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complex supported by a [2+2] Schiff-base

Turning on ROP activity in a bimetallic Co/Zn

Homo-dinuclear Co and Zn complexes derived from the macrocycle LH₂, {[2-(OH)-5-(R)-C₆H₂-1,3-(CH)₂][CH₂CH₂(2-C₆H4N)₂]}₂ (R = Me, tBu), revealed near inactivity for the ring opening polymerization (ROP) of the cyclic esters δ -valerolactone (δ -VL) and ϵ -caprolactone (ϵ -CL). By contrast, the hetero-bimetallic complexes [LCo(NCMe)(μ -Br)ZnBr]·*n*MeCN (*n* = 3 or 3.25) were found to be efficient catalysts for the ROP of ϵ -CL and δ -VL.

The production of aliphatic polyesters has become a very topical area given their biodegradability and biocompatibility,¹ and given the current global issues with plastic pollution, this is likely to remain the case for the foreseeable future.² One viable route to such polymers is via the metal-catalyzed ring opening polymerization (ROP) of cyclic esters.³ The choice of metal catalyst is influenced by a number factors, such as price, toxicity, activity and control. Frameworks that are capable of simultaneously binding multiple metal centres continue to be of great interest in various fields of catalysis, and this stems from the possible presence of favourable cooperative effects.⁴ We have become interested in the use of Schiff-base macrocycles given that they possess multiple binding sites,⁵ and our studies have been focusing on the simplest members of this family, the so-called Robson type macrocycles, derived from the [2+2] condensation of a diamine/dianiline with a dialdehyde.⁶ In terms of catalysis (ROP of E-CL), we observed beneficial cooperative effects when alkylaluminium centres are bound in a specific way to a Schiff-base macrocycle (LH₂, Scheme 1, left) derived from the dianiline $[(CH_2CH_2)(2-C_6H_4NH_2)_2]$, whereas the presence of aluminoxane type (Al-O-Al) bonding in such a system proved detrimental.⁷ Furthermore, we noted that manganese complexes of such macrocycles were far less active with conversions for the ROP

Scheme 1 Macrocycle LH_2 (R = Me, tBu) and the Zn–Mg complex reported by Williams *et al.*

of ε -CL < 15%.⁸ It is noteworthy that the structural chemistry of this particular macrocycle is underexplored, indeed a search of the CSD revealed no hits,⁹ other than our previously mentioned chemistry.^{7,8} We have selected the metals cobalt and zinc given their relatively low cost and biocompatibility. Further, we note that the use of Zn complexes for the ROP of ε -CL is well established,³ whilst reports on ROP using Co species is scant.¹⁰

Recent work by Williams et al. has shown how the use of hetero-dinuclear complexes can result in enhanced catalytic performance.^{11a} In particular, it was reported that an *in situ* generated catalyst comprising the hetero-dinuclear Zn-Mg complex bearing a diphenolate tetraamine macrocycle (Scheme 1, right) used in conjunction with its homo-dinuclear Zn-Zn and Mg-Mg counterparts performed better for the copolymerization of CO2 with epoxides than did the homo-dinuclear complexes alone. Given the very similar solubility properties of the three species, it was not possible to crystallize selectively the Mg-Zn hetero-dinuclear complex. However, subsequent studies by the same group have shown that it is possible to access such species via mono-metalation, followed by the addition of the second metal,^{11b} and the molecular structures of a number of mixed-metal species were reported.^{11c-e} Interestingly, Williams et al. also observed that for ROP of E-CL and r-LA, a mixed Ti/Zn system displayed moderate/high activity whilst the mono-Ti system was inactive.^{11c} We also note that cooperative effects have also been observed for a homodinuclear zinc complex in lactide polymerization.12

Given this, we have re-focused our efforts on the [2+2] Schiffbase systems and have extended our studies in an attempt to

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[†] Electronic supplementary information (ESI) available: Full experimental details for complex synthesis and ROP studies. CCDC 1829365–1829367 (**1tBu**·0.5MeCN, **2tBu**·4.5MeCN, and **5tBu**·3.25MeCN), 1849421 (**4tBu**·0.25MeCN) and 1921189– 1921192. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9cc04494a



access mixed-metal systems. Herein, we report that homodinuclear cobalt and zinc complexes bearing the macrocycle L (1-3, Scheme 2) are readily accessible. Furthermore, on reacting 1 with Br₂Zn a complex 4 related to 1 was formed differing only in the composition (partial occupancy Co:Zn = 68:32) of the anion, whereas with Et₂Zn, it proved possible to isolate and structurally characterize the mixed-metal Co-Zn complexes 5 (Scheme 2 right). Interestingly, the homo-dinuclear species 1 and 3 (R = Me and tBu) were inactive when screened for the ROP of ε -CL (and virtually inactive for ε -VL), whereas the mixed-metal complexes 5Me and 5tBu were efficient catalysts when screened under the same conditions (130 °C, 24 h). We note that poly(εcaprolactone), PCL and PVL are favoured polymers given both their biodegradability, and are considered as potential environmentally friendly commodity plastics.¹³ Beyond ROP, Co-Zn species are of interest in gas sensors, semiconductors, dyes and pigments, as well as in other catalytic processes.¹⁴

Reaction of the [2+2] Schiff-base macrocycle {[2-(OH)-5-(R)- $C_6H_2-1,3-(CH)_2$ [CH₂CH₂(2-C₆H₄N)₂]₂ (R = Me, tBu) with 2.1 equivalents of CoBr2 afforded, following work-up, green prisms on recrystallization from a saturated solution of acetonitrile at 0 °C in about 70% yield. The molecular structure of 1tBu 0.5MeCN is shown in Fig. 1, with selected bond lengths and angles given in the caption; for 1Me 4MeCN see ESI,† Fig. S1. The complex is a salt of formula [CoBrL^{tBu}][CoBr₃(NCMe)]·0.5MeCN (1tBu·0.5MeCN). In the cation, the cobalt centre is five-coordinate with a trigonal bipyramidal geometry; the apical sites are occupied by O atoms of phenolates, with the bromide and two N atoms in the equatorial sites. Concentration of the mother-liquor afforded more of 1tBu-0.5MeCN plus small amounts of an orange/red product, identified as [CoBrL^{tBu}]₂[CoBr₃(NCMe)][Br]·4.5MeCN (2tBu 4.5MeCN), the structure of which is similar to that observed for 1tBu 0.5MeCN, differing mainly in the composition of the anions, namely Br⁻ and CoBr₃(NCMe)⁻; the molecular structure is shown in Fig. S2 (ESI[†]). Similar interaction of LH₂ with 2.1 equivalents of ZnBr₂ afforded, following work-up, yellow prisms of [ZnL^{tBu}Br][ZnBr₃(NCMe)]·MeCN (3tBu·MeCN) in good yield. Use of excess $ZnBr_2$ (>4 equivalents) also afforded 3tBu MeCN as the only crystalline product. Again, the structure (ESI,† Fig. S4) is very reminiscent of 1tBu 0.5MeCN, with the



Fig. 1 Molecular structure of $1tBu\-$ 0.5MeCN. Solvent omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Co(1)-Br(1) 2.4847(6), Co(1)-O(1) 2.004(2), Co(1)-O(2) 2.043(2), Co(1)-N(1) 2.088(3), Co(1)-N(3) 2.105(3); O(1)-Co(1)-O(2) 178.52(9), N(1)-Co(1)-N(3) 108.77(11), O(1)-Co(1)-Br(1) 92.98(7), N(3)-Co(1)-Br(1) 128.17(8), N(1)-Co(1)-Br(1) 122.54(8), N(1)-Co(1)-N(3) 108.77(11).

zinc adopting a trigonal bipyramidal geometry in the cation; for the structure of 3Me MeCN, see Fig. S3 (ESI⁺). Having isolated and characterized these homo-dinuclear products, we then targeted the formation of a mixed-metal system. Complex 1tBu was reacted with ZnBr₂ to afford a yellow product, however the structure, namely [CoBrL^{fBu}][Co_{0.68}Zn_{0.32}Br₃(NCMe)]·0.25MeCN (4tBu 0.25MeCN), turned out to be very similar to 1 differing only in the composition of the anion, the latter having cobalt:zinc occupancy 68.4:32.6(17) (ESI,† Fig. S5). We note that the structures of both 3Me/tBu and 4tBu are analogous to the equivalent manganese complex (see CUVYID in CCDC).7c Given this disappointing result, both 1Me and 1tBu were treated with Et₂Zn (one equivalent) and on work-up (acetonitrile), brown/red products were isolated in good yield. Single crystals were grown from acetonitrile on prolonged standing (3 days) at ambient temperature. The molecular structure of 5tBu-3.25MeCN is shown in Fig. 2, with bond lengths/angles given in the caption; for 5Me-3MeCN see Fig. S6, ESI.† In 5tBu-3.25MeCN, the macrocycle binds two metals (Co and Zn) in an ordered way. The Co²⁺ is bound in distorted octahedral geometry by two *cis* phenolates and two cis imines of the macrocycle, a rather distant bromide (Co(1)-Br(1) 2.9383(5) Å), and a single



Fig. 2 The molecular structure of **5tBu**-3.25MeCN. Solvent omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Co(1)–O(1) 2.133(2), Co(1)–O(2) 1.947(2), Co(1)–N(3) 2.058(2), Co(1)–N(4) 2.126(2), Co(1)–N(5) 2.108(3), Zn(1)–Br(1) 2.3873(4), Zn(1)–Br(2) 2.3412(5), Zn(1)–O(1) 1.9792(19), Zn(1)–N(1) 2.015(3); Co(1)–O(1)–Zn(1) 103.93(8), N(3)–Co(1)–N(4) 107.92(9), O(2)–Co(1)–N(3)90.50(9), O(2)–Co(1)–N(5) 167.52(9), O(1)–Zn(1)–N(1) 93.30(9), Br(1)–Zn(1)–Br(2) 113.655(18).

molecule of acetonitrile. The Zn ion is in close proximity to the Co ion: the bromide and one of the phenolates each coordinate to the Zn. The tetrahedral coordination about the Zn is completed by an imine and a mono-dentate bromide. One might describe the octahedron of Co(1) and the tetrahedron around Zn(1) as sharing a common edge (O(1) and Br(1)). The two metals are separated at a distance 3.2399(5) Å. The magnetic moments of 5 (R = Me, *t*Bu) are in the range 5.1–5.3 $\mu_{\rm B}$



Fig. 3 Plot of ln[VL]₀/[VL]_t vs. time and ln[CL]₀/[CL]_t vs. time using complex **1tBu**, **3tBu** and **5tBu** ([monomer] : [Cat] : [BnOH] = 500 : 1 : 1); 130 °C.

Fable 1	ROP of δ-VL	using	complexes	1-5
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consistent with high spin Co(II) complexes,¹⁵ whilst the ¹H NMR spectra are broad and spread over a large window (+140 to -40 ppm). The cobalt and zinc complexes 1, 3 and 5 (R = Me, tBu) have been screened for their ability to ring open polymerize δ-VL and ε-CL; runs were conducted in the presence of benzyl alcohol (BnOH). For complexes 1 and 3, a variety of conditions were used in the attempted ROP of δ -VL including temperatures in the range 40 to 130 °C, differing ratios of $[\delta$ -VL]: [Cat]: [BnOH] and over different times, however on each occasion there was no sign of polymer upon work-up. However, for the mixed-metal system 5, activity was observed when the temperature reached 130 °C, in the presence of one equivalent of BnOH (at this temperature, no activity was observed for 1 and 3 - see Fig. 3 for the relative rates of the tBu derivatives). Data for runs is given in Table 1 (see also Fig. S19-S24, ESI[†]) and reveals that 5tBu out-performs 5Me, which is thought to be due to the increased solubility of the former in the reaction solvent. In these mixed-metal systems, the Co to Zn distance may favour coordination of a monomer to both metal centres, and then as in the ROP of propylene oxide,¹⁶ one metal acts a as Lewis acid with the other using its M-OR function to attack the carbonyl group. Highest conversions were achieved with ratios between 100:1:1 and 500:1:1 at 130 °C, with all the runs showing good control with PDIs in range 1.15-1.30; above and below this temperature only trace polymer was observed. Use of either 12 h (run 6) or no solvent (i.e. a melt, run 7) was less controlled. Analysis of the polymer indicated the presence of benzyloxy and hydroxyl end groups (Fig. S22, ESI[†]). There was evidence of transesterification and all observed $M_{\rm n}$ values were significantly lower than the calculated values (see Fig. S21, ESI[†]). In the case of ɛ-CL, the situation was more pronounced with no conversion evident by ¹H NMR spectroscopy for catalyst systems 1 and 3. By contrast, systems using 5Me and 5tBu were efficient catalysts at 130 °C over 24 h, with similar conversion results observed using the ratios between 50:1:1 and 500:1:1; above and below this temperature only trace polymer was observed. As for the δ -VL runs, good control was observed, except for when using either 12 h or a melt. From a kinetic study, it was observed that the polymerization rate exhibited near first order dependence of the CL concentration at 130 °C. The rate of polymerization for ε -CL ($K_{obs} = 2.12 \times 10^{-3} (h^{-1})$ for 5*t*Bu) was less than half that for δ -VL ($K_{obs} = 6.10 \times 10^{-3} (h^{-1})$ for 5*t*Bu),

	5						
Cat.	[δ-VL]:[Cat]:[BnOH]	T (°C)	<i>t</i> (h)	$\operatorname{Conv.}^{a}(\%)$	$M_{ m n} imes 10^{3b}$	$M_{ m nCalcd} imes 10^{4c}$	PDI^d
5 <i>t</i> Bu	50:1:1	130	24	88.7	1.35	0.45	1.16
5 <i>t</i> Bu	100:1:1	130	24	92.8	2.14	0.93	1.15
5 <i>t</i> Bu	250:1:1	130	24	98.7	5.19	2.46	1.22
5 <i>t</i> Bu	500:1:1	130	24	99.4	6.89	4.97	1.23
5 <i>t</i> Bu	1000:1:1	130	24	77.9	5.33	7.79	1.43
5 <i>t</i> Bu	500:1:1	130	12	92.7	0.45	4.64	1.53
5 <i>t</i> Bu	500:1:1 (melt)	130	24	96.2	7.11	4.82	1.79
5 <i>t</i> Bu	500:1:1	70	24	76.1	0.76	3.80	1.19
5Me	250:1:1	130	24	97.0	2.68	2.43	1.30
5Me	500:1:1	130	24	91.4	3.35	4.57	1.15
1 <i>t</i> Bu	500:1:1	130	24	38.8	0.45	1.94	1.42
3 <i>t</i> Bu	500:1:1	130	24	4.4	_	0.22	_
	Cat. 5tBu 5tBu 5tBu 5tBu 5tBu 5tBu 5tBu 5tBu	Cat. [δ-VL]:[Cat]:[BnOH] 5tBu 50:1:1 5tBu 100:1:1 5tBu 250:1:1 5tBu 500:1:1 5tBu 500:1:1	Cat. [δ-VL]:[Cat]:[BnOH] T (°C) 5tBu 50:1:1 130 5tBu 100:1:1 130 5tBu 250:1:1 130 5tBu 500:1:1 130	Cat. [δ-VL]:[Cat]:[BnOH] T (°C) t (h) 5tBu 50:1:1 130 24 5tBu 100:1:1 130 24 5tBu 250:1:1 130 24 5tBu 500:1:1 130 24 5Me 250:1:1 130 24 5Me 500:1:1 130 24 5Me 500:1:1 130 24 5Mu 500:1:1 130 24 5Mu 500:1:1 130 24 5Mu 500:1:1 130 24	Cat. [δ-VL]:[Cat]:[BnOH] T (°C) t (h) Conv. ^a (%) 5tBu 50:1:1 130 24 88.7 5tBu 100:1:1 130 24 98.7 5tBu 250:1:1 130 24 98.7 5tBu 500:1:1 130 24 99.4 5tBu 500:1:1 130 24 92.7 5tBu 500:1:1 130 24 96.2 5tBu 500:1:1 130 24 97.0 5tBu 500:1:1 130 24 97.0 5tBu 500:1:1 130 24 91.4 1tBu 500:1:1 130 24 38.8 3tBu 500:1:1 130 24 4.4	Cat.[δ -VL]:[Cat]:[BnOH] T (°C) t (h)Conv. ^a (%) $M_n \times 10^{3b}$ 5tBu50:1:11302488.71.355tBu100:1:11302492.82.145tBu250:1:11302498.75.195tBu500:1:11302499.46.895tBu500:1:11302492.70.455tBu500:1:11301292.70.455tBu500:1:11302496.27.115tBu500:1:11302497.02.685Me250:1:11302491.43.355tBu500:1:11302491.43.355tBu500:1:11302491.43.455Me500:1:11302491.43.455tBu500:1:11302491.43.455tBu500:1:11302491.43.455tBu500:1:11302491.43.455tBu500:1:11302491.43.455tBu500:1:11302491.43.455tBu500:1:11302491.43.455tBu500:1:11302494.4	Cat.[δ -VL]:[Cat]:[BnOH] T (°C) t (h)Conv. ^a (%) $M_n \times 10^{3b}$ $M_{nCaled} \times 10^{4c}$ 5tBu50:1:11302488.71.350.455tBu100:1:11302492.82.140.935tBu500:1:11302498.75.192.465tBu500:1:11302499.46.894.975tBu500:1:11302492.70.454.645tBu500:1:11302496.27.114.825tBu500:1:11302497.02.682.435tBu500:1:11302491.43.354.575tBu500:1:11302491.43.354.575tBu500:1:11302491.43.251.945tBu500:1:11302491.43.251.945tBu500:1:11302491.43.251.945tBu500:1:11302491.43.251.945tBu500:1:11302491.43.251.945tBu500:1:11302491.43.251.945tBu500:1:11302491.43.251.945tBu500:1:11302491.43.251.945tBu500:1:11302491.43.251.945tBu500:1:1130244.4

^{*a*} By ¹H NMR spectroscopic analysis. ^{*b*} M_n values were determined by GPC in THF νs . PS standards and were corrected with a Mark–Houwink factors (0.58 for poly(δ -VL)). ^{*c*} (F.W.[M]/[BnOH])(conversion). ^{*d*} Polydispersity index (M_w/M_n) were determined by GPC.

Table 2 ROP of ε-CL using complexes 1-5

Run	Cat.	[ɛ-CL]:[Cat]: BnOH	$T(^{\circ}C)$	<i>t</i> (h)	Conv. ^{<i>a</i>} (%)	$M_{ m n} imes$ 10 ^{3 b}	$M_{ m nCalcd} imes 10^{4c}$	PDI ^d
1	5tBu	50:1:1	130	24	99.3	1.14	0.57	1.14
2	5 <i>t</i> Bu	100:1:1	130	24	99.6	2.65	1.01	1.13
3	5 <i>t</i> Bu	250:1:1	130	24	99.6	4.10	2.86	1.13
4	5 <i>t</i> Bu	500:1:1	130	24	99.8	6.56	5.05	1.34
5	5tBu	1000:1:1	130	24	88.7	3.61	8.87	1.12
6	5tBu	500:1:1	130	12	48.0	2.28	2.74	1.80
7	5tBu	500:1:2	130	24	71.5	3.48	1.78	1.15
8	5tBu	500:1:1 (melt)	130	24	98.2	7.87	4.98	1.66
9	5tBu	500:1:1	70	24	72.7	_	3.63	_
10	5Me	250:1:1	130	36	97.6	4.83	2.44	1.34
11	5Me	500:1:1	130	36	99.2	5.16	4.96	1.96
12	1 <i>t</i> Bu	500:1:1	130	24	_			_
13	1Me	500:1:1	130	24	—	—	_	—

^{*a*} By ¹H NMR spectroscopic analysis. ^{*b*} M_n values were determined by GPC in THF *vs.* PS standards and were corrected with a Mark–Houwink factors (0.56 for poly(ε -CL)). ^{*c*} (F.W.[M]/[BnOH])(conversion). ^{*d*} Polydispersity index (M_w/M_n) were determined by GPC.

which is consistent with other reports.¹⁷ The observed molecular weights were lower than the calculated values, suggesting the presence of a chain transfer agent (H₂O or BnOH). This was also evident in the MALDI-TOF mass spectra, were a number of families of peaks were observed separated by 114 mass units (Fig. S26 and S27, ESI†); the highest were typically about 7000. For example, in the case of *5t*Bu (run 4, Table 2), peaks in the spectrum can be assigned to 4926, 5039, and 5154 using the formula C₆H₆–CH₂O[O(CH₂)₄-CO]_nOH for n = 42, 43 and 44 respectively. The ¹H NMR spectra of the PCL (*e.g.* Fig. S28, ESI†) revealed the presence of benzyloxy and OH end groups. It also proved possible to ROP *r*-LA using the mixed-metal systems, albeit in much poorer yields. Moreover, co-polymerization of ϵ -VL and ϵ -CL was possible as was ϵ -CL with *r*-LA (see Table S1 and Fig. S33–S43, ESI† for preliminary results).

In conclusion, we have isolated and structurally characterized homo-dinuclear cobalt and zinc complexes as well as rare examples of mixed-metal (Co/Zn) complexes of a [2+2] macrocyclic Schiff-base. Screening of these complexes for the ROP of the cyclic esters δ -valerolactone (δ -VL) and ϵ -caprolactone (ϵ -CL) revealed that whilst the homo-dinuclear complexes are either virtually inactive (δ -VL) or inactive (ϵ -CL), the mixed-metal systems are efficient catalysts at 130 °C, suggestive that the metals are able to 'turn each other on'.

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Conflicts of interest

There are no conflicts to declare.

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