Coordination chemistry of [2 + 2] Schiff-base macrocycles derived from the dianilines 
[(2-NH₂C₆H₄)₂X] (X = CH₂CH₂, O): structural studies and ROP capability towards cyclic esters†

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Reaction of the [2 + 2] Schiff-base macrocycles ([(2-(OH)-5-(R)-C₆H₄-1,3-(CH)₂]₂[CH₂CH₂(2-C₆H₄N)₂]₆)₆ (R = Me, L₁H₂; tBu, L₂H₂) with FeBr₃ afforded the complexes [FeBr(L₁H₂)]₂[FeBr₃]₂O·2MeCN (1·2MeCN), [FeBr(L₂H₂)][X] (X = 0.5(FeBr₃)₂O, 2·0.5MeCN, X = Br, 3·5.5MeCN), respectively. Reaction of L₃H₃ with [KFe(OTBu)₃(THF)] (formed in situ from FeBr₂ and KOTBu), following work-up, led to the isolation of the complex [Fe(L₅)₂O·3MeCN (4·3MeCN), whilst with [CuBr₂] affording [CuBr(L₂H₂)][CuBr₂]·2MeCN (5·2MeCN). Attempts to form mixed Co/Ti species by reaction of [CoBr₂]Br[CoBr₃(NCMe)] with TiCl₄ resulted in [L₅H₄]Br[CoBr₃]·2MeCN (6·2MeCN). Use of the related oxy-bridged Schiff-base macrocycles ([(2-(OH)-5-(R)-C₆H₄-1,3-(CH)₂]₂O(2-C₆H₄N)₂]₆ (R = Me, L₁H₂; tBu, L₂H₂) with CoBr₂ led to the isolation of the complexes [(CoBr₂)L₃H₂]·2C₃H₆O (7·2C₃H₆O), [Co(NCMe)₂(L₂H₂)][CoBr₃]·5MeCN (8·5MeCN), [Co(NCMe)₃][CoBr₃(MeCN)]·2MeCN (9·2MeCN). For comparative structural/polymerisation studies, the complexes [CoBr(NCMe)₂L₅H₂]·2MeCN (10·2MeCN) and [Co(NCMe)₂L₅H₆][CoBr₃(MeCN)]·2MeCN (11·2MeCN) where L₅H = 2,6-(CHO)₂-4-R-C₆H₄OH, as well as the chelate-free salt [Fe(NCMe)₂][FeBr₂OFeBr₃] (13) have been isolated and structurally characterized. The ability of these complexes to act as catalysts for the ring opening polymerisation (ROP) of ε-caprolactone (ε-CL) and δ-valerolactone (δ-VL) was investigated, as well as co-polymerisation of ε-CL with rac-lactide (r-LA) and vice versa.

Introduction

Global issues over plastic pollution continue to drive the search for alternative, more environmentally-friendly materials.1 As part of our search for new catalysts capable of affording biodegradable polymers via the ring opening polymerisation (ROP) of cyclic esters, we have initiated investigations into the coordination chemistry of Schiff-base macrocycles derived from the [2 + 2] condensation of the dianilines [(X)(2-C₆H₄NH₂)₂] (X = CH₂CH₂, O) with the diformylphenols 2,6-(CHO)₂-4-R-C₆H₄OH (R = Me, tBu) (Chart 1).2 To date, we have reported how remote alkylaluminium centres bound to the macrocycle (X = CH₂CH₂) exhibited beneficial cooperative effects in the ROP of ε-caprolactone (ε-CL), whereas aluminox-ane type (Al–O–Al) bonding proved to be detrimental.3 Manganese complexes bearing these macrocycles were far less active (conversions <15%).4 However, studies of mixed cobalt/zinc systems revealed interesting catalytic properties, with homo-binuclear systems exhibiting inactivity while mixed-metal systems proved to be efficient for the ROP of ε-CL and δ-valerolactone (δ-VL).5 It is also noteworthy that the structural chemistry of macrocycles of this type remains underexplored; a

Chart 1 Synthesis of ligands L₅H₄-L₅H prepared herein.
search of the CSD revealed no hits, other than our reported aluminium, manganese and cobalt systems. Given this, we have re-focused our efforts on such Schiff-base systems and have extended our studies to iron, cobalt and copper complexes bearing [2 + 2] macrocycles derived from the dianilines [(X)(2-C₆H₄NH₂)₂] (X = CH₂CH₂, O, Chart 2). Herein, we report the molecular structures of these complexes, and have screened a number of them for their capability in the ROP of ε-CL, δ-VL and rac-lactide (r-LA), and for the co-polymerisation of ε-CL with r-LA and vice versa. Poly(ε-caprolactone), PCL, and poly(lactide), PLA, are favoured polymers given their biodegradability properties, and their co-polymers are considered as potential environmentally-friendly commodity plastic.

Results and discussion

-CH₂CH₂– bridged systems

Iron

Use R = Me L₁H₂. Iron is a cheap, earth abundant metal and its complexes have shown potential in the ROP of cyclic esters. Given this, we have initiated studies on the iron chemistry of our [2 + 2] macrocyclic systems. The reaction of the macrocycle [{2-(OH)-5-Me-C₆H₂-1,3-(CH)₂}CH₂CH₂{2-C₆H₄N}₂]₂ (L₁H₂) with two equivalents of FeBr₂ in refluxing toluene afforded, following work-up (MeCN), a brown crystalline solid in moderate yield. Single crystals were grown from a saturated solution of acetonitrile on standing at ambient

![Chart 2](https://example.com/chart2.png)

Chart 2 Structures of iron and cobalt complexes 1–13 prepared herein.
temperature for 3 days. The molecular structure is shown in Fig. 1, with selected bond lengths and angles given in the caption. There are two macrocyclic iron complexes in the asymmetric unit, related by a pseudosymmetric translation of c/2 (see ESI†), plus an anion of $[{\text{Br}}_{3}{\text{FeOFeBr}}_{3}]^{-}$ and two molecules of acetonitrile. Of the macrocyclic bound iron centres, both Fe1 and Fe2 adopt a distorted trigonal bipyramidal geometry ($\tau = 0.69$),

9 bound by a bromide and two nitrogen atoms and two oxygen atoms of the macrocyclic, apical sites are occupied by O atoms, with the bromide and N atoms in the equatorial sites. The composition is thus $[{\text{FeBr}}_{2}{\text{L}}_{2}{\text{H}}_{2}]_{2} [{\text{Br}}_{3}{\text{FeOFeBr}}_{3}]^{-} · 2{\text{MeCN}}$ (1-2MeCN). In terms of charge, the $2^+ \text{ available from the anion which contains two }$ Fe3+ centres, is balanced by the two cations ($2x + 1$), each of which contains an Fe(n) centre.

Use of $[\text{KFe(OtBu)}_{3}(\text{THF})]$. Given alkoxide species play a central role in metal-catalysed ROP, we attempted to generate an iron alkoxide species. Reaction of $L^2H_2$ with in situ generated $[\text{KFe(OtBu)}_3(\text{THF})]$ in refluxing toluene resulted, after work-up, red needles in good yield. Crystals suitable for X-ray diffraction were grown from a saturated solution of acetonitrile at ambient temperature. A view of the molecular structure is shown in Fig. 2, and bond lengths and angles are given in the caption. The crystal comprises FeBr3 cations, (FeBr3)O anions and MeCN solvent molecules. The anions lie about a centre of symmetry and the solvent molecule sites refine best with half-occupancy; the bromide ligands is disordered over two sites, in an 82 : 18 occupancy ratio. The nearest neighbours of the bromide atoms are atoms of the disordered r-butyl group.

Similar treatment of $[[2-(\text{OH})-5-(\text{tBu})-\text{C}_6\text{H}_2-1,3-(\text{CH}_3)]]_2 \text{O}_2$ with 2.1 equivalents of FeBr3 afforded, following work-up, red needles in good yield. Crystals suitable for X-ray diffraction were grown from a saturated solution of acetonitrile at ambient temperature. A view of the molecular structure is shown in Fig. 2, and bond lengths and angles are given in the caption. The crystal comprises FeBr3 cations, (FeBr3)O anions and MeCN solvent molecules. The anions lie about a centre of symmetry and the solvent molecule sites refine best with half-occupancy; the molecular formula is therefore $[\text{FeBr}(L^2H_2)]_2 0.5[\text{FeBr}_3]_2 \text{O}^{-} 0.5(\text{MeCN})$ (2.05MeCN), and like 1-2MeCN, is a mixed oxidation state Fe(n)/Fe(u) system. The iron atom in the cation is five-coordinate with a trigonal bipyramidal pattern ($\tau = 0.82$),

9 the apical sites are occupied by O atoms, with the bromide and N atoms in the equatorial sites. There is a pseudo-two-fold symmetry axis along the Fe–Br bond. In the macrocyclic ligand, there are four N atoms, each involved in a double bond, viz. C11=N2 1.298(5) C52=N1 1.287(6) C26=N3 1.296(6) C37=N4 1.308 (7), N1 and N3 are coordinated to the Fe atom, while N2 and N4 are bonded to two C atoms (one with a double bond) and a hydrogen atom. The hydrogen atoms were included in the structure factor calculations in a planar, trigonal fashion, and their $U_{iso}$ values were refined freely and satisfactorily; it is believed that both these groups are charged C=NH=C groups. Both these hydrogen atoms are involved in intramolecular hydrogen bonds.

The $[\text{FeBr}_3]_2 \text{O}$ anion lies about a centre of symmetry. One of the bromide ligands is disordered over two sites, in an 82 : 18 occupancy ratio. The nearest neighbours of the bromide atoms are atoms of the disordered r-butyl group.

Similar treatment of $[[2-(\text{OH})-5-(\text{tBu})-\text{C}_6\text{H}_2-1,3-(\text{CH}_3)]]_2 \text{O}_2$ with 1.1 equivalents, led to the isolation of the Fe(n) salt $[\text{FeBr}(L^2H_2)]_2 \text{Br}3\text{MeCN}$ (5.5MeCN). The molecular structure is provided in the ESI (Fig. S2†).
The molecular structure of the salt 6 comprises a protonated macrocycle \( \text{L}^3 \text{H}_2 \) and the Co(n) containing anion \([\text{CoBr}_4]^{2-}\); see ESI (Fig. S4†) for details.

**–O– bridged systems**

We have also initiated a programme to investigate the coordination chemistry of the oxy-bridged macrocycles \([2-(\text{OH})-5-(\text{R}):(\text{C}_6\text{H}_2-1,3-(\text{CH})_2)[\text{O}(2\text{-C}_6\text{H}_4\text{N})_2]]_2 \text{ (R = Me L}^3 \text{H}_2, \text{ tBu L}^4 \text{H}_2)\). Reaction of \( \text{L}^4 \text{H}_2 \) with two equivalents of CoBr2 afforded, following work-up (acetone), the complex \([\text{CoBr}_2]_2\text{C}_6\text{H}_6 \text{O} (7\text{-2C}_6\text{H}_4\text{O})\), containing two Co(n) centres, as black crystals in ca. 40% isolated yield. Single crystals can be grown from a saturated solution of acetone at ambient temperature, and the molecular structure is shown in Fig. 5; selected bond lengths and angles are given in the caption. Both cobalt centres adopt distorted trigonal bipyramidal with a bromide at each apex (\( \tau = 0.59 \) and 0.53 for Co1 and Co2, respectively).9

In the case of \( \text{L}^3 \text{H}_2 \) reaction with CoBr2 afforded, following work-up (MeCN), two sets of crystals (ca 90:10). Both sets were subjected to single crystal X-ray diffraction, and the major product, as shown in Fig. 6, was found to be the Co(n) containing salt \([\text{Co(NCMe)}_2(\text{L}^3 \text{H}_2)][\text{CoBr}_4]·5\text{MeCN} (8\text{-5MeCN})\). In the cation, the cobalt centre is distorted octahedral, and is bound by two phenoxide oxygens and the two nitrogens N(1) and N(3) of the macrocycle plus two bound acetonitrile ligands. In the solid-state, there are C–H⋯Br interactions present. The minor product was found to be Co(n) containing salt \([\text{Co}
(NCMe)₆[CoBr₃NCMe]₂·2MeCN (9·2MeCN), details of this structure can be found in the ESI (Fig. S4†).

'Dialdehyde' systems

To probe the role played by the presence of the macrocycle during catalysis (see ROP section), we have also prepared cobalt complexes bearing chelate ligands derived from the 4-tert-butyl-2,6-diformylphenol 2,6-(CHO)₂-4-Bu-C₆H₄OH (L²H). Reaction of L²H with CoBr₂ in the presence of excess Et₃N afforded, after work-up (MeCN), the Co(n) complex [[CoBr(NCMe)₂L₅]₂·2MeCN (10·2MeCN) as orange/brown prisms in good yield. The molecular structure is shown in Fig. 7, with selected bond lengths and angles given in the caption. Each cobalt centre is distorted octahedral, and are bound by oxygens from two L ligands, a bromide and an MeCN ligand. The ligand arrangement is such that one bromide and an MeCN ligand reside above the Co₂O₆ plane and one bromide and an NCMe ligand are below this plane.

If the same reaction is conducted with FeBr₂ in the presence of Et₃N, then, following work-up (MeCN), green prisms are isolated in good yield. The molecular structure (Fig. S5†) revealed the structure of the Fe(n) complex to be [FeBr(NCMe)₆]L²₃·2MeCN (12·2MeCN). Each iron centre in the cation is distorted octahedral, bound by oxygens from two L ligands, a bromide and an acetonitrile ligand.

Finally, for comparative catalytic studies, the salt [Fe(NCMe)₆]_2[FeBr₃(OFeBr)₃] (13) was prepared from L¹H₂ and FeBr₃.

Ring opening polymerisation (ROP) of ε-CL and δ-VL

The Fe, Cu and Co complexes 1, 2, 4, 5, 9–13 have been screened for their ability to ring open polymerise ε-caprolactone (ε-CL) and δ-valerolactone (δ-VL); runs were conducted in the presence of benzyl alcohol (BnOH). For complexes 1, 2 and 4, a variety of conditions were used in the attempted ROP of ε-
CL including differing ratios of [ε-CL]:[Cat]:[BnOH] and run times, and it was found that the Fe compounds were far more active than the other metal complexes screened herein. ROP systems based on Fe, Cu and Co have been reported with mixed success.

The polymerisation data for the ε-CL runs is given in Table 1. Highest conversion was achieved using 2 in run 5 using the ratio 500:1:1 at 130 °C over 24 h, albeit with less control than observed in run 6 using 250:1:1. Systems employing 1 and 4 were also less controlled, whilst the non-macrocyclic cobalt systems 9–11 proved to be inactive under the conditions employed herein. Interestingly, the non-macrocyclic iron complexes 12 and 13 proved to be poorly active with low conversions for ε-CL. However, for δ-VL, a 32% conversion (affording small molecular weight oligomers) was observed for 13, whereas 12 was inactive. The MALDI-TOF spectra can be interpreted using the formula C₆H₆–CH₂O[O(CH₂)₅CO]–VL, a 32% conversion of ε-CL or δ-CL or δ-VL concentration at 130 °C, and PDI were determined by GPC.

Table 1 Synthesis of polycaprolactone using catalysts 1, 2, 4, 9–13

| Run | Cat. | [Monomer]:[Cat]:BnOH | T (°C) | t/h | Conv. (%) | Mₙ × 10³ | Mₛ/ₙ × 10⁴ | PDI |
|-----|------|----------------------|--------|-----|-----------|----------|-------------|-----|
| 1   | 1    | 500:1:1              | 130    | 24  | 63.2      | 3.70     | 3.61        | 1.95|
| 2   | 1    | 250:1:1              | 130    | 24  | 88.7      | 2.95     | 2.54        | 3.28|
| 3   | 1    | 500:1:1              | 130    | 12  | 79.4      | 0.97     | 4.53        | 1.11|
| 4   | 1    | 500:1:1              | 130    | 12  | 66.3      | 0.70     | 3.79        | 1.17|
| 5   | 2    | 500:1:1              | 130    | 24  | 99.3      | 5.92     | 5.66        | 1.56|
| 6   | 2    | 250:1:1              | 130    | 24  | 55.0      | 2.60     | 1.58        | 1.06|
| 7   | 4    | 500:1:1              | 130    | 24  | 68.9      | 8.67     | 3.94        | 1.75|
| 8   | 4    | 250:1:1              | 130    | 24  | 87.6      | 7.52     | 2.50        | 1.58|
| 9   | 9    | 500:1:1              | 130    | 24  | —         | —        | —           | —   |
| 10  | 10   | 500:1:1              | 130    | 24  | —         | —        | —           | —   |
| 11  | 12   | 500:1:1              | 130    | 24  | 8.4       | —        | 0.45        | —   |
| 12  | 12   | 500:1:1              | 130    | 24  | 15.3      | —        | 0.87        | —   |

Conversion was confirmed by ¹H NMR spectroscopy. * Determined by GPC analysis calibrated with polystyrene standards and multiplied by correction factor of 0.58. © W. F.W. ([M]/[BnOH])(conversion) + BnOH. Polydispersity index (Mₛ/Mₙ) were determined by GPC.

Table 2 ROP of δ-VL using complexes 1, 2, 4, 5, 9–13

| Run | Cat. | [VL]:[Cat]:BnOH | T (°C) | t/h | Conv. (%) | Mₙ × 10³ | Mₛ/ₙ × 10⁴ | PDI |
|-----|------|------------------|--------|-----|-----------|----------|-------------|-----|
| 1   | 1    | 500:1:1          | 130    | 24  | 98.6      | 2.52     | 4.94        | 1.14|
| 2   | 1    | 250:1:1          | 130    | 24  | 94.3      | 3.10     | 2.36        | 1.28|
| 3   | 1    | 500:1:1          | 130    | 12  | 39.7      | 2.00     | —           | —   |
| 4   | 2    | 500:1:1          | 130    | 24  | 96.1      | 6.00     | 4.92        | 1.38|
| 5   | 2    | 250:1:1          | 130    | 24  | 93.2      | 4.53     | 2.41        | 1.23|
| 6   | 2    | 500:1:1          | 130    | 12  | 83.8      | —        | 4.20        | —   |
| 7   | 4    | 500:1:1          | 130    | 24  | 34.5      | 2.59     | 1.84        | 1.25|
| 8   | 4    | 250:1:1          | 130    | 24  | 23.5      | 2.51     | 0.60        | 1.27|
| 9   | 5    | 500:1:1          | 130    | 24  | —         | —        | —           | —   |
| 10  | 9    | 500:1:1          | 130    | 24  | —         | —        | —           | —   |
| 11  | 10   | 500:1:1          | 130    | 24  | —         | —        | —           | —   |
| 12  | 11   | 500:1:1          | 130    | 24  | —         | —        | —           | —   |
| 13  | 12   | 500:1:1          | 130    | 24  | —         | —        | —           | —   |
| 14  | 13   | 500:1:1          | 130    | 24  | 32.0      | 0.76     | 2.18        | 1.26|

Conversion was confirmed by ¹H NMR spectroscopy. * Determined by GPC analysis calibrated with polystyrene standards and multiplied by correction factor of 0.58. © W. F.W. ([M]/[BnOH])(conversion) + BnOH. Polydispersity index (Mₛ/Mₙ) were determined by GPC.
The iron complexes outperformed the other metal systems and complexes were also prepared for comparative catalytic studies. An oxy bridge. A number of non-macrocyclic Fe and Co complexes were prepared from a related dianiline containing further illustrated by 13C NMR spectroscopy (Fig. S17 and S22, ESI†).

| Run | Composition | Catalyst | t (h) | Incorporated amount | $M_n \times 10^3$ | PDI |
|-----|-------------|----------|-------|---------------------|-----------------|------|
| 1   | Poly (e-CL + r-LA) | 1        | 24 + 24: | e-CL : r-LA = 47 : 53 | 3.75 | 2.22 |
| 2   | Poly (δ-VL + r-LA) | 1        | 24 + 24 : | δ-VL : r-LA = 14 : 86 | 5.51 | 1.73 |
| 3   | Poly (r-LA + e-CL) | 2        | 24 + 24 | r-LA : e-CL = 49 : 51 | 10.55 | 1.51 |
| 4   | Poly (r-LA + e-CL) | 2        | 24 + 24 | r-LA : e-CL = 49 : 51 | 10.55 | 1.51 |
| 5   | Poly (r-LA + e-CL) | 2        | 24 + 24 | r-LA : e-CL = 93 : 7 | 6.20 | 1.82 |
| 6   | Poly (r-LA + e-CL) | 2        | 24 + 24 | r-LA : e-CL = 60 : 40 | 9.31 | 1.64 |
| 7   | Poly (r-LA + e-CL) | 2        | 24 + 24 | r-LA : e-CL = 63 : 37 | 12.63 | 3.02 |
| 8   | Poly (r-LA + e-CL) | 2        | 24 + 24 | r-LA : e-CL = 55 : 45 | 3.40 | 1.26 |
| 9   | Poly (r-LA + e-CL) | 2        | 24 + 24 | r-LA : e-CL = 88 : 12 | 2.57 | 2.56 |
| 10  | Poly (r-LA + e-CL) | 4        | 24 + 24 | r-LA : e-CL = 100 : 0 | 4.61 | 1.23 |
| 11  | Poly (r-LA + e-CL) | 4        | 24 + 24 | r-LA : e-CL = 90 : 10 | 3.61 | 1.18 |

*a Conversion was confirmed by 1H NMR spectroscopy. b Determined by GPC analysis calibrated with polystyrene standards and multiplied by correction factor of 0.56.

**Synthesis of block co-polymers**

The co-polymerisation of e-CL with r-LA and of δ-VL with r-LA was also examined (Table 3). Noteworthy, the co-polymerisation of e-CL with r-LA is much easier than δ-VL with r-LA when using the Fe complexes. In the presence of complex 2, the $M_n$ of the block co-poly(e-CL + r-LA) reached around 12 000. Complexes 1 and 4 were less active in these co-polymerisations. As observed by 1H NMR spectroscopy (Fig. S14 and S24†), the co-polymers were also capped by benzyloxy and hydroxyl end groups. The composition of the copolymer was further illustrated by 13C NMR spectroscopy (Fig. S17 and S25†). From the MALDI-ToF mass spectrum (positive mode) of poly(e-CL + r-LA) a gap of 144 corresponding to the molecular weight of e-CL was evident, whilst running the spectra in negative mode revealed a gap of 114 corresponding to the molecular weight of r-LA (Fig. S12 and 13†). The MALDI-ToF mass spectrum for co-poly (δ-VL + r-LA) was also recorded, see Fig. S26†. The 2D J-resolved 1H NMR spectrum for the copolymer was recorded and the peaks were assigned to the corresponding tetrads (see Fig. S17 and S22, ESI†) according to literature reports,12 which revealed an atactic LA–LA chain.

**Conclusion**

In conclusion, we have successfully synthesised iron, cobalt and copper complexes bearing [2 + 2] Schiff-base macrocycles derived from dianilines containing CH$_2$CH$_2$ bridges. Cobalt complexes were prepared from a related dianiline containing an oxy bridge. A number on non-macrocyclic Fe and Co complexes were also prepared for comparative catalytic studies. The iron complexes outperformed the other metal systems herein for the ring opening polymerisation of both e-caprolactone and δ-valerolactone. Best results were obtained using the iron salt 2, however the non-macrocyclic system 12 also performed well. Complex 2 was also capable of the copolymerisation of e-CL (or δ-VL) with rac-lactide, affording copolymers appreciable amounts of each monomer incorporated.

**Experimental**

**General**

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Toluene was refluxed over sodium, whilst acetonitrile was refluxed over calcium hydride. IR spectra (nujol mulls, KBr windows) were recorded on a Nicolet Avatar 360 FT-IR spectrometer; 1H and 13C NMR spectra were recorded at room temperature on a Varian VX 400 S spectrometer at 400 MHz or a Gemini 300 NMR spectrometer or a Bruker Advance DPX-300 spectrometer. The 1H NMR spectra were calibrated against the residual proton impurity of the deuterated solvent. Elemental analyses were performed by the elemental analysis service at the London Metropolitan University, the Chemistry Department at the University of Hull or Nanjing University. The precursors 2,6-difluorobenzylidene (CHO)$_2$, 4-R-C$_6$H$_4$OH (R = Me, tBu) and 2,2′-ethyleneoxydimine (or 2,2′-oxidadimine) and the Schiff-base pro-ligands were prepared by the literature.13,14,15 For the iron and cobalt complexes, all manipulations were carried out under an atmosphere of dry nitrogen using conventional Schlenk and cannula techniques or in a conventional nitrogen-filled glove box. All solvents were distilled and degassed prior to use (Table 2).
Synthesis of [FeBr(L\textsuperscript{1}H\textsubscript{2})\textsubscript{2}][FeBr\textsubscript{2}O]-2(MeCN) (1:2MeCN)

L\textsubscript{1}H\textsubscript{2} (0.52 g, 0.77 mmol) and FeBr\textsubscript{2} (0.34 g, 1.58 mmol) were combined in a Schlenk and toluene (20 mL) was added. After refluxing for 12 h, the volatiles were removed in vacuo, and the residue was extracted into MeCN (20 mL). Prolonged standing at room temperature afforded orange/brown prisms. Yield: 0.72 g, 78%. Elemental analysis calculated for C\textsubscript{106}H\textsubscript{107}Br\textsubscript{8}Fe\textsubscript{4}N\textsubscript{9}O\textsubscript{5}: C 57.4 (w), 53.4 (w), 50.2 (m), 48.6 (w), 45.5 (w). M.S. (MALDI-ToF): 817 (M\textsuperscript{+}). Magnetic moment: 6.35 B.M.\textsuperscript{16}

Synthesis of [FeBr(L\textsuperscript{2}H\textsubscript{2})\textsubscript{2}][FeBr\textsubscript{2}O]-0.5MeCN (2:0.5MeCN)

To the pro-ligand L\textsubscript{2}H\textsubscript{2} (0.50 g, 0.65 mmol) in toluene was added 2.1 equivalents of FeBr\textsubscript{2} (0.30 g, 1.39 mmol), and the system was refluxed for 12 h. On cooling, the volatiles were removed under vacuum, and the residue was extracted into acetonitrile (30 ml) to afford 2:0.5MeCN as red needles (0.48 g, 56%). Elemental analysis calculated for C\textsubscript{104}H\textsubscript{101}Fe\textsubscript{4}N\textsubscript{8}O\textsubscript{4} (sample dried \textit{in-vacuo}, cm\textsuperscript{-1}): 3171 (m), 2922 (s), 2853 (s), 2726 (w), 1704 (m), 1620 (m), 1587 (m), 1542 (s), 1462 (s), 1377 (s), 1317 (w), 1260 (w), 1233 (m), 1214 (m), 1180 (m), 1103 (w), 977 (m), 873 (w), 801 (m), 754 (m), 722 (m), 688 (w), 622 (w), 574 (w), 534 (w), 502 (m), 486 (w), 455 (w). M.S. (MALDI-ToF): 817 (M\textsuperscript{+}). Magnetic moment: 6.35 B.M.\textsuperscript{16}

Synthesis of [FeBr(L\textsuperscript{2}H\textsubscript{2})\textsubscript{2}][FeBr\textsubscript{2}O]-Br·3MeCN (5:3MeCN)

As for 2, but using L\textsubscript{2}H\textsubscript{2} (0.52 g, 0.68 mmol) and FeBr\textsubscript{2} (0.16 g, 0.74 mmol) affording 3:5.5MeCN as brown prisms. Yield: 0.52 g, 65%. IR (KBr, cm\textsuperscript{-1}): 3168 (m), 2925 (s), 2854 (s), 2726 (w), 1704 (m), 1620 (m), 1587 (m), 1542 (s), 1462 (s), 1377 (s), 1317 (w), 1260 (w), 1233 (m), 1214 (m), 1180 (m), 1103 (w), 933 (w), 890 (w), 839 (w), 799 (m), 744 (m), 722 (m), 526 (w), 449 (m). M.S. (MALDI-ToF): 901 (M – anion). Magnetic moment: 5.86 B.M.\textsuperscript{16}

Synthesis of [FeBr(L\textsuperscript{2}H\textsubscript{2})\textsubscript{2}][FeBr\textsubscript{2}O]-Br·3MeCN (5:3MeCN)

To FeBr\textsubscript{2} (1.00 g, 4.64 mmol) was added KO\textsubscript{Bu} (1.04 g, 9.27 mmol) in THF (30 ml) at 0 °C and the system was stirred for 5 h. Following removal of the volatiles, L\textsubscript{2}H\textsubscript{2} (3.57 g, 0.30 mmol) in toluene was added and the residue was refluxed for 12 h. On cooling, the volatiles were removed and the residue was extracted into cold acetonitrile (30 ml). Prolonged standing at ambient dark brown block. Yield: 1.84 g, 46.6%. IR (KBr, cm\textsuperscript{-1}): 3377 (w), 2958 (s), 2854 (s), 2726 (w), 1630 (m), 1587 (m), 1462 (s), 1377 (s), 1260 (s), 1202 (w), 1093 (s), 1019 (s), 863 (m), 800 (s), 755 (w), 740 (w), 2723 (m), 705 (w), 662 (w), 556 (w), 530 (w), 504 (w), 465 (w). MS (MALDI): 1584 (M + H\textsuperscript{+}). Magnetic moment: 5.07 B.M.\textsuperscript{16}

Synthesis of [Co(NCMe\textsubscript{2})\textsubscript{2}L\textsubscript{2}H\textsubscript{2}]\textsubscript{2}[CoBr\textsubscript{4}]·5MeCN (8:5MeCN)

To the pro-ligand L\textsubscript{2}H\textsubscript{2} (1.00 g, 1.52 mmol) in toluene was added 2.1 equivalents of CoBr\textsubscript{2} (0.70 g, 3.20 mmol), and the system was refluxed for 12 h. On cooling, the volatiles were removed and the residue was extracted into acetonitrile (30 ml) to afford 8:5MeCN as black crystals (0.98 g, 62%). Single crystals can also be grown from a saturated acetone solution of 7. Elemental analysis calculated for C\textsubscript{42}H\textsubscript{30}Br\textsubscript{2}Co\textsubscript{2}N\textsubscript{4}O\textsubscript{4}: C 54.10, H 3.24, N 6.01%. Found C 53.88, H 3.19, N 6.25%. IR (KBr, cm\textsuperscript{-1}): 3171 (m), 2922 (s), 2854 (s), 2726 (w), 2359 (w), 1636 (w), 1618 (s), 1594 (m), 1574 (w), 1538 (s), 1462 (s), 1377 (s), 1333 (s), 1285 (m), 1260 (m), 1183 (s), 1102 (m), 1063 (m), 1021 (m), 873 (m), 799 (s), 756 (m), 722 (m), 688 (w), 668 (w), 624 (w), 576 (w), 558 (w), 522 (w). M.S. (MALDI): 847 (M – CoBr\textsubscript{2}). 766.97 (M – CoBr\textsubscript{4}). Magnetic moment: 5.05 B.M.\textsuperscript{18}

Synthesis of [CuBr(L\textsubscript{2}H\textsubscript{2})][CuBr\textsubscript{2}]-2MeCN (5:2MeCN)

As for 1, but using L\textsubscript{2}H\textsubscript{2} (0.52 g, 0.68 mmol) and CuBr\textsubscript{2} (0.30 g, 1.34 mmol) affording 5 as brown prisms. Yield 0.69 g, 84%. Elemental analysis calculated for C\textsubscript{52}H\textsubscript{54}Br\textsubscript{4}Co\textsubscript{2}N\textsubscript{4}O\textsubscript{2}: C 55.18, H 4.63, N 4.95%. Found C 54.59, H 4.48, N 4.93%. IR (KBr, cm\textsuperscript{-1}): 3171 (m), 2922 (s), 2853 (s), 2727 (s), 2671 (w), 2350 (w), 1633 (s), 1618 (s), 1594 (s), 1463 (s), 1377 (s), 1336 (w), 1285 (m), 1260 (w), 1249 (m), 1239 (w), 1183 (m), 1156 (w), 1103 (m), 1062 (m), 1022 (w), 977 (w), 950 (w), 938 (w), 876 (s), 846 (m), 830 (m), 794 (m), 754 (s), 738 (w), 722 (s), 688 (m), 623 (m), 594 (w), 575 (m), 558 (m), 550 (m). M.S (ESI): 908 (M – anion), 827 (M – anion – Br). Magnetic moment: 1.19 B.M.\textsuperscript{17}
Synthesis of \([\text{CoBr(NCMe)L}_5]^2\cdot2\text{MeCN}\) (10-2MeCN)

To \(\text{L}^1\)H (1.00 g, 4.85 mmol) and \([\text{CoBr}_2]\) (1.05 g, 4.85 mmol) was added toluene (20 mL) and Et₃N (0.3 ml, 0.22 mmol) and the system was refluxed for 12 h. Following removal of volatiles \(\text{in vacuo}\), the residue was extracted into MeCN (20 mL), and on standing at ambient temperature large orange/brown prisms of \(10\cdot3\text{MeCN}\) formed. Isolated yield: 1.41 g, 68%. Elemental analysis calculated for \(\text{C}_{32}\text{H}_{38}\text{Br}_2\text{Co}_2\text{N}_4\text{O}_6\) (sample dried \(\text{in vacuo}\) - 2Co). Magnetic moment: 6.94 B.M.¹⁸

Synthesis of \([\text{Fe(NCMe)}_6]\)[\(\text{FeOBr}_3\)]\(_2\) (13)

L\(_1\)H\(_2\) (0.52 g, 0.77 mmol) and \([\text{FeBr}_3]\) (0.47 g, 1.58 mmol) were combined in a Schlenk and toluene (20 mL) was added. After refluxing for 12 h, the volatiles were removed \(\text{in vacuo}\), and the residue was extracted into MeCN (20 mL). Prolonged standing at room temperature afforded brown prisms; isolated yield 0.39 g 81%. Elemental analysis calculated for \(\text{C}_{12}\text{H}_{18}\text{Br}_6\text{Fe}_3\text{N}_6\text{O}(\text{sample dried in vacuo for 2 h})\): C 15.85, H 2.12, N 9.31%. IR (KBr, cm\(^{-1}\)): 2926 (s), 2854 (s), 2339 (s), 1868 (s), 1844 (s), 1830 (m), 1772 (w), 1750 (m), 1734 (m), 1717 (m), 1684 (m), 1669 (m), 1653 (m), 1646 (m), 1635 (m), 1616 (m), 1576 (s), 1559 (s), 1540 (s), 1521 (s), 1506 (s), 1497 (m), 1489 (m), 1457 (s), 1419 (m), 1377 (s), 1260 (s), 1089 (s), 800 (s), 668 (s).

ROP procedure

e-Caprolactone and \(\delta\)-valerolactone. Typical polymerisation procedure in the presence of one equivalent of benzyl alcohol (Table 1, run 1) is as follows. A toluene solution of 1 (0.010 mmol, in 1.0 mL toluene) and BnOH (0.010 mmol) were added into a Schlenk tube in the glove-box at room temperature. The solution was stirred for 2 min, and then e-caprolactone (2.5 mmol) or \(\delta\)-valerolactone along with 1.5 mL toluene was added to the solution. The reaction mixture was then placed into an oil bath pre-heated to the required temperature, and the solution was stirred for the prescribed time. The polymerisation mixture was then quenched by addition of an excess of glacial acetic acid (0.2 mL) into the solution, and the resultant solution was then poured into cold methanol (200 mL). The resultant polymer was then collected on filter paper and was dried \(\text{in vacuo}\).

Co-polymerisations

A toluene solution of catalyst (0.010 mmol, in 1.0 mL toluene) was added into a Schlenk tube in the glove-box at room temperature. The solution was stirred for 2 min, and then 1 equivalent of BnOH (from 1 mmol BnOH in 100 mL toluene) and monomer were added, after 24 h the other monomer was added to the solution. The reaction mixture was then placed into an oil bath pre-heated to the 130 °C, and the solution was stirred for another 24 h. The polymerisation mixture was then quenched by addition of an excess of glacial acetic acid (0.2 mL) into the solution, and the resultant solution was then poured into cold methanol (200 mL). The resultant polymer was then collected on filter paper and was dried \(\text{in vacuo}\).

Kinetic studies

The polymerisations were carried out at 130 °C in toluene (1 mL) using 0.010 mmol of complex. The molar ratio of monomer to initiator was fixed at 500 : 1, and at appropriate time intervals, 0.5 μL aliquots were removed (under N\(_2\)) and...
Table 4  Crystallographic data

| Compound | 1·2MeCN | 2·0.5MeCN | 3·5.5MeCN | 4·3MeCN |
|----------|---------|-----------|-----------|---------|
| Formula  | C₁₀₆H₁₀₀Br₄Fe₄N₁₀O₂₄ | C₁₂₃H₁₃₂Br₄Fe₁₆N₃₀O₃₂ | C₁₄₅H₁₄₅Br₄Co₄N₄₀O₄₄ | C₁₆₈H₁₄₈Br₄N₄₀O₄₄ |
| Formula weight | 1705.9 | 5315.9 | 5315.9 | 5315.9 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | P₂₁/n | P₂₁/n | P₂₁/n | P₂₁/c |
| Unit cell dimensions | | | | |
| a (Å) | 13.645(1) | 14.2077(6) | 11.487(1) | 12.190(6) |
| b (Å) | 15.630(1) | 16.5179(8) | 15.630(1) | 15.630(1) |
| c (Å) | 37.473(2) | 41.824(7) | 41.824(7) | 41.824(7) |
| α (°) | 90 | 90 | 90 | 90 |
| β (°) | 90 | 90 | 90 | 90 |
| γ (°) | 90 | 90 | 90 | 90 |
| V (Å³) | 2707.0(2) | 1124.84(6) | 100.817(3) | 9273.8(6) |
| Z | 4 | 4 | 4 | 4 |
| Temperature (K) | 100(2) | 100(2) | 100(2) | 140(1) |
| Wavelength (Å) | 1.54184 | 0.71075 | 0.71073 | 0.71073 |
| Calculated density (g cm⁻³) | 1.667 | 1.503 | 1.222 | 1.222 |
| Absorption coefficient (mm⁻¹) | 9.439 | 3.531 | 0.223 | 0.223 |
| Tmin, Tmax | 0.755, 1.000 | 0.71073, 1.000 | 0.71073, 0.71073 | 0.71073, 0.71073 |
| Crystal size (mm³) | 0.08 × 0.05 × 0.02 | 0.30 × 0.015 × 0.01 | 0.26 × 0.015 × 0.01 | 0.26 × 0.015 × 0.01 |
| θ(max) (°) | 68.2 | 27.5 | 27.5 | 27.5 |
| Reflections measured | 16805 | 12337 | 12466 | 12466 |
| Unique reflections | 4174 | 3567 | 3567 | 3567 |
| Rint | 0.056 | 0.067 | 0.305 | 0.305 |
| Number of parameters | 1127 | 556 | 556 | 556 |
| R₁ [F² > 2σ(F²)] | 0.070 | 0.088 | 0.088 | 0.088 |
| wR2 (all data) | 1.766 | 1.904 | 1.904 | 1.904 |
| GOOF, S | 1.023 | 1.011 | 1.011 | 1.011 |
| Largest difference peak and hole (e Å⁻³) | 1.42 and −0.86 | 1.33 and −0.80 | 1.42 and −0.86 | 1.33 and −0.80 |

Compound | 5·2MeCN | 6·2MeCN | 7·2C₃H₆O | 8·3MeCN |
|----------|---------|---------|----------|---------|
| Formula  | C₅₆H₅₄Br₃Cu₄N₄O₂ | C₅₂H₄₈Br₄Co₄N₄O₂·2(C₂H₃N) | C₆₂H₅₂Br₂Co₂N₄O₄·2(C₃H₆O) | C₆₄H₅₂Br₄Co₄N₄O₄ |
| Formula weight | 1213.89 | 1145.56 | 1048.56 | 1465.8 |
| Crystal system | Triclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | P1 | P1 | P2₁/c | P2₁/c |
| Unit cell dimensions | | | | |
| a (Å) | 10.080(2) | 12.2629(5) | 11.4774(8) | 11.7781(10) |
| b (Å) | 15.001(4) | 13.2489(6) | 14.5787(10) | 15.4787(10) |
| c (Å) | 18.660(5) | 17.0384(7) | 26.021(3) | 26.021(3) |
| α (°) | 71.442(2) | 71.442(2) | 90 | 90 |
| β (°) | 82.738(2) | 82.738(2) | 100.235(8) | 100.235(8) |
| γ (°) | 76.600(2) | 76.600(2) | 90 | 90 |
| V (Å³) | 2598.2(1) | 2707.2(2) | 4284.6(6) | 4284.6(6) |
| Z | 4 | 4 | 4 | 4 |
| Temperature (K) | 100(2) | 100(2) | 100(2) | 100(2) |
| Wavelength (Å) | 1.54178 | 0.71075 | 1.54178 | 0.71075 |
| Calculated density (g cm⁻³) | 1.552 | 1.405 | 1.516 | 1.516 |
| Absorption coefficient (mm⁻¹) | 4.572 | 0.176 | 0.176 | 0.176 |
| Tmin, Tmax | 0.149, 1.000 | 0.652, 1.000 | 0.652, 1.000 | 0.652, 1.000 |
| Crystal size (mm³) | 0.70 × 0.60 × 0.15 | 0.10 × 0.015 × 0.01 | 0.404, 1.000 | 0.404, 1.000 |
| θ(max) (°) | 68.3 | 27.5 | 27.5 | 27.5 |

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### Table 4 (Contd.)

| Compound | 5·2MeCN | 6·2MeCN | 7·2C₃H₆O | 8·3MeCN |
|----------|---------|---------|---------|---------|
| Reflections measured | 44 092 | 10 619 | 6241 | 147 825 |
| Unique reflections | 9337 | 10 619 | 3471 | 16 480 |
| $R_{int}$ | 0.083 | 0.179 | 0.054 | 0.047 |
| Number of parameters | 622 | 564 | 526 | 762 |
| $R_1 [F^2 > 2\sigma(F^2)]$ | 0.066 | 0.114 | 0.128 | 0.032 |
| $wR_2$ (all data) | 0.184 | 0.297 | 0.371 | 0.064 |
| GOOF, $S$ | 1.062 | 1.098 | 1.226 | 1.023 |
| Largest difference peak and hole (e Å⁻³) | 3.45 and −1.24 | 1.02 and −1.54 | 2.52 and −2.02 | 0.52 and −0.46 |

| Compound | 910·2MeCN | 11·2MeCN | 12·2MeCN | 13 |
|----------|-----------|-----------|-----------|---|
| Formula | C₂₀H₃₀Br₆Co₃N₁₀·2MeCN | C₂₈H₃₂Br₂Co₂N₂O₆·2(C₂H₃N) | C₃₆H₄₄Br₆Co₄N₆O₆ | C₃₂H₃₈Br₂Fe₂N₄O₆ |
| Formula weight | 1066.79 | 852.34 | 1371.95 | 846.18 |
| Crystal system | Monoclinic | Triclinic | Triclinic | Trigonal |
| Space group | P₂₁/n | P | P | P |
| Unit cell dimensions | | | | |
| $a$ (Å) | 8.34720(10) | 8.4718(5) | 10.416(2) | 12.39520(10) |
| $b$ (Å) | 18.8457(3) | 9.2109(3) | 11.156(4) | 9.20980(10) |
| $c$ (Å) | 12.5811(2) | 12.2495(5) | 11.7384(4) | 12.1881(2) |
| $α$ (°) | 90 | 101.186(3) | 101.186(3) | 90 |
| $β$ (°) | 108.941(2) | 102.715(4) | 97.208(4) | 90 |
| $γ$ (°) | 90 | 102.715(4) | 97.208(4) | 120 |
| $V$ (Å³) | 1871.95(5) | 900.47(7) | 1257.87(2) | 4061.92(8) |
| Z | 2 | 1 | 1 | 6 |
| Temperature (K) | 100(2) | 100(2) | 100(2) | 100(2) |
| Wavelength (Å) | 0.71075 | 1.54184 | 1.51481 | 1.54184 |
| Calculated density (g cm⁻³) | 1.893 | 1.572 | 1.572 | 1.572 |
| Absorption coefficient (mm⁻¹) | 7.743 | 10.197 | 10.197 | 10.197 |
| $T_{min}$, $T_{max}$ | 0.154, 0.733 | 0.423, 1.000 | 0.725, 0.820 | 0.646, 1.000 |
| Crystal size (mm²) | 0.216 × 0.125 × 0.10 | 0.32 × 0.16 × 0.10 | 0.31 × 0.13 × 0.09 | 0.30 × 0.20 × 0.10 |
| $θ$(max) (°) | 27.49 | 68.2 | 29.2 | 70.3 |
| Reflections measured | 48 302 | 15 481 | 11602 | 32 046 |
| Unique reflections | 4301 | 3240 | 6632 | 30 046 |
| $R_{int}$ | 0.0235 | 0.066 | 0.044 | 0.0324 |
| Number of parameters | 183 | 217 | 268 | 217 |
| $R_1 [F^2 > 2\sigma(F^2)]$ | 0.017 | 0.042 | 0.035 | 0.0299 |
| $wR_2$ (all data) | 0.0037 | 0.119 | 0.072 | 0.0622 |
| GOOF, $S$ | 1.170 | 1.072 | 1.091 | 1.091 |
| Largest difference peak and hole (e Å⁻³) | 0.79 and −0.35 | 0.85 and −0.83 | 0.84 and −0.63 | 0.413 and −0.69 |
| | 0.38 and −0.51 |
were quenched with wet CDCl$_3$. The percent conversion of monomer to polymer was determined by $^1$H NMR spectroscopy.

**Mass spectrometry**

Polymer samples were run at the University of Hull using MALDI-TOF MS analysis. Samples were dissolved in THF, and the matrix, 2-(4-hydroxyphenylazo) benzoic acid (HPABA) with added NaOAc was employed, which was dissolved in THF to give a saturated solution. 50 µL of the sample solution was then mixed with 50 µL matrix solution, and 1 µL of the mixed solution applied to the sample target. The sample was allowed to dry in air before analysis. The co-poly (5-VL + r-LA) (run 7) sample was analysed by MALDI in positive-linear and reflectron modes, with DCTB matrix and NaOAc additive. The sample was fully soluble in THF at 10 mg mL$^{-1}$.

**X-ray crystallography**

Single-crystal X-ray diffraction data for the structures (except for 4 and 11) were collected at the UK National Crystallography service on a range of Rigaku Oxford Diffraction ultra-high intensity instruments employing modern areas detectors. Samples were held at 100 K for data collection. For 4, data were from a Rigaku Oxford Diffraction Xcalkub-3 CCD diffractometer at 140 K. For 11, data were from a Stoe IPSD2 image plate diffractometer utilising monochromated Mo radiation ($\lambda = 0.71073$ Å). In all cases standard procedures were employed for integration and processing of data. Crystallographic data for all samples are collated in Table 4.

Crystal structures were solved using direct methods (in SHELXS$^{19e}$) or dual space methods implemented within SHELXT.$^{19b}$ Completion of structures was achieved by performing least squares refinement against all unique $F^2$ values using SHELXL-2018.$^{20}$ All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed using a riding model. Where the location of hydrogen atoms was obvious from difference Fourier maps, C-H and O-H bond lengths were refined subject to chemically sensible restraints. Minor disorder was treated using standard methods.

The crystal of 5 examined was the best of those available. The crystal was split and intensity data from the major component were used for refinement. The final refinement has good quality of fit ($R_1 = 6.66\%$) but it is not perfect because of the imperfect nature of the crystals available.

**Conflicts of interest**

There are no conflicts of interest to declare.

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