

Please cite the Published Version

Fazekas, Eszter, Etcheverry-Berrios, Alvaro, Nichol, Gary S, Piligkos, Stergios, Brechin, Euan K and Garden, Jennifer A  (2025) Robust Y and Lu TrenSal catalysts for ring-opening polymerisation. *Polyhedron*, 266. 117308 ISSN 0277-5387

DOI: <https://doi.org/10.1016/j.poly.2024.117308>

Publisher: Elsevier BV

Version: Published Version

Downloaded from: <https://e-space.mmu.ac.uk/637231/>

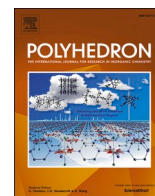
Usage rights:  [Creative Commons: Attribution 4.0](https://creativecommons.org/licenses/by/4.0/)

Additional Information: This is an open access article which first appeared in *Polyhedron*

Data Access Statement: CCDC contains the supplementary crystallographic data for YLCHO, Y2L and Lu2L. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Enquiries:

If you have questions about this document, contact openresearch@mmu.ac.uk. Please include the URL of the record in e-space. If you believe that your, or a third party's rights have been compromised through this document please see our Take Down policy (available from <https://www.mmu.ac.uk/library/using-the-library/policies-and-guidelines>)



Robust Y and Lu TrenSal catalysts for ring-opening polymerisation

Eszter Fazekas^a, Alvaro Etcheverry-Berrios^b, Gary S. Nichol^a, Stergios Piligkos^c,
Euan K. Brechin^a, Jennifer A. Garden^{a,*}

^a EaStCHEM School of Chemistry, University of Edinburgh, David Brewster Road, EH9 3FJ Edinburgh, UK

^b Faculty of Science and Engineering, Manchester Metropolitan University, Chester Street, M1 5GD Manchester, UK

^c Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen, Denmark

ARTICLE INFO

Dedicated to Prof. Robert E. Mulvey, an inspirational chemist, colleague and mentor, on the occasion of his 65th birthday.

Keywords:

Yttrium
Lutetium
TrenSal ligand
Metal–organic cage
Polymerisation

ABSTRACT

Mono and bimetallic cage-like TrenSal complexes based on rare-earth metals Y and Lu were synthesised and fully characterised by single crystal and powder X-ray diffraction, multinuclear NMR and IR spectroscopy, and MALDI-ToF mass spectrometry. These robust and air-stable complexes are active catalysts for the ring-opening polymerisation of *rac*-lactide. While the polymerisation activity is low, the complexes remain active in air using unpurified monomers, and are highly unusual examples of metal–organic cages applied in polymerisation. MALDI-ToF mass spectrometry studies of the obtained polymers revealed H and OBn end-capped chains suggesting that an ‘activated monomer’ mechanism predominates when BnOH is used as an exogenous initiator.

1. Introduction

Renewable and biodegradable polyesters such as poly(lactic acid) (PLA) are at the forefront of research to tackle the global plastic problem, and are typically synthesised *via* the ring-opening polymerisation (ROP) of cyclic esters such as lactide (LA) [1]. Most catalysts are metal based, including highly active mono- and bimetallic complexes based on metals from across the periodic table [2]. Rare-earth metal complexes often display excellent catalytic performance [3], which has been attributed to their large ionic radii and high Lewis acidity due to the empty orbitals and high oxophilicity [4]. Both features promote the coordination of cyclic ester monomers, which is a key mechanistic step in ROP [3,5–7]. Most metal-based catalysts operate *via* a coordination-insertion mechanism (CIM, Scheme 1, right), which requires a labile M-alkyl/alkoxide/amide initiating group [1]. However, a drawback is that these complexes are typically air- and moisture-sensitive, and thus challenging to prepare and handle. It would therefore be advantageous to develop more robust rare-earth metal catalysts.

TrenSal is a popular ligand framework due to the chelate effect and stabilisation provided by the three phenoxyimine moieties, which can afford robust, air-stable complexes (Fig. 1, left). A range of TrenSal complexes have been reported, including main group metals (Na, Al, Zn,

Ga) [8–10], transition metals (V, Cr, Mn, Fe, Co, Ni, Rh, Re) [8,10–13] and lanthanides (Ce, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) [14–22]. TrenSal complexes have a host of applications. The magnetic properties of the rare-earth metal complexes (particularly Yb) have been extensively studied as potential qubits in quantum computing applications [15,18,23,24], while actinide U(IV) TrenSal complexes have been employed in CO₂ reduction [25]. However, there is only one report of TrenSal complexes being used for cyclic ester ROP [9]. This is somewhat surprising, as there are structural similarities between TrenSal ligands and the salen ligands that are ubiquitously used in LA ROP [2,26].

Unusually, the heterobimetallic Na/Al TrenSal complex reported for LA polymerisation operates *via* an ‘activated monomer mechanism’ (AMM, Scheme 1, left), mediated by BnOH. Whether a CIM or an AMM occurs is generally dictated by the nature of the metal-alkoxide bond. Complexes featuring strong M–OR bonds typically follow an AMM, whereas those with labile M–OR bonds favour a CIM [27,28]. As TrenSal complexes are chelating and feature strong M–OR bonds, contributing to their robustness, this can favour an AMM. Mechanistic studies have indicated that in the AMM, both the monomer and the exogenous nucleophile (ROH) can be activated by coordination to a single metal centre. Bimetallic complexes, where one metal coordinates the monomer, and the other coordinates the initiator, thus have the potential to

* Corresponding author.

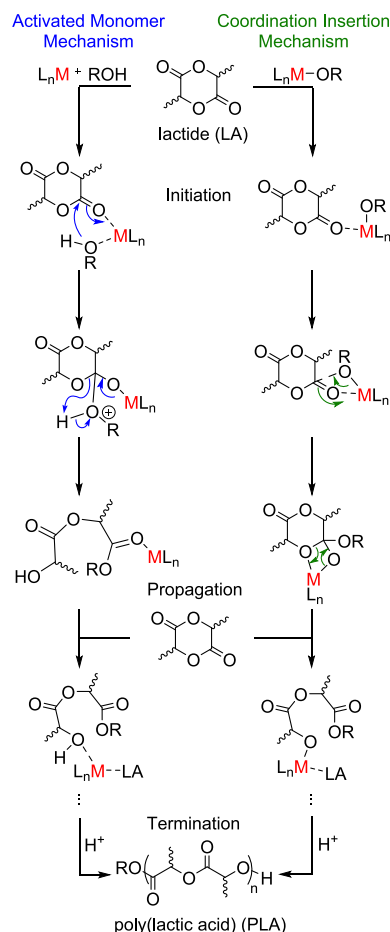
E-mail address: j.garden@ed.ac.uk (J.A. Garden).

<https://doi.org/10.1016/j.poly.2024.117308>

Received 13 September 2024; Accepted 14 November 2024

Available online 17 November 2024

0277-5387/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).



Scheme 1. Potential mechanisms for metal-catalysed LA ROP. Left, activated monomer mechanism (AMM). Right, coordination-insertion mechanism (CIM). L refers to ligand, M refers to metal and RO refers either to the initiator or the growing polymer chain.

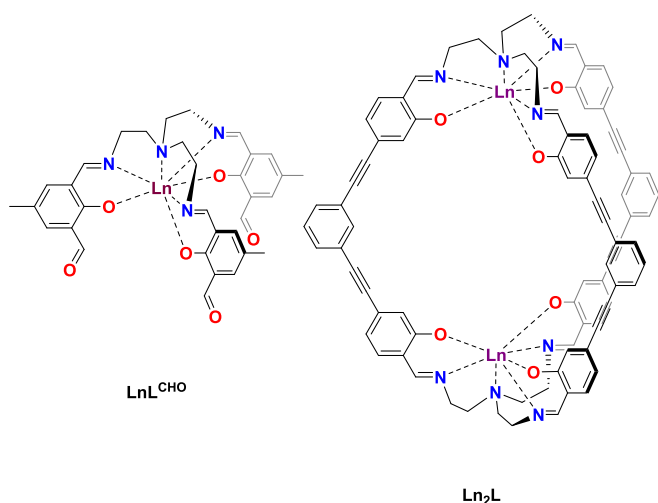


Fig. 1. Structures of mono- and bimetallic complexes (Ln = Y or Lu).

show good activity in the AMM. While some bi- or polymetallic catalysts based on rare-earth metals have been reported for cyclic ester ROP, these are generally air- and moisture-sensitive complexes featuring labile initiating groups [29,30].

Herein, we describe the synthesis and application of mono- and

bimetallic Y and Lu TrenSal complexes as robust catalysts for LA ROP. Due to the tris-anionic TrenSal framework, these M(III) complexes do not possess a conventional M-alkyl/alkoxide/amide initiating group, which is characteristic for most rare-earth metal ROP catalysts reported to date. A ligand backbone containing two TrenSal pockets was designed to provide a framework for a bimetallic system, where both metals are accessible and are separated enough to enable coordination thus activation of the monomer and the alcohol initiator at the two proximal metal centres. Through benchmarking studies with monometallic analogues, we investigate the possible benefits of having two metals in one cage.

2. Results and discussion

2.1. Complex synthesis and characterisation

The novel bimetallic TrenSal complexes, **Ln₂L**, were synthesised using a metal-templated Schiff base reaction between the corresponding dialdehyde and tris(2-aminoethyl)amine (Tren) in the presence of excess Ln(OTf)₃ (where Ln = Y or Lu, Fig. 1, refer to ESI for further synthetic details). For comparative purposes, the monometallic analogues **LnL^{CHO}** were also synthesised [18]. All reactions were carried out under standard benchtop conditions in the presence of air, and the reagents were used from commercial sources without extra purification or drying steps.

The bimetallic **Ln₂L** complexes were synthesised through a one-pot synthesis using two different methods. Heating the reactions using DMF as solvent in an oven at 120 °C for 60 h afforded orange block crystals suitable for single-crystal X-ray diffraction studies. While this method afforded high-quality single crystals, the yields were rather low (<10 %). Scaling up the reaction using this method afforded samples contaminated with the empty cage. This was circumvented by employing microwave irradiation, which afforded pure polycrystalline samples with higher yields (58 %). Powder X-ray diffraction measurements of samples obtained by both methods are in full agreement with the simulated diffractograms (Figs. S29 and S30).

The monometallic **LnL^{CHO}** analogues were synthesised following a reported procedure [18]. While the molecular structure of **LuL^{CHO}** has been reported, **YL^{CHO}** has not, and thus the procedure was modified to obtain single crystals of **YL^{CHO}**. After reducing the volume of the solution, the reaction was removed from the heat and Et₃N was added, delivering yellow hexagon-shaped crystals overnight. Powder X-ray diffraction analysis confirmed excellent agreement between the polycrystalline samples and the simulated diffractograms (Figs. S27 and S28).

The molecular structures of **YL^{CHO}** and **Ln₂L** were determined by single-crystal X-ray diffraction studies (Fig. 2, Tables S1–S7). Monometallic **YL^{CHO}** crystallises in the trigonal space group $P\bar{3}$, with two complexes in the unit cell (Fig. 2a, Table S1). The crystallographic C_3 axis passes through the molecular C_3 axis such that one-third of the complex is contained in the asymmetric unit. The Y(III) complex is heptacoordinated by the ligand with three O-atoms and four N-atoms, with the geometry of a monocapped trigonal antiprism. In accordance with previously reported complexes, the three aldehyde groups point away from the Y centre and do not coordinate to the metal (Fig. 2b) [18]. Here, the bond distances around the Y(III) ion resemble those in the previously reported molecular structure of **LnL^{CHO}** [11], with Y–O, Y–N_{imine} and Y–N_{apical} bond lengths of 2.1835(15), 2.4675(19), and 2.637(3) Å, respectively (see Tables S2 and S3 for a list of selected bond lengths and angles).

Both **Ln₂L** complexes crystallise in the monoclinic space group $P2_1/c$, with four complexes in the unit cell and with five molecules of DMF in the asymmetric unit (Fig. 2c,d, Tables S1 and S4–S7). The framework of the cage is composed of two TrenSal moieties, joined by three dialkynylbenzene units. The geometry around the metal centre in

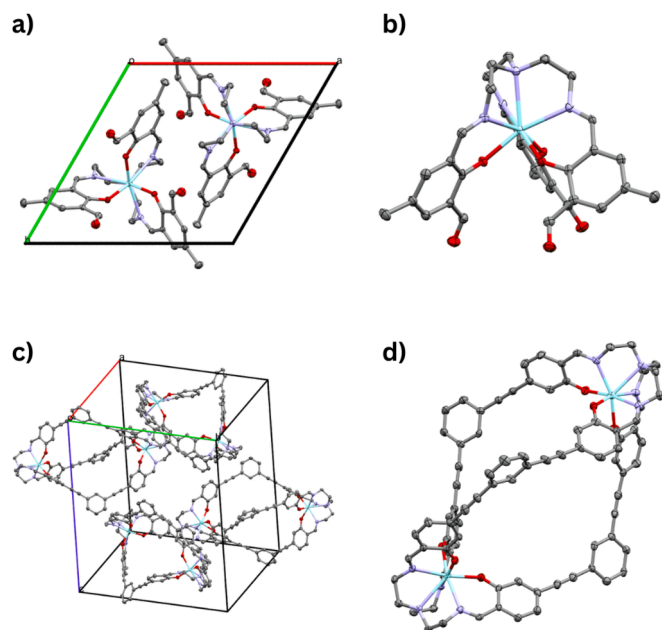


Fig. 2. (a) Unit cell of YL^{CHO} viewed along the crystallographic c axis. (b) Molecular structure of YL^{CHO} . (c) Unit cell of Y_2L . (d) Molecular structure of Y_2L . Colour code: Y, cyan; N, lilac; O, red; C, grey. Hydrogen atoms and solvent molecules have been omitted for clarity, and thermal ellipsoids have been set to 50 % probability. ((Colour online.))

both complexes is monocoordinated trigonal antiprismatic for 7-coordinate centres. The aromatic backbone is highly distorted, with the planes of the phenolic rings twisted (to varying degrees) with respect to the plane formed by the central diethynylbenzene group (Fig. 2d). Similarly to other Ln-TrenSal complexes, the Ln(III) centre is heptacoordinated by the ligand with a pseudo- C_3 molecular axis passing through the Ln(III) ions. The two metal centres are crystallographically independent with Ln–O, Ln–N_{imine} and Ln–N_{apical} bond distances ranging from 2.177(4)–2.212(4), 2.438(5)–2.479(5), and 2.672(5)–2.727(5) Å for Y_2L ; and 2.141(3)–2.180(3), 2.398(3)–2.434(3), and 2.645(3)–2.692(3) Å for Lu_2L , respectively (see Tables S4–S7 for selected bond lengths and angles). For all the complexes, the bond lengths around the metal centre are within the range of values observed for similar complexes [18,19,31–36], with longer metal–O/N bond lengths observed for the Y complexes due to the larger ionic radius, compared to the Lu complexes [37]. The single crystal X-ray data reveals that the Lu–Lu distance in the full cage is 15.2961(3) Å. Intriguingly, this distance is almost twice as long as the shortest metal–metal distance between cages in the solid phase, 8.1286(3) Å. Similarly, in the Y_2L complex the intramolecular Y–Y distance is 15.2198(10) Å and the shortest intermolecular Y–Y distance is 8.1099(9) Å.

In addition to crystallographic characterisation, the bimetallic Ln_2L complexes were characterised by MALDI-ToF and IR spectroscopy. MALDI-ToF data shows both the $[M + H]^+$ and the $[M + Na]^+$ signals (Figs. S25 and S26). No signals attributed to the monometallic or empty cage were found. The IR spectra shows bands around 1650 cm^{-1} confirming the presence of the imine groups (Figs. S20 and S21). While the poor solubility of the Ln_2L complexes in conventional laboratory solvents such as $CDCl_3$ and DMSO prevented NMR spectroscopic characterisation, both at ambient and elevated temperatures, the monometallic analogues were characterised by NMR spectroscopy. Complex LuL^{CHO} matched the previously reported NMR data and complex YL^{CHO} showed similar 1H NMR resonances (Figs. S1 and S12). The IR spectra of both monometallic complexes show bands around 1620 and 1670 cm^{-1} , confirming the presence of imine and aldehyde groups, respectively (Figs. S17 and S18). MALDI-ToF data for YL^{CHO} and LuL^{CHO} showed $[M+Na]^+$ signals, along with much lower intensity signals for $[M+H]^+$

and $[M+K]^+$ (Figs. S22 and S23).

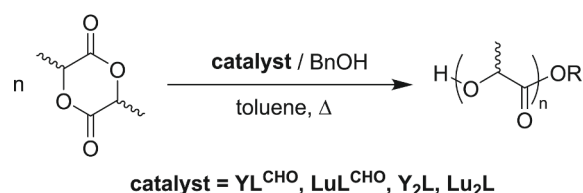
2.2. Polymerisation studies

The polymerisation affinities of all four TrenSal complexes were investigated in the ROP of *rac*-lactide (*rac*-LA). Initial studies were performed with bimetallic Lu_2L , using protocols that have previously shown success in polymerising *rac*-LA (Scheme 2) [38,39]. Control reactions performed without an exogenous initiator showed that using Lu_2L alone gave either no, or very low conversion of *rac*-LA to PLA (Table 1, entries 1–2). This suggests that Lu_2L is inefficient at polymerising *rac*-LA through a coordination-insertion mechanism, which is consistent with literature precedent for complexes with strong metal-alkoxide bonds such as metal-phenoxides or carboxylates [9,27,40]. In contrast, a dramatic activity enhancement was observed upon introducing BnOH as an exogenous initiator. For example, using 5 equiv. of BnOH (vs Lu_2L) gave 94 % conversion of *rac*-LA vs 9 % without BnOH (entry 5 vs entry 2), under otherwise identical conditions.

MALDI-ToF mass spectrometry analysis showed that α -benzyloxy, ω -hydroxy end-capped PLA chains were generated with BnOH (Fig. S35), which could either arise from an AMM or a CIM following deprotonation of BnOH by the TrenSal ligand. While the limited solubility of the bimetallic complexes restricted reactivity studies with Lu_2L and Y_2L , the reaction of BnOH with LuL^{CHO} or YL^{CHO} was investigated by 1H and DOSY NMR analysis (5 equiv. of BnOH, $CDCl_3$ solvent, room temperature and 60 °C). In all cases, no reaction was observed; the resonances corresponding to LnL^{CHO} did not change. DOSY NMR analysis clearly showed that BnOH retains a different diffusion coefficient to the LuL^{CHO} and YL^{CHO} complexes, indicating that it does not remain coordinated in the solution state (Figs. S32 and S33). The pK_a values of 9.11–11.91 predicted for structurally related TrenSal ligands in H_2O also suggest that the formation of Ln-OBn species is unlikely [41]. Taken together, the lack of Ln-benzoxide formation, the observation of BnO/H end groups and the pK_a values all point towards AMM being the major polymerisation mechanism. The catalyst remained active upon increasing the monomer loading to 100 equivalents, although the monomer conversion plateaued at 35 % (entry 11). Here, this is attributed to the steric bulk of the propagating PLA chain disfavoured diffusion into the Lu_2L cage structure.

Complexes YL^{CHO} , LuL^{CHO} , Y_2L and Lu_2L were subsequently tested using the optimised reaction parameters (Table 2, entries 1–8). While all four complexes were active catalysts, monometallic YL^{CHO} achieved the highest conversions, affording 34 % and 77 % conversion after 90 min and 20 h, respectively (Table 2, entry 1–2). Notably, YL^{CHO} was significantly more active than the LuL^{CHO} analogue, which only gave 14 % conversion after 20 h (entry 4). This may be due to the larger ionic radius of Y [37,42,43]; metals with larger ionic radii have been widely shown to facilitate monomer coordination and enhance catalyst activity in LA ROP [2,26,44]. Monometallic YL^{CHO} also outperformed bimetallic Y_2L , which gave 29 % conversion after 20 h (vs 77 %, entries 2 and 6). This likely arises from the improved accessibility of the metal centres in the half-cage complex compared to the full cage structure. However, the Lu complexes do not show the same trend, and the bimetallic Lu complex even displays a slightly higher conversion than the monometallic species (22 % vs 14 % after 20 h, entries 3–4 and 7–8).

It is important to note that the molecular weights of the obtained



Scheme 2. Ring-opening polymerisation of *rac*-lactide.

Table 1

Optimisation of reaction parameters in the ring-opening polymerisation of *rac*-lactide using Lu_2L .

Entry	Loading (eq.)	t (h)	T (°C)	Conv. (%)	TON	TOF (/h)
1 ^a	40	4	75	0	0	0.0
2 ^a	40	24	120	9	4	0.2
3	40	4	75	4	2	0.4
4	40	24	75	18	7	0.3
5	40	24	120	94	38	1.6
6	100	0.5	120	7	7	14.0
7	100	1.5	120	11	11	7.3
8	100	2	120	14	14	7.0
9	100	16	120	22	22	1.4
10	100	20	120	24	24	1.2
11	100	72	120	35	35	0.5

Conditions: [monomer] = 1 M in toluene, $[\text{Lu}_2\text{L}]:[\text{BnOH}]:[\text{monomer}] = 1:5:40$ –100 (refer to ESI for additional details). Conversions were calculated using ¹H NMR spectroscopy. ^a Reactions performed without BnOH additive.

Table 2

Comparison of mono and bimetallic catalysts in the ring-opening polymerisation of *rac*-lactide.

Entry	Catalyst	t (h)	Conv. (%)	TON	TOF (/h)
1	Y^{CHO}	1.5	34	34	22.7
2	Y^{CHO}	20	77	77	3.9
3	Lu^{CHO}	1.5	9	9	6.0
4	Lu^{CHO}	20	14	14	0.7
5	Y_2L	1.5	1	1	0.7
6	Y_2L	20	29	29	1.5
7	Lu_2L	1.5	11	11	7.3
8	Lu_2L	20	22	22	1.1
9 ^a	Y^{CHO}	20	90	90	4.5
10 ^a	Lu^{CHO}	20	49	49	2.5
11 ^a	Y_2L	20	80	80	4.0
12 ^a	Y_2L	96	95	95	1.0
13 ^a	Lu_2L	20	32	32	1.6
14 ^b	Lu_2L	24	28	56	2.3

Conditions: [monomer] = 1 M in toluene, $[\text{catalyst}]:[\text{BnOH}]:[\text{monomer}] = 1:5:100$, 120 °C (refer to ESI for additional details). Conversions were calculated using ¹H NMR spectroscopy. ^a Reactions performed under air using unpurified *rac*-lactide and wet toluene. ^b Reactions performed without solvent using 200 equiv. monomer.

polymers are low, and significantly lower than the theoretical values (Table S8), which differs from other reports on Ln catalysts. This is, however, consistent with reports using vanadium clusters as ROP catalysts [45], where the lower-than-expected M_n values were attributed to the rate of transesterification side-reactions being competitive with the propagation rate under the relatively harsh reaction conditions and long reaction times. Indeed, MALDI-ToF mass spectrometry analysis of the resultant PLA shows the presence of half lactide (lactic acid) repeat units (72 Da), providing evidence for transesterification (Fig. S35) and affording atactic PLA chains. The SEC traces are bimodal (Fig. S34), although the dispersities are relatively moderate ($D = 1.2$ – 1.9 , Table S2) compared to some other lanthanide catalysts; various Y and Lu catalysts have been reported with dispersities of up to 4.2 [3]. While the origin of the bimodal distributions is not completely clear, this may be due to the presence of trace water (as the catalysts were prepared in the presence of air and moisture), or from the formation of cyclic polymer *via* a small amount of initiation from the metal-phenoxide unit, as some ROP activity was observed in the control reaction without BnOH [27].

To probe the robustness of these catalysts, the polymerisation was investigated using unpurified *rac*-LA, wet toluene and under air instead of an argon atmosphere (entries 9–13). For both the mono- and bimetallic catalysts the activity increased under these conditions (e.g. entry 11 vs 6), which can be attributed to the presence of water, lactic acid and other impurities facilitating alternative initiation or chain transfer mechanisms. Polymerisation was also investigated under neat (solvent-

free) conditions, using 200 equivalents of molten *rac*-LA at 120 °C affording a significant increase in the turnover number (TON = 56, entry 14 vs TON = 38, Table 1 entry 5).

While these catalysts are less active than some other lanthanide complexes reported [3,46–48], they are unusual examples of rare-earth metal catalysts operating through an AMM, and Y_2L and Lu_2L are rare examples of metal–organic cage catalysts for cyclic ester ROP. Very few metal-based cage compounds have been reported for LA ROP, and these are generally aggregated metal-oxo or metal-alkoxide species based on Li, Zn, Ti, or mixed-metal Na/Ln species [30,49–54]. The presence of Lewis donors is well known to influence the aggregation state of metal complexes, but here, the metal–metal proximity is fixed through three rigid 1,3-diethynylbenzene connectors. The strong chelation and steric shielding of the metal centre by the TrenSal ligand indicates that polymerisation occurs inside the cage structure, providing promise for the use of metal–organic cages in cyclic ester polymerisation so long as the metal centres remain accessible for activation of the monomer and the active polymer chain end.

3. Conclusions

Applying straightforward one-pot synthetic strategies, mono- and bimetallic TrenSal complexes of Y and Lu were synthesised. Crystallographic characterisation of the monometallic Y and homobimetallic Y and Lu complexes shows that the metal centres are heptacoordinate in all cases, and feature a monocapped trigonal antiprism geometry. Despite their low solubility, all four catalysts showed activity in the ring-opening polymerisation of *rac*-lactide. Very few cage complexes have shown catalytic activity for *rac*-lactide polymerisation, and these have been almost exclusively limited to aggregated metal-oxo or alkoxo structures based on alkali metals, zinc and titanium. Here, the full-cage structures are strikingly different, as the two metal centres are seated within two TrenSal units bridged by organic spacer ligands. While the polymerisation control was limited, these robust, air- and moisture-stable catalysts maintained activity with the use of unpurified monomers. This study serves as a promising first step in this area, and future work will involve varying the ligand substituents to enhance the activity by improving solubility and enabling detailed mechanistic studies.

Author contributions

The project was conceived by E.F., A.E.B., S.P., E.K.B. and J.A.G. A.E.B. carried out the synthesis and characterisation of the complexes. E.F. carried out the polymerisation studies. A.E.B. and G.S.N. collected and analysed the single crystal X-ray data for all the compounds. The manuscript was written by E.F., A.E.B., E.K.B. and J.A.G., with contributions from all the authors.

CRedit authorship contribution statement

Eszter Fazekas: Writing – original draft, Investigation, Conceptualization. **Alvaro Etcheverry-Berrios:** Writing – original draft, Investigation, Conceptualization. **Gary S. Nichol:** Formal analysis. **Stergios Piligkos:** Conceptualization. **Euan K. Brechin:** Writing – review & editing, Supervision, Conceptualization. **Jennifer A. Garden:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

E.F. and J. A. G. thank the UKRI Future Leaders Fellowship (MR

\T042710\1), J. A. G. thanks the British Royal Society (Grant RSG\R1\180101) and A.E.B. thanks the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no. 882686 (MaSCHiP) for funding. S. P. thanks Independent Research Fund Denmark – Technology and Production (DFF-FTP) for research grant 0136-00061B DFF-Forskningsprojekt1. We thank Prof. Paul Lusby for useful discussions.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2024.117308>.

References

- [1] M.J. Stanford, A.P. Dove, *Chem. Soc. Rev.* 39 (2010) 486–494.
- [2] U. Yolsal, P.J. Shaw, P.A. Lowy, R. Chamenahalli, J.A. Garden, *ACS Catal.* 14 (2024) 1050–1074.
- [3] D.M. Lyubov, A.O. Tolpygin, A.A. Trifonov, *Coord. Chem. Rev.* 392 (2019) 83–145.
- [4] K.P. Kepp, *Inorg. Chem.* 55 (2016) 9461–9470.
- [5] S.J. Gray, K. Brown, F.Y.T. Lam, J.A. Garden, P.L. Arnold, *Organometallics* 40 (2021) 948–958.
- [6] N.Y. Rad'kova, A.V. Cherkasov, A.A. Trifonov, *Russ. J. Coord. Chem.* 49 (2023) 710–717.
- [7] R.N. Kularatne, S. Taslimy, A. Bhadrans, J.M.O. Cue, C. Bulumulla, E.L. Calubaquib, R. Gunawardhana, M.C. Biewer, M.C. Stefan, *Polym. Chem.* 14 (2023) 3962–3970.
- [8] A. Mustapha, K. Busch, M. Patykiewicz, A. Apedaile, J. Reglinski, A.R. Kennedy, T. J. Prior, *Polyhedron* 27 (2008) 868–878.
- [9] Y. Zhou, G.S. Nichol, J.A. Garden, *Eur. J. Inorg. Chem.* 2022 (2022) e202200134.
- [10] D.F. Cook, D. Cummins, E.D. McKenzie, *Dalton Trans.* (1976), <https://doi.org/10.1039/DT9760001369>, 1369–1375.
- [11] G. Brewer, C. Luckett, *Inorg. Chim. Acta* 358 (2005) 239–245.
- [12] K. Ramesh, R. Mukherjee, *Dalton Trans.* (1991), <https://doi.org/10.1039/DT9910003259>, 3259–3262.
- [13] G. Hunter, N. Kilcullen, *Dalton Trans.* (1989), <https://doi.org/10.1039/DT9890002115>, 2115–2119.
- [14] S. Chicco, G. Allodi, A. Chiesa, E. Garlatti, C.D. Buch, P. Santini, R. De Renzi, S. Piligkos, S. Carretta, *J. Am. Chem. Soc.* 146 (2024) 1053–1061.
- [15] B.E. Bode, E. Fusco, R. Nixon, C.D. Buch, H. Weihe, S. Piligkos, *J. Am. Chem. Soc.* 145 (2023) 2877–2883.
- [16] Z. Liu, F. Yin, J. Yang, X.-Q. Guo, L.-P. Zhou, C.-B. Tian, Q.-F. Sun, *Dalton Trans.* 52 (2023) 8670–8675.
- [17] C.D. Buch, K. Kundu, J.J. Marbey, J. van Tol, H. Weihe, S. Hill, S. Piligkos, *J. Am. Chem. Soc.* 144 (2022) 17597–17603.
- [18] C.D. Buch, S.H. Hansen, C.M. Tram, D. Mitcov, S. Piligkos, *Inorg. Chem.* 59 (2020) 16328–16340.
- [19] J.K. Molloy, C. Philouze, L. Fedele, D. Imbert, O. Jarjayes, F. Thomas, *Dalton Trans.* 47 (2018) 10742–10751.
- [20] E. Lucaccini, J.J. Baldoví, L. Chelazzi, A.-L. Barra, F. Grepioni, J.-P. Costes, L. Sorace, *Inorg. Chem.* 56 (2017) 4728–4738.
- [21] N. Jori, D. Toniolo, B.C. Huynh, R. Scopelliti, M. Mazzanti, *Inorg. Chem. Front.* 7 (2020) 3598–3608.
- [22] P.V. Bernhardt, B.M. Flanagan, M.J. Riley, *Aust. J. Chem.* 54 (2001) 229–232.
- [23] J.G.C. Kragoskow, J. Marbey, C.D. Buch, J. Nehr Korn, M. Ozerov, S. Piligkos, S. Hill, N.F. Chilton, *Nat. Commun.* 13 (2022) 825.
- [24] B.M. Flanagan, P.V. Bernhardt, E.R. Krausz, S.R. Lüthi, M.J. Riley, *Inorg. Chem.* 41 (2002) 5024–5033.
- [25] N. Jori, M. Falcone, R. Scopelliti, M. Mazzanti, *Organometallics* 39 (2020) 1590–1601.
- [26] E. Fazekas, P.A. Lowy, M. Abdul Rahman, A. Lykkeberg, Y. Zhou, R. Chamenahalli, J.A. Garden, *Chem. Soc. Rev.* 51 (2022) 8793–8814.
- [27] Y. Zhou, G.S. Nichol, J.A. Garden, *Eur. J. Org. Chem.* 2021 (2021) 5557–5568.
- [28] F.M. García-Valle, R. Estivill, C. Gallegos, T. Cuenca, M.E.G. Mosquera, V. Taberner, J. Cano, *Organometallics* 34 (2015) 477–487.
- [29] J. Wang, H. Sun, Y. Yao, Y. Zhang, Q. Shen, *Polyhedron* 27 (2008) 1977–1982.
- [30] H. Peng, Z. Zhang, R. Qi, Y. Yao, Y. Zhang, Q. Shen, Y. Cheng, *Inorg. Chem.* 47 (2008) 9828–9835.
- [31] K. Masatoshi, Y. Toshiro, *Chem. Lett.* 28 (1999) 137–138.
- [32] M. Kanesato, H. Houjou, Y. Nagawa, K. Hiratani, *Inorg. Chem. Commun.* 5 (2002) 984–988.
- [33] S. Mizukami, H. Houjou, M. Kanesato, K. Hiratani, *Chem. – Eur. J.* 9 (2003) 1521–1528.
- [34] M. Kanesato, K. Nagahara, K. Igarashi, K.-I. Sato, Y. Kikkawa, M. Goto, *Inorg. Chim. Acta* 367 (2011) 225–229.
- [35] D. Lionetti, M.W. Day, T. Agapie, *Chem. Sci.* 4 (2013) 785–790.
- [36] J.K. Molloy, L. Fedele, O. Jarjayes, C. Philouze, D. Imbert, F. Thomas, *Inorg. Chim. Acta* 483 (2018) 609–617.
- [37] S.A. Cotton, P.R. Raithby, A. Shield, J.M. Harrowfield, *Coord. Chem. Rev.* 455 (2022) 214366.
- [38] E. Fazekas, G.S. Nichol, J.A. Garden, M.P. Shaver, *ACS Omega* 3 (2018) 16945–16953.
- [39] W. Gruszka, A. Lykkeberg, G.S. Nichol, M.P. Shaver, A. Buchard, J.A. Garden, *Chem. Sci.* 11 (2020) 11785–11790.
- [40] J. Collins, O. Santoro, T.J. Prior, K. Chen, C. Redshaw, *J. Mol. Struct.* 1224 (2021) 129083.
- [41] Q. Yang, Y. Li, J.-D. Yang, Y. Liu, L. Zhang, S. Luo, J.-P. Cheng, *Angew. Chem. Int. Ed.* 59 (2020) 19282–19291.
- [42] M. Li, J. Hong, Z. Chen, X. Zhou, L. Zhang, *Dalton Trans.* 42 (2013) 8288–8297.
- [43] H. Sheng, F. Xu, Y. Yao, Y. Zhang, Q. Shen, *Inorg. Chem.* 46 (2007) 7722–7724.
- [44] W. Gruszka, J.A. Garden, *Nat. Commun.* 12 (2021) 3252.
- [45] M.A. Glenister, J.W.A. Frese, M.R.J. Elsegood, A.B. Canaj, E.K. Brechin, C. Redshaw, *Dalton Trans.* 53 (2024) 5351–5355.
- [46] L. Clark, M.G. Cushion, H.E. Dyer, A.D. Schwarz, R. Duchateau, P. Mountford, *Chem. Commun.* 46 (2010) 273–275.
- [47] R. Ligny, M.M. Hänninen, S.M. Guillaume, J.-F. Carpentier, *Chem. Commun.* 54 (2018) 8024–8031.
- [48] M. Mazzeo, R. Tramontano, M. Lamberti, A. Pilone, S. Milione, C. Pellicchia, *Dalton Trans.* 42 (2013) 9338–9351.
- [49] M.-T. Chen, C.-T. Chen, *Dalton Trans.* 46 (2017) 10181–10184.
- [50] S. Ghosh, A. Spannenberg, E. Mejía, *Helv. Chim. Acta* 100 (2017) e1700176.
- [51] S. Pappuru, V. Ramkumar, D. Chakraborty, *Polym. Adv. Technol.* 32 (2021) 3392–3401.
- [52] R.R. Gowda, D. Chakraborty, V. Ramkumar, *Inorg. Chem. Commun.* 14 (2011) 1777–1782.
- [53] T. Xing, C. Jiang, M.R.J. Elsegood, C. Redshaw, *Inorg. Chem.* 60 (2021) 15543–15556.
- [54] A. Arbaoui, C. Redshaw, *Polym. Chem.* 1 (2010) 801–826.