Multinuclear alkylaluminium macrocyclic Schiff base complexes: influence of procatalyst structure on the ring opening polymerisation of ε-caprolactone†

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Two remote dialkylaluminium centres supported by a macrocyclic Schiff base ligand exhibited beneficial cooperative effects, whilst aluminoxane-type bonding proved to be detrimental to activity for the ring opening polymerisation of ε-caprolactone.

Poly(lactide) and poly(ε-caprolactone) are amongst the most studied and desirable biodegradable polymers due to their biomedical applications and their potential as alternatives to well-established, non-degradable poly(olefin)s.[1–6]

Dinuclear catalysts have attracted recent attention in the field of the ring opening polymerisation (ROP) of cyclic esters and epoxides due to the possible cooperative effect that can occur between metal centres linked through M–O–M′ type bonds.[7–9] In particular, reports have shown dinuclear organoaluminium species to be highly active for the ROP of ε-caprolactone and lactide;[4] however, structural and catalytic studies on multinuclear aluminium complexes and, consequently, observations of cooperative effects and motifs which promote them are scant.[3,10]

We report herein the synthesis, structural characterisation and catalytic activity of a series of multinuclear aluminium complexes supported by macrocyclic Schiff base ligands (Scheme 1). These complexes were designed to prevent catalyst aggregation and to provide a suitable environment that could lead to cooperative effects between metal centres. Their catalytic activities were compared to those of known, structurally related mono- and dinuclear species.

Reaction of 2,6-dicarboxy-4-*tert*-butylphenol and 2,2′-ethylenedianiline in a 1 : 1 ratio afforded the macrocyclic ligand $\mathbf{L}H_2$, in high yield as a yellow powder. Treatment of $\mathbf{L}H_2$ with two equivalents of AlR_3 afforded the complexes $[\mathbf{L}(AlR_2)_2]$ (R = Me (**1**), Et (**2**)) in moderate to good yields. In solution, ^{1}H NMR spectra of **1** and **2** both display C_2 symmetry, as demonstrated by the two sets of signals for the four Al–R groups (−0.77 ppm and −1.15 ppm for **1**). The two-fold axis is located between the mid-points of the ethylene bridges.

Reaction of $\mathbf{L}H_2$ with 4 equivalents of $AlMe_3$ afforded a mixture of the complexes $[\mathbf{L}'(AlMe_2)_x]$ (x = 2 (**3**), 4 (**4**)) in moderate to good yields; complex **3** was extracted from the reaction mixture using cold acetonitrile, affording analytically pure **4**. Crystals of **3** and **4** suitable for X-ray diffraction studies were grown from saturated acetonitrile solutions (Fig. 1).‡ In both **3** and **4**, the complexation involves a methyl transfer from the $AlMe_3$ reagent to two imine moieties.[11–14] This methyl transfer occurs selectively on imine groups originally from the same dianiline, affording complexes **3** and **4**, both with potential C_2 symmetry in the solid state. An approximate two-fold axis is located between the mid-points of the C(27)–C(28) and C(57)–C(58) bonds in both **3** and **4**. Interestingly, complexes **3** or **4** could not be obtained by reacting complex **1** with excess $AlMe_3$. In both complexes, the aluminium centres are distorted tetrahedral. In complex **3**, the two aluminium centres are bound to opposite phenolic moieties and to the two remaining imino nitrogens. In complex **4**, the two remaining coordination sites are occupied by two aluminium centres coordinated to opposite phenolic oxygens and to the amino nitrogens. In solution, the C_2 symmetry is retained for both complexes **3** and **4**.

Subsequent hydrolysis of **4** afforded the new macrocyclic ligand $\mathbf{L}'H_4$ in high yield.

The aluminium complexes **1**–**4** were screened for the ROP of ε-caprolactone. All complexes exhibited good control over the polymerisation process (Tables 1–3 and ESI†) with the corrected average molecular mass[15] of the polymers obtained close to the calculated values, and with narrow polydispersities (IP < 2).

At high temperature (80 °C), the polymerisation catalysed by complex **4** was found to be almost quantitative after 20 min (>90% conversion, Table 1 entry 4). The increase in temperature shortened the polymerisation time, but had a detrimental effect on the control of the molecular weight obtained (Table 1, entries 4 and 5), reflecting the importance of transfer reactions at high temperature (80 °C). In solvent-free conditions (Table 1, entry 5), complex **4** was shown to be slightly less active, owing to increasing viscosity.

Complex **4** was still active at low catalyst concentration, although it was found to be less active than the fluorous diamino dialkoxy based aluminium complex reported by Carpentier and co-workers.[16] At a monomer/metal ratio of 1100, conversions of 7% after 24 h at room temperature (Table 2, entry 5), and 68% after 48 h at 60 °C were obtained. At high monomer/aluminium ratio (*i.e.* 700 to 1100), the recorded average molecular weight is half the calculated one suggesting that, at those low catalyst concentrations, both Al–Me bonds on one aluminium centre are involved in the polymerisation process.

Without benzyl alcohol, complex **4** was still active at room temperature (Table 3, entry 6) despite a dramatic increase

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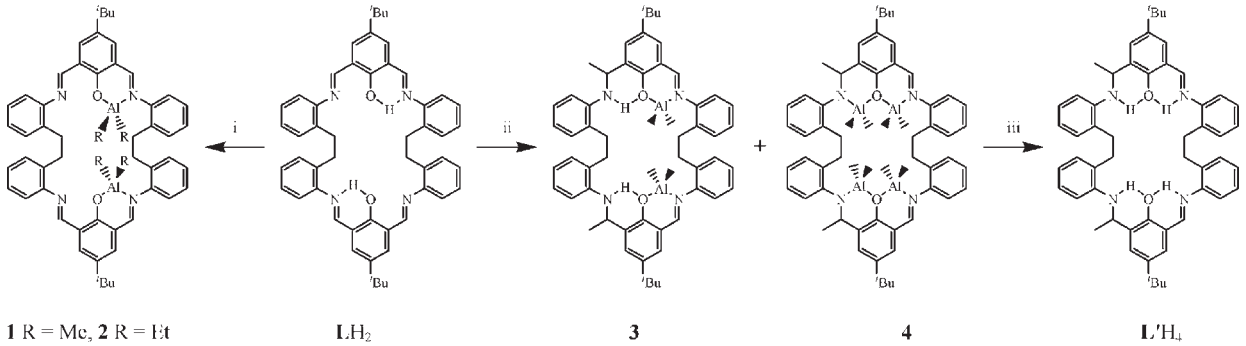
† Electronic supplementary information (ESI) available: Experimental details, spectroscopic data of **1**–**4**, **6**, **7**, $\mathbf{L}H_2$ and $\mathbf{L}'H_4$; *in situ* IR polymerisation data for **4**. CCDC reference numbers 692213–692214. For ESI and crystallographic data in CIF format see DOI: 10.1039/b810417d



Scheme 1 Conditions: (i) AlR_3 (2 equivalents), toluene, reflux for 12 h; (ii) $AlMe_3$ (4 equivalents), toluene, reflux for 12 h; (iii) H_2O–CH_2Cl_2, stirring at room temperature for 30 min.

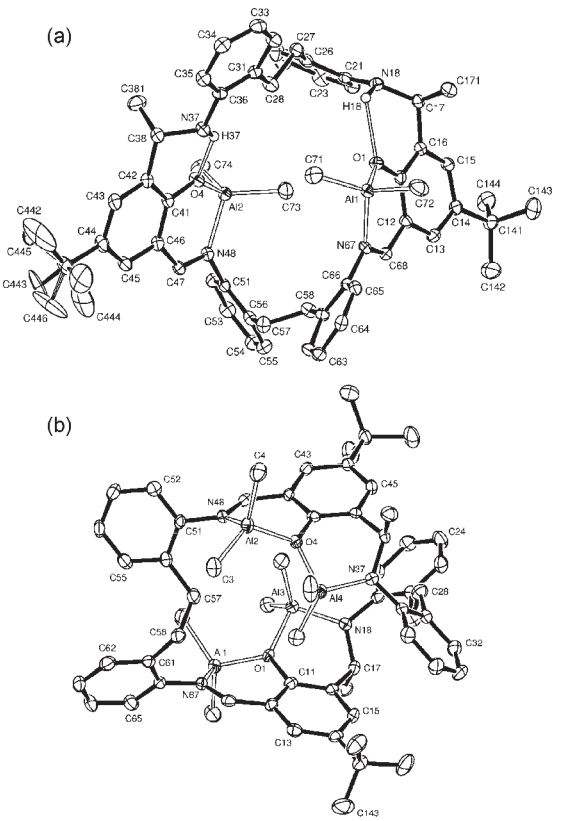


Fig. 1 (a) X-Ray crystal structure of **3**; (b) X-ray crystal structure of **4**. Thermal ellipsoids are represented at the 50% level and hydrogen atoms (other than those involved in hydrogen bonds) have been omitted for clarity. See ESI† for bond lengths and angles.‡

in the polydispersity index. The ^{1}H NMR spectrum of a polymer obtained for a monomer/aluminium ratio of 40 displayed a single peak at 5.11 ppm assigned to benzylic protons: ROP by complex **4** follows a coordination/insertion mechanism.

The ROP of ε-caprolactone initiated by **4** was monitored by *in situ* IR spectroscopy. At room temperature and for a monomer/metal ratio of 500, complex **4** exhibited a turnover frequency of 105 h^{-1} up to 20% monomer conversion. The subsequent decrease in activity was attributed to an increase in viscosity.

In order to assess the potential cooperative effect from metal centres in a close proximity, the known complex [{2-(C_6H_5N=CH)C_6H_4O}$AlMe_2$], **5**, (Fig. 2) was screened for the ROP of ε-caprolactone under the same conditions (Table 3, entry 7). As reported by Baugh and Sissano,[17] complex **5** was found to be inactive under these conditions.

We have previously reported the synthesis of mono- and dinuclear organoaluminium species bound to phenoxy bis-imine ligands that can be seen as acyclic analogues of **1**, **3** and **4**.[14] Similarly, treatment of 2,6-(2,6-*i*$Pr_2C_6H_3N$=CH)$_2$-4-*t*BuC_6H_2OH with $AlMe_3$ afforded, after work-up, **6** and **7** (Fig. 2), the structures of which were deduced from ^{1}H NMR spectra, elemental analyses and mass spectrometry data.

Complexes **1** and **2** exhibited low but similar activities; however, their catalytic performance is greater than that of complex **5**, their acyclic analogue (Table 3). Complexes **6** and **7** showed lower activities than the macrocyclic complexes **3** and **4**. These results suggest that a cooperative effect is in operation so long as the aluminium centres are not linked in an aluminoxane [Al–O–Al] type fashion (*e.g.* procatalyst **6** performs better than **7**). This is in accordance with the poor activity reported for MAO (methyl aluminoxane) in the ROP of ε-caprolactone[18] and in turn reflects the higher activity reported for complex **3** (Table 3, entry 3), which possesses the favourable metal arrangement (Al···Al distance of 5.7818(10) Å) in contrast to complex **4** where the closer Al···Al interactions hinder the polymerisation process (Al···Al

Table 1 ε-Caprolactone polymerisation data for complex **4** at various temperatures[a]

Run	Temperature/°C	Time	Conversion (%)	M_n measured[b]/g mol^{-1}	M_n calculated/g mol^{-1}	IP
1	25	24 h	98	60 750	55 870	1.5
2	40	24 h	98	52 650	55 870	1.4
3	60	24 h	98	58 050	55 870	1.9
4	80	20 min	91	15 400	52 210	1.1
5[c]	80	20 min	71	15 900	40 620	1.3

[a] Conditions: monomer/metal = 500; 40 mL of toluene; 5 mL of ε-caprolactone; 1 equivalent of benzyl alcohol. [b] M_n measured = 0.45 × M_n GPC. [c] Solvent-free.

Table 2 ε-Caprolactone polymerisation data for complex **4** at various complex concentrations[a]

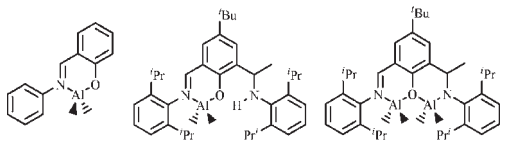
Run	Monomer/metal molar ratio	Conversion (%)	M_n measured[b]/g mol^{-1}	M_n calculated/g mol^{-1}	IP
1	300	100	26 500	34 390	1.3
2	500	98	60 750	56 200	1.5
3	700	17	5 760	13 840	1.1
4	900	18	7 740	18 800	1.1
5	1100	7	5 090	9 040	1.1

[a] Conditions: 40 mL of toluene; 5 mL of ε-caprolactone; 1 equivalent of benzyl alcohol (from a 0.97 M solution in toluene); 25 °C; 24 h. [b] M_n measured = 0.45 × M_n GPC.

Table 3 ε-Caprolactone polymerisation data for complexes **1**–**7**[a]

Run	Catalyst	Polymerisation time/h	Conversion[b] (%)	M_n measured[c]/g mol^{-1}	M_n calculated/g mol^{-1}	IP
1	**1**	11	24	14 360	13 730	1.1
2	**2**	11	28	10 670	16 020	1.5
3	**3**	1	14	7 470	8 010	1.1
4	**3**	12	99	49 500	56 650	1.7
5	**4**	11	64	23 630	36 610	1.1
6[d]	**4**	24	46	44 640	26 440	2.6
7	**5**	20	—	—	—	—
8	**6**	11	50	26 690	28 600	1.1
9	**7**	11	37	24 480	21 170	1.2

[a] Conditions: monomer/metal = 500; 40 mL of toluene; 5 mL of ε-caprolactone; 1 equivalent of benzyl alcohol (from a 0.97 M solution in toluene); 25 °C; 24 h. [b] Calculated using ^{1}H NMR spectroscopy. [c] M_n measured = 0.45 × M_n GPC. [d] Without benzyl alcohol.



5 **6** **7**

Fig. 2 Complexes **5**–**7**.

distances of 3.2129(13) and 3.2270(14) Å). When complex **3** is used, the Al···Al distance may favour the coordination of a single monomer to both catalytic centres from the same complex: one being used as a Lewis acid and the other one using its Al–R functionality to attack the carbonyl group. A similar mechanism has been suggested for the ROP of propylene oxide by discrete mononuclear aluminium complexes.[19,20]

In summary, we have demonstrated that highly active systems for ε-caprolactone polymerisation are accessible using a combination of macrocyclic Schiff-base ligand and trimethylaluminium. Beneficial cooperative effects are observed for multi-metallic systems where aluminoxane-type bonding is absent. Further studies using diamines with differing length of backbone are in progress to gain further insight into the influence of the inter-aluminium distance.

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Notes and references

‡ *Crystal data for compound* **3**: $C_{58}H_{70}Al_2N_4O_2$, M = 909.1, triclinic, a = 10.8444(9), b = 12.1356(11), c = 12.3556(11) Å, α = 113.895(9), β = 109.772(8), γ = 99.385(7)°, V = 1311.2(2) Å^3, T = 140(1) K, space group $P\bar{1}$ (no. 1), Z = 1, 17 941 reflections measured, 11 514 unique (R_{int} = 0.019) which were used in all calculations. Final wR_2 = 0.082 and R_1 = 0.044 for all data. CCDC number 692213.

Crystal data for compound **4**: $C_{66}H_{86}Al_4N_6O_2$, M = 1103.3, monoclinic, a = 20.7137(6), b = 13.6334(3), c = 23.6742(7) Å, β = 107.436(3)°, V = 6378.4(3) Å^3. T = 140(1) K, space group $P2_1/n$ (equiv. to no. 14), Z = 4, 65 005 reflections measured, 11 208 unique (R_{int} = 0.114) which were used in all calculations. Final wR_2 = 0.106 and R_1 = 0.128 for all data. CCDC number 692214.†

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