sup>t</sup>Bu), 31.67 (-CH<sub>3</sub> <sup>t</sup>Bu), 29.59 (-CH<sub>3</sub> <sup>t</sup>Bu), 28.74  $(-CH_2-CH_2-CH_2-)$  25.34  $(-CH_2, butyl)$ . FAB<sup>+</sup>-MS: m/z = 1182 [M<sup>+</sup>]. IR (KBr, cm<sup>-1</sup>): 3355 (br), 2947 (st), 2860 (m), 1629 (st), 1444 (st), 1438 (st), 1359 (m), 1250 (m), 1230 (m), 1176 (m), 1172 (m), 1022 (w), 970 (s), 874 (s), 826 (s), 824 (s), 771 (m), 1052.0 (w), 727 (s), 694 (s), 643(m).

#### 2.3.2. $L(AlMe_2)_4$ (1)

A solution of Me<sub>3</sub>Al (27.4 mg, 0.38 mmol, 4.5 equiv.) in 20 mL of hexane was added dropwise to a stirred solution of L-H<sub>4</sub> (100 mg,  $0.085\,mmol,\,1\,equiv.)$  in 20 mL of hexane. The reaction mixture was stirred for 6 h at room temperature followed by filtration, the volatiles in the filtrate were removed under dynamic vacuum resulting in a vellow powder, which was rinsed with diethyl ether  $(3 \times 5 \text{ mL})$  and decanted to remove any residue of free ligand, the powder was left under dynamic vacuum for 4 h to remove the volatiles (100 mg, 0.071 mmol, yield = 84%, MW: 1406.01). m.p. 115–120 °C. <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>): δ 8.14 (s, 4H, *H*-C=N), 7.52 (d, 4H, Ph-*H*), 7.01 (d, 4H, Ph-H), 3.60 (t, 8H, =N-CH<sub>2</sub>), 2.50 (q, 8H, -CH<sub>2</sub>-N), 2.46 (s, 4H,  $-N-CH_2$ ), 1.89 (q, 8H,  $=N-CH_2-CH_2$ ), 1.41 (s, 36H,  $-CH_3$ <sup>t</sup>Bu), 1.37 (s, 4H, N-CH<sub>2</sub>-CH<sub>2</sub>), 1.29 (s, 36H, -CH<sub>3</sub> <sup>t</sup>Bu), -0.74 (s, 24H, Al-(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  171.85 (C=N), 161.23 (C-O, Ph), 140.49 (C-C(CH<sub>3</sub>)<sub>3</sub>, Ph), 139.06 (C-C(CH<sub>3</sub>)<sub>3</sub>, Ph), 131.78 (C-H, Ph), 1258.54 (C-H, Ph), 118.32 (C-C=N, Ph), 57.68 (= N-C), 54.22 (-N-C), 51.60 (-CH<sub>2</sub>-CH<sub>2</sub>-N-), 35.17 (-C(CH<sub>3</sub>)<sub>3</sub> <sup>t</sup>Bu), 34.25 (-C(CH<sub>3</sub>)<sub>3</sub> <sup>t</sup>Bu), 31.49 (-CH<sub>3</sub> <sup>t</sup>Bu), 29.44 (-CH<sub>3</sub> <sup>t</sup>Bu), 28.24 (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-) 25.34 (-CH<sub>2</sub>, butyl), -9.24 (Al-(CH<sub>3</sub>)<sub>2</sub>). EI-MS: m/  $z = 1391 [M^+ - CH_3]$ . IR (KBr, cm<sup>-1</sup>): 2945 (st), 2857 (m), 1617 (st), 1543 (m), 1438 (st), 1440 (m), 1358 (s), 1255 (s), (m), 1173 (m), 850 (m), 670 (w).

#### 2.3.3. L(GaMe<sub>2</sub>)<sub>4</sub> (2)

A solution of Me<sub>3</sub>Ga (39.0 mg, 0.34 mmol, 4 equiv.) in 20 mL of hexane was added dropwise to a stirred solution of L-H<sub>4</sub> (100 mg, 0.085 mmol, 1 equiv.) in 20 mL of hexane. The reaction mixture was stirred for 6 h at room temperature followed by filtration, the volatiles in the filtrate were removed under dynamic vacuum resulting in a yellow powder, which was rinsed with diethyl ether  $(3 \times 5 \text{ mL})$  and decanted to remove any residue of free ligand, the powder was left under dynamic vacuum for 4h to remove the volatiles (120 mg, 0.076 mmol, yield = 90%, MW: 1576.97). m.p. 76 °C. <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  8.00 (s, 4H, *H*-C=N), 7.45 (d, *J* = 2.6 Hz, 4H, Ph-H), 6.88 (d, J = 2.6 Hz, 4H, Ph-H), 3.55 (t, 8H, =N-CH<sub>2</sub>), 2.47 (q, 8H, -CH<sub>2</sub>-N), 2.44 (s, br, 4H, -N-CH<sub>2</sub>), 1.81 (q, 8H, =N-CH<sub>2</sub>-CH<sub>2</sub>), 1.42 (s, 36H, -CH<sub>3</sub> <sup>t</sup>Bu), 1.40 (s, 4H, N-CH<sub>2</sub>-CH<sub>2</sub>), 1.28 (s, 36H, -CH<sub>3</sub> <sup>t</sup>Bu), -0.30 (s, 24H, Ga-(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 25 °C, CDCl<sub>3</sub>): *δ* 169.88 (*C*=N), 164.35 (*C*-O, Ph), 141.15 (*C*-C(CH<sub>3</sub>)<sub>3</sub>, Ph), 137.30 (C-C(CH<sub>3</sub>)<sub>3</sub>, Ph), 131.06 (C-H, Ph), 128.76 (C-H, Ph), 117.32 (C-C=N, Ph), 57.28 (=N-C), 53.88 (-N-C), 51.29 (-CH<sub>2</sub>-CH<sub>2</sub>-N-), 35.51 (-C(CH<sub>3</sub>)<sub>3</sub> <sup>t</sup>Bu), 34.04 (-C(CH<sub>3</sub>)<sub>3</sub> <sup>t</sup>Bu), 31.52 (-CH<sub>3</sub> <sup>t</sup>Bu), 29.48 (-CH<sub>3</sub> <sup>t</sup>Bu), 27.92 (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 25.09 (-CH<sub>2</sub>, butyl), -6.62 (Ga- $(CH_3)_2$ ). FAB<sup>+</sup>-MS:  $m/z = 1561 [M^+ - CH_3]$ . IR (KBr, cm<sup>-1</sup>): 2948 (m), 2899 (w), 2860 (w), 1619 (st), 1536 (m), 1440 (m), 1434 (m), 1411 (m), 1384 (m), 1360 (m), 1359 (w), 1314 (w), 1255 (m), 1176 (w), 1170 (m), 1067 (w), 1014 (w), 873 (m), 839 (w), 784 (m), 743 (m), 682 (w).

#### 2.3.4. L(ZnEt(CH<sub>3</sub>CN)<sub>0.5</sub>)<sub>4</sub> (3)

A solution of Et<sub>2</sub>Zn (41.99 mg, 0.34 mmol) in 20 mL of a 1:1 toluene and acetonitrile mixture was added dropwise to a stirred solution of L-H<sub>4</sub> (100 mg, 0.085 mmol) in 20 mL of toluene. The reaction mixture was stirred for 6h at room temperature, filtered, concentrated and stored at -25 °C. After two days transparent yellow crystals were obtained from the solution, the crystals were collected on a frit, rinsed with cold toluene (3  $\times$  3 mL), and the volatiles removed under dynamic vacuum (104 mg, 0.064 mmol, 75%, MW: 1637.68): m.p. 115-120 °C. <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>): δ 8.06 (s, 4H, *H*-C=N), 7.30 (m, 4H, Ph-H), 6.87 (s, 4H, Ph-H), 4.47 (m, 4H, =N-CH<sub>2</sub>), 3.48-3.14 (m, 4H, = N-CH2), 2.86-2.51 (m, 12H, -CH2-N, -N-CH2-CH2), 2.36 (s, 3H, CH<sub>3</sub>CN), 1.97–1.63 (m, 8H, =N–CH<sub>2</sub>–CH<sub>2</sub>), 1.48–1.34 (m, 44H, –CH<sub>3</sub> <sup>t</sup>Bu, -CH<sub>2</sub>CH<sub>3</sub>), 1.32–1.16 (m, 52H, -CH<sub>3</sub> <sup>t</sup>Bu, -CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>): δ 169.92 (C=N), 168.85 (C-OH, Ph), 141.91 (C-C(CH<sub>3</sub>)<sub>3</sub>, Ph), 135.72 (C-C(CH<sub>3</sub>)<sub>3</sub>, Ph), 130.08 (C-H, Ph), 129.69 (C-H, Ph), 118.43 (C-C=N, Ph), 60.09 (=N-C), 50.98

 $(-CH_2-CH_2-N-), 36.32 \ (-C(CH_3)_3 \ ^tBu), 34.44 \ (-C(CH_3)_3 \ ^tBu), 32.14 \\ (-CH_3 \ ^tBu), 30.40 \ (-CH_3 \ ^tBu), 26.36 \ (-CH_2-CH_2-CH_2-), 11.85 \\ (Zn-(CH_2CH_3), 4.41 \ (Zn-(CH_2CH_3). FAB^+-MS: m/z = 1525 \ [M^+ - Et, -2CH_3CN]. IR \ (KBr, cm^{-1}): 2947 \ (m), 2899 \ (w), 2858 \ (w), 1616 \ (st), 1528 \ (m), 1435 \ (st), 1410 \ (m), 1382 \ (m), 1358 \ (m), 1324 \ (w), 1254 \ (m), 1231 \ (w), 1197 \ (w), 1162 \ (m), 1086 \ (m), 911 \ (w), 871 \ (w), 834 \ (m), 789 \\ (m), 741 \ (m), 697 \ (w).$ 

#### 2.4. Ring-opening polymerization studies

The catalytic activity was studied in toluene in Ace pressure reactors under argon atmosphere. The monomer, initiator, solvent, and benzyl alcohol were loaded into the Ace reactor in an MBraun glovebox, the reactor was taken out of the glovebox and immersed in an oil bath at 70 °C. After the selected stirring time, the reactor was let to cool down to room temperature and opened to quench the reaction by addition of a few drops of diluted HCl. An aliquot was taken, and the volatiles were removed under dynamic vacuum, the residue was dissolved in CDCl<sub>3</sub> and analyzed by <sup>1</sup>H NMR spectroscopy to determine the percentage of conversion. The PLA was precipitated in the remaining solution by addition of cold methanol, the polymer was collected by filtration and the volatiles were removed under dynamic vacuum, samples from the residue were taken for additional characterization by gel permeation chromatography (GPC).

# 3. Results and discussion

The reaction of polydentate ligand L-H<sub>4</sub> with four equivalents of MMe<sub>3</sub> or ZnEt<sub>2</sub> resulted in tetranuclear complexes L(MMe<sub>2</sub>)<sub>4</sub> (M = Al (1), Ga (2)), and L(ZnEt(CH<sub>3</sub>CN)<sub>0.5</sub>)<sub>4</sub> (3), (Scheme 1) as corroborated by mass spectrometry (MS), infrared and <sup>1</sup>H, <sup>13</sup>C nuclear magnetic resonance spectroscopy as well as X-ray crystallographic analysis for **3**. The Zn(II) tetranuclear complex was synthesized in an attempt to obtain crystals suitable for Single Crystal X-ray diffraction studies, since the analogous tetranuclear complexes of Al and Ga did not resulted on good quality crystals. The MS studies indicate the presence of tetranuclear complexes with *m*/*z* values of 1391 and 1561 [M<sup>+</sup> – CH<sub>3</sub>] corresponding to the loss of a Me group from MMe<sub>2</sub> organometallic fragment in **1** and **2** respectively, and 1525 [M<sup>+</sup> – Et, –2CH<sub>3</sub>CN] from loss of two acetonitrile and one Et group for **3** (Fig. S1). The <sup>1</sup>H NMR

spectrum provides further evidence of a clean metallation due to the disappearance of the O–H signal at about 14 ppm of the proligand L-H<sub>4</sub> and the appearance of a single set of signals for the complexes in <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR (Figs. 1 and S2–3), which is indicative of a symmetric product, proposed as the tetranuclear complex. <sup>1</sup>H NMR signals of Me substituents on the metal are singlets at -0.74 and -0.30 ppm for 1 and 2 respectively, the Et substituent on Zn, complex 3, overlaps with ligand signals at 1.38 and 1.28 ppm. The disappearance of the IR absorption band, in all cases, around 3355 cm<sup>-1</sup> is an additional indication that metallation took place (Fig. S4–7), since such band is assigned to the stretching of the O–H bond of the proligand. Crystals of **3** suitable for Single Crystal X-ray diffraction studies were obtained from saturated 1:1 (vol) acetonitrile:toluene solution (Table S1).

The asymmetric unit of **3** consists of a tetranuclear complex (Fig. 2) with Zn ions in distorted tetrahedral coordination environments with angles in the range of 90.59–126.42° and 87.03–135.59° for Zn1 and Zn2, respectively. The ligand wraps around Zn1 in a tridentate fashion with *O*,*N*,*N* donor atoms from phenolate, imine and amine groups, with the remaining coordination site occupied by Et; while binding in a bidentate fashion to Zn2 having *O*,*N* as donor atoms from a phenolate and imine groups, with the remaining sites occupied by an ethyl group and acetonitrile. Similar structures are expected for the additional tetranuclear complexes 1 and 2, but having all the metal centers with the same coordination environment with two methyl groups and the *N*,*O* chelation from imine-phenoxy moiety as shown in Scheme 1. The proposed structure for 1 and 2 correlates with the <sup>1</sup>H NMR data which shows a single set of signals, indicative of equivalent coordination environment for all the metal centers.

The catalytic activity was studied in toluene. The typical ratio of monomer to initiator used was M/I = 100/1 or 400/1, addition of benzyl alcohol was necessary because the alkyl complexes resulted inactive in the ROP. The *in-situ* generation of main group alkoxide complexes is a common strategy to obtain more active initiators due to increased nucleophilicity of the OR group which more easily migrates to the carbonyl carbon of the monomer in comparison with the R alkyl group.[27] The conversion was followed by <sup>1</sup>H NMR analysis of the methine proton for *rac*-LA and PLA (Figs. 3 and S8, S9), which have distinctive chemical shifts of 5.02 and 5.15–5.25 ppm, respectively. Complex **1** was the most active catalyst of the series, the polymerization results are included in Table **1**, complex **2** and **3** showed low activity



Scheme 1. Synthetic route for tetranuclear complexes.



Fig. 1. <sup>1</sup>H NMR spectra for 1 (400 MHz, CDCl<sub>3</sub>, 25 °C).



**Fig. 2.** Solid-state structure for **3**, with ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. Color code = Zn: pink, N: blue, O: red, C: grey. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

after 24 h even in the presence of benzyl alcohol.

The tacticity of polymers was determined using homonuclear decoupled <sup>1</sup>H NMR by analyzing the methine region following the ZelÍs method. The value of the integral corresponding to *rmr* was taken for five tetrad populations and  $P_r$  was calculated ( $P_r = (2 \times rmr)^{0.5}$ ) ( $P_r + P_m = 1$ ), see Figs. 4 and S10.

Values for  $P_r$  and  $P_m$  indicate the tacticity of polymers (atactic:  $P_r$  or  $P_m = 0.5$ ; heterotactic:  $P_r = 1.0$ ,  $P_m = 0$ ; isotactic:  $P_r = 0$ ,  $P_m = 1.0$ ). The PLA polymer obtained was predominantly isotactic for M/I ratios of 100/1 (Entries 1 and 2, Table 1). Compound 1 shows moderate activity for the ROP of *rac*-LA in experimental conditions shown in entry 1 (Table 1), with calculated  $M_n$  close to the experimental value, and good  $\mathcal{D} = 1.16$  and  $P_m = 0.60$ . Increasing the amount of benzyl alcohol maintained isotacticity about the same ( $P_m = 0.67$ ) but caused wider molecular weight distribution ( $\mathcal{D} = 1.60$ , Entry 2, Table 1), indicating that chain transfer is a significant degradation pathway. The M/I ratio was increased to probe the catalysts closer to actual polymerizations conditions, but a wide molecular weight distribution was obtained

(D = 1.66), the tacticity decreased and became close to atactic (Entry 3, Table 1).

The low activity of present complexes can, to some extend, be correlated to the solid-state structure. In the case of 3, the Zn centers are far away at a minimum of 7.01 Å, which might be too long for the metal centers to act cooperatively on ROP of rac-LA. There are also ligand segments between Zn ions that might block the alkoxide migration, necessary to observe cooperativity. The tertiary nitrogen site coordinates to Zn center in some cases as observed in the solid-state structure. This asymmetry is also observed in solution by <sup>1</sup>H NMR studies. In contrast, the tertiary nitrogen most likely does not coordinate to the metal center in compounds 1 and 2, therefore resulting in a different structure than compound 3. The low ROP activity of 1 and 2 suggests the absence of cooperativity effects, probably due to the reasons pointed out for 3. Alkoxide migration is very important for accelerating ROP, it was proposed in previous studies that the ROgroup bound to an aluminum center migrates an attacks lactide coordinated to the adjacent Al resulting in cooperativity which accelerates ring opening of lactide in a back and forth process [11,13,14,16].

Attempts to obtain monometallated complex, L-H<sub>3</sub>Al-Me<sub>2</sub>, for evaluation of its activity in ROP of *rac*-LA, resulted in a mixture of metallated species that cannot be isolated by fractional crystallization techniques (Fig. S11). Thus, the control experiment for ROP of *rac*-LA with monometallated complex was not performed, and a comparison with catalysts having similar coordination sphere is presented instead. The activity of **1** is similar to related dialkylaluminum mononuclear complexes with bidentate phenoxide-imine **N**,**O** ligands [13]. It can then be inferred that the low activity of complex L(AlMe<sub>2</sub>)<sub>4</sub> (1) most likely is due to having ROP independently on each metal site, as the activity is at least one order of magnitude higher for bimetallic aluminum complexes that show cooperativity.

In the case of **3**, thus, in analogous complexes **1** and **2** the ROP most likely proceeds by individual metal sites without cooperativity.

#### 4. Conclusions

Three new tetranuclear Al, Ga, Zn complexes of polynucleating ligand with four N,O bidentate sites have been prepared and investigated as precatalysts in the presence of benzyl alcohol for the ring-opening polymerization of *rac*-lactide. Complex 1 was the best catalyst in this



Fig. 3. <sup>1</sup>H NMR spectrum for PLA obtained with catalyst 1 (Table 1, entry 1, 400 MHz, CDCl<sub>3</sub>, 25 °C).

| Table 1               |      |          |            |
|-----------------------|------|----------|------------|
| rac-LA polymerization | with | aluminum | complex 1. |

| Entry  | Cat <sup>a</sup> | [LA] <sub>0</sub> /[cat.] <sub>0</sub> /[BnOH] <sub>0</sub> | <i>t</i> (h) | Conv <sup>b</sup> (%) | M <sub>n</sub> (calcd) <sup>c</sup> (g/mol) | M <sub>n</sub> (obsd) <sup>d</sup> (g/mol) | $D^{\mathrm{d}}$ | $P_{\rm m}^{\rm e}$ |
|--------|------------------|-------------------------------------------------------------|--------------|-----------------------|---------------------------------------------|--------------------------------------------|------------------|---------------------|
| 1      | 1                | 100:1:4                                                     | 24           | 95<br>01              | 3531                                        | 3698                                       | 1.165            | 0.60                |
| 3      | 1                | 400:1:4                                                     | 26<br>24     | 98                    | 14,233                                      | 10,919                                     | 1.659            | 0.87                |
| 4<br>5 | 2<br>3           | 100:1:4<br>100:1:4                                          | 48<br>48     | 93<br>14              | 3450<br>_f                                  | f                                          | -                | 0.56<br>-           |
|        |                  |                                                             |              |                       |                                             |                                            |                  |                     |

<sup>a</sup> Reactions were performed in 5 mL of toluene,  $[cat.]_0 = 0.0173$  mM, at 70 °C.

<sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy.

 $^{c}$  Calculated by  $M_{\text{rac-LA}} \times ([\text{LA}]_0/[\text{BnOH}]_0) \times \text{conversion} + M_{\text{BnOH}}.$ 

<sup>d</sup> Measured by GPC in THF calibrated with polystyrene standards.

<sup>e</sup> Determined by analysis of all the tetrad signals in the methine region of the homonuclear-decoupled <sup>1</sup>H NMR spectrum.

<sup>f</sup> Polymer could not be isolated.



Fig. 4. Deconvolution of the methine region of the homonuclear-decoupled <sup>1</sup>H NMR spectrum for PLA obtained with catalyst 1 (Table 1, entry 1).

family of complexes, the better performance is due to the Al-OR site in **1** being more active than in the Ga complex **2**. For compound **1**, increasing the amount of benzyl alcohol or *rac*-LA, independently, caused high  $\mathcal{D}$ . The increase in *rac*-LA also caused the formation of polymer close to atactic. Zn complex **3** might not be stable as alkoxide Zn-OR, thus resulting in low activity in the ROP of *rac*-LA. Cooperativity between metal centers in the ROP of *rac*-LA was not observed in the tetranuclear complexes due to having long distance between metal centers and also having ligand segments between metal centers which impede direct interaction of the growing chain with at least two metals simultaneously. Ongoing studies include ligand modifications to enhance metal cooperativity in the ROP of *rac*-LA.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2019.02.007.

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