Sterically variable dizinc complexes bearing bis(iminopyridyl)phenolate ligands: synthesis, structures and reactivity studies†

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A series of chiral dizinc complexes of the type [(2,6-{ArN=C(Me)C_5H_3N}$_2C_6H_3O$)Zn_2(μ-Cl)Cl_2] [Ar = 2,6-*i*-$Pr_2C_6H_3$ (**1a**), 2,6-$Me_2C_6H_3$ (**1b**), 2,4,6-Me_3-C_6H_2 (**1c**), 2,4-$Me_2C_6H_3$ (**1d**)] can be conveniently prepared in good yield by the template reaction of 2,6-{O=C(Me)C_5H_3N}$_2C_6H_3$OH with an excess of the corresponding aniline and two equivalents of zinc dichloride in *n*-BuOH at elevated temperature. Alternatively, the pro-ligands, 2,6-{(ArN=C(Me)C_5H_3N}$_2C_6H_3$OH [Ar = 2,6-*i*-$Pr_2C_6H_3$ (L1-H), 2,6-$Me_2C_6H_3$ (L2-H), 2,4,6-$Me_3C_6H_2$ (L3-H), 2,4-$Me_2C_6H_3$ (L4-H)], can be isolated and then treated with two equivalents of zinc dichloride to afford **1a–1d**. Interaction of **1a** with two equivalents of NaOAc in the presence of $TlBF_4$ gives the diacetate-bridged salt [(L1)Zn_2(μ-OAc)$_2$](BF_4) (**2**) while with Nadbm (dbm = dibenzoylmethanato) the bis(dbm)-chelated salt [(L1)Zn_2(dbm)$_2$](BF_4) (**3**) is obtained. Hydrolysis occurs on reaction of **1a** with TlOEt to furnish [(L1)Zn_2(μ-OH)Cl_2] (**4**) as the only isolable product. Conversely, reaction of **1a** with Tlhp (hp = 2-pyridonate) affords the neutral bis(pyridonate)-bridged trimetallic complex [(L1)Zn_3(μ-hp)$_2Cl_3$] (**5**) as the major product along with **4** as the minor one. Complex **4** and mixtures of **4**/**5** act as modest activators for the ring-opening polymerisation of ε-caprolactone. Single crystal X-ray diffraction studies have been performed on **1b**, **1c**, **2**, **3**, **4** and **5** reveal Zn ··· Zn separations in the range: 3.069(4)–4.649(6) Å.

1 Introduction

The rational design and synthesis of ligand frameworks that are capable of housing two (or more) zinc centres in close proximity (between 3 and 5 Å) have long been the subject of research activity due, in the main, to the connection the resulting complexes[1] have to the binuclear metal sites found in a number of zinc hydrolytic enzymes (*e.g.*, metallo-β-lactamases,[2,3] some aminopeptidases,[4] phosphotriesterase[5] and alkaline phosphatase[6]). More recently, these bio-inspired families of compartmental ligands and related frameworks have been used to develop dizinc complexes that can be employed in other fields including as molecular sensors,[7] and as catalysts for a variety of transformations including the ring-opening polymerisation[8] of cyclic esters (*e.g.*, *rac*-lactide, ε-caprolactone), epoxide/CO_2 copolymerisations[9] and for C–C bond forming reactions.[10]

As part of our programme we have been targeting new preorganised binucleating manifolds[11–13] that are potentially amenable to systematic variation in their steric and electronic properties[14] with a view to preparing bimetallic oligomerisation/polymerisation catalysts. For example, we have shown that diiron(II), dicobalt(II) and dinickel(II) complexes of the 2,6-diisopropylphenyl derivative of the monoanionic bis(iminopyridyl)phenolate [Lx, Fig. 1] ligand, L1, display, on treatment with methylaluminoxane, some activity for the oligomerisation of ethylene.[13] A preliminary attempt at preparing a dizinc(II) complex bearing L1 has also led to the isolation of [(L1)Zn_2(μ-Cl)Cl_2] (**1a**).[13]

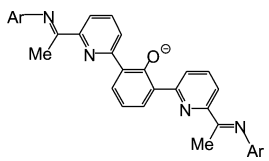

Fig. 1 Bis(iminopyridyl)phenolate, Lx.

Herein, we report a new route to **1a** and expand the family of complexes of type [(Lx)Zn_2(μ-Cl)Cl_2] (**1**) to cover a range of aryl group substitution patterns (*viz.* Ar = 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 2,4-$Me_2C_6H_3$). In addition, the coordination chemistry of trichloride **1a** is probed by exploring its reactivity towards acetate, dibenzoylmethanato, ethoxide and 2-pyridonate; the capacity of some of the derivatives to act as initiators for the ring opening polymerisation of ε-caprolactone is also examined.

2 Results and discussion

(a) Synthesis of 1

The template reaction of 2,6-{O=C(Me)C_5H_3N}$_2C_6H_3$OH with two equivalents of $ZnCl_2$ in the presence of an excess of $ArNH_2$ (Ar = 2,6-*i*-$Pr_2C_6H_3$, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 2,4-$Me_2C_6H_3$) in *n*-butanol at elevated temperature gave complexes [(Lx)Zn_2(μ-Cl)Cl_2] [Lx = L1 (**1a**), L2 (**1b**), L3 (**1c**), L4 (**1d**)] in good yield, respectively (Scheme 1). Alternatively, **1b–1d** can also be prepared in a manner similar to that previously reported for **1a**,[13] by firstly

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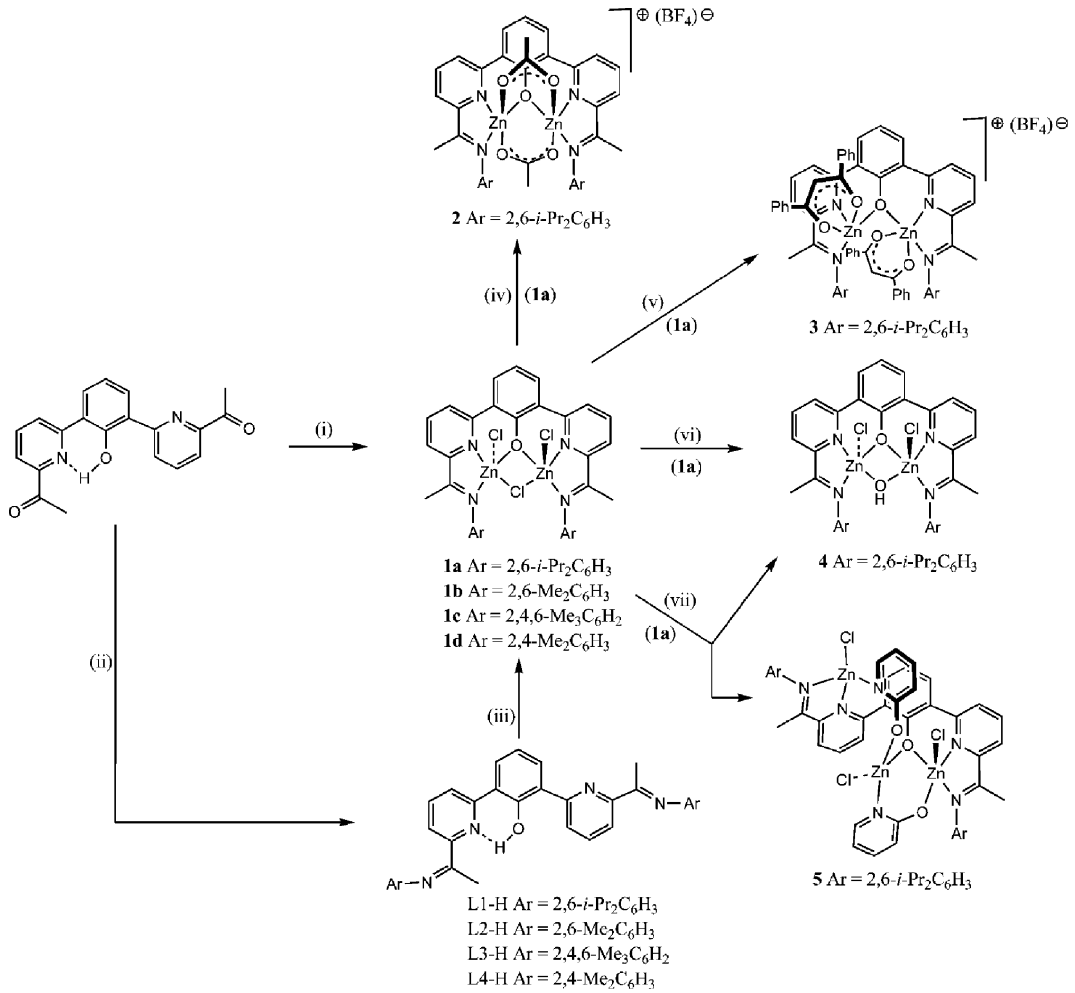

Scheme 1 *Reagents and conditions*: (i) 10 $ArNH_2$, 2 $ZnCl_2$, *n*-BuOH, 120 °C, 2 days; (ii) xs. $ArNH_2$, 160 °C, cat. H^+, 30 min.; (iii) 2 $ZnCl_2$, *n*-BuOH, 100 °C, 1 h; (iv) $TlBF_4$, 2 NaOAc, MeCN, RT, 12 h; (v) TlOEt, CH_2Cl_2, RT, 12 h; (vi) $TlBF_4$, 2 Nadbm, MeCN, RT, 12 h; (vii) Tlhhp (made *in-situ*), MeCN, RT, 12 h.

reacting 2,6-{O=C(Me)C_5H_3N}$_2C_6H_3OH$ with the corresponding aniline to form 2,6-{(ArN=C(Me)C_5H_3N}$_2C_6H_3OH$ [Ar = 2,6-*i*-$Pr_2C_6H_3$ (L1-H), 2,6-$Me_2C_6H_3$ (L2-H), 2,4,6-$Me_3C_6H_2$ (L3-H), 2,4-$Me_2C_6H_3$ (L4-H)] and then treating these pro-ligands with two equivalents of zinc dichloride (Scheme 1). All new pro-ligands (L2-H, L3-H, L4-H) and complexes (**1b–1d**) have been characterised by ^{1}H NMR, IR spectroscopy, mass spectrometry and gave satisfactory microanalytical data (see Experimental section). In addition, complexes **1b** and **1c** have been the subject of single crystal X-ray diffraction studies.

Single crystals of **1b** and **1c** suitable for X-ray determination were grown by slow cooling (to ambient temperature) of hot concentrated acetonitrile solutions containing the corresponding complex. Two independent molecules are apparent in the asymmetric unit of both **1b** and **1c** with only minor variations (*vide infra*) in bond parameters apparent between molecules; in the case of **1c** the second molecule (B) adopts the enantiomeric twin form of molecule A. A view of **1b** is depicted in Fig. 2; selected bond distances and angles are listed for both molecules in **1b** and **1c** in Table 1. The structures are similar and will be discussed together using molecule A in each case as the representative example.

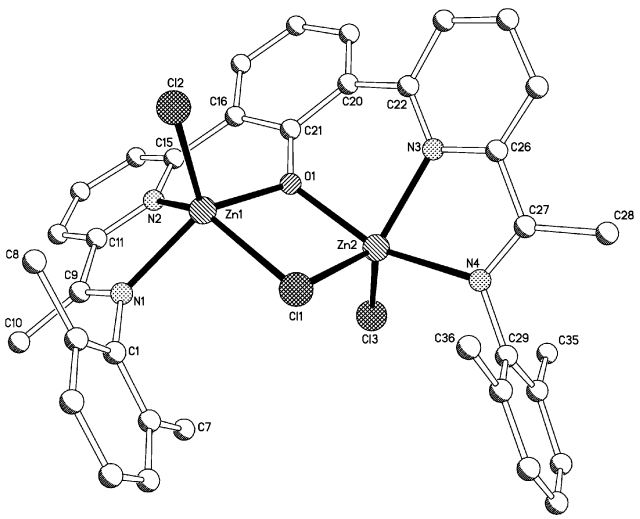

Fig. 2 Molecular structure of **1b** (molecule A) with a partial atom labeling scheme; all hydrogen atoms have been omitted for clarity.

Table 1 Selected bond distances (Å) and angles (°) for **1b** and **1c**

	1b		**1c**	
	Molecule A	Molecule B	Molecule A	Molecule B
Zn(1)–O(1)	2.017(3)	1.996(4)	2.031(4)	2.051(4)
Zn(1)–Cl(1)	2.4610(16)	2.4827(17)	2.439(3)	2.429 (3)
Zn(1)–Cl(2)	2.2372(16)	2.2456(18)	2.246(2)	2.238(2)
Zn(1)–N(1)	2.120(4)	2.110(5)	2.143(6)	2.119(6)
Zn(1)–N(2)	2.107(4)	2.130(4)	2.121(5)	2.118(5)
Zn(1)···Zn(2)	3.341(4)	3.280(4)	3.327(5)	3.325(5)
Zn(2)–O(1)	2.064(3)	2.063(4)	2.075(4)	2.056(4)
Zn(2)–Cl(1)	2.3690(16)	2.3511(17)	2.368(3)	2.371(3)
Zn(2)–Cl(3)	2.2413(17)	2.2209(18)	2.241(3)	2.242(2)
Zn(2)–N(3)	2.123(4)	2.135(5)	2.120(6)	2.118(6)
Zn(2)–N(4)	2.169(4)	2.145(4)	2.177(6)	2.169(5)
C(9)–N(1)	1.285(7)	1.271(7)	1.285(8)	1.279(8)
C(27)–N(4)	1.281(6)	1.286(7)	1.283(8)	1.273(8)
N(1)–Zn(1)–O(1)	140.66(16)	141.99(17)	141.0(2)	139.76(19)
N(1)–Zn(1)–N(2)	77.96(17)	78.10(18)	78.1(2)	77.3(2)
N(1)–Zn(1)–Cl(1)	92.29(12)	94.91(14)	91.99(18)	92.58(17)
N(1)–Zn(1)–Cl(2)	113.34(13)	110.70(14)	112.63(16)	112.44(17)
N(2)–Zn(1)–Cl(1)	140.93(12)	139.15(13)	140.20(15)	141.30(15)
N(2)–Zn(1)–Cl(2)	107.75(12)	113.16(13)	107.01(16)	107.11(16)
N(2)–Zn(1)–O(1)	83.90(16)	82.94(16)	83.51(19)	83.72(19)
Cl(2)–Zn(1)–Cl(1)	110.82(5)	106.99(7)	112.34(8)	111.23(8)
N(4)–Zn(2)–O(1)	157.12(15)	156.24(16)	157.0(2)	156.96(19)
N(4)–Zn(2)–Cl(1)	97.29(11)	99.18(13)	97.86(14)	97.26(14)
N(4)–Zn(2)–Cl(3)	101.94(12)	103.63(13)	103.18(16)	102.73(15)
N(3)–Zn(2)–Cl(3)	125.34(13)	129.18(13)	120.92(16)	123.06(15)
Cl(3)–Zn(2)–Cl(1)	112.56(6)	113.66(7)	115.59(11)	115.09(10)
Zn(1)–O(1)–Zn(2)	109.89(15)	107.84(17)	108.2(2)	108.14(19)
Zn(1)–Cl(1)–Zn(2)	87.50(5)	85.43(5)	87.60(7)	87.69(7)

The molecular structures comprise two zinc atoms supported on monoanionic Lx [Lx = L2 (**1b**), L3 (**1c**)] with the phenolate oxygen atom [O(1)] bridging the metals and the two separate pyridyl-imine units acting as chelates. Each metal centre is further bound by one terminal chloride and one bridging chloride so as to complete two independent five-coordinate geometries. Some differences in the coordination sphere at each metal centre are observed with the geometry at Zn(1) being described as square pyramidal [$\tau = 0.01$ (**1b**), 0.01 (**1c**)][15] while at Zn(2) the geometry is more distorted and tending towards trigonal pyramidal [$\tau = 0.53$ (**1b**), 0.60 (**1c**)]. The imino-pyridyl chelating moieties in Lx are almost planar [tors.: N(1)–C(9)–C(11)–N(2) 3.12° (**1b**), 4.49° (**1c**); N(3)–C(26)–C(27)–N(4) 11.64° (**1b**), 11.78° (**1c**)] with the *N*-aryl groups *quasi*-orthogonal to these planes [tors.: C(2)–C(1)–N(1)–C(9) 101.84° (**1b**), 99.03° (**1c**); C(34)–C(29)–N(4)–C(27) 91.66° (**1b**), 88.39° (**1c**)]. These inclinations of the aryl groups have the effect that one *ortho*-methyl substituent per aryl group points in a similar direction as a terminal chloride. With regard to the central phenolate plane, each pyridyl-imine unit is twisted away from planarity [tors.: C(21)–C(20)–C(22)–N(3) 35.42° (**1b**), 35.94° (**1c**); N(2)–C(15)–C(16)–C(21) 21.98° (**1b**), 20.48° (**1c**)], which compares to the more uneven variation in **1a** (1.6 *vs.* 36.2°).[13] As would be expected, the Zn–Cl (bridging) distances in **1b** and **1c** are longer than the Zn–Cl (terminal) distances with some asymmetry apparent between the Zn–Cl (bridging) distances [Zn(1)–Cl(1) 2.4610(16) *vs.* Zn(2)–Cl(1) 2.3690(16) Å (**1b**); 2.439(3) *vs.* 2.368(3) Å (**1c**)]. A similar asymmetry is observed for the Zn–O (bridging) distances with the Zn(1)–O(1) bond [2.017(3) Å (**1b**); 2.031(4) Å (**1c**)] in this case being shorter than the Zn(2)–O(1) bond length [2.064(3) Å (**1b**); 2.075(4) Å (**1c**)]. The intermetallic Zn···Zn distances for both molecules of **1c** are similar [3.327(5) Å, 3.325(5) Å], while in **1b** there is a notable variation in the Zn···Zn distance between independent molecules (*ca.* 0.061 Å); the reported range for complexes containing the Zn(μ-$O_{phenolate}$)(μ-Cl)Zn motif is 3.209–3.348 Å.[8b,13] This variation in intermetallic separation in **1b** is also reflected by the Zn–O–Zn angles [109.89(15)° (molecule A), 107.84(17)° (molecule B)]. The N(1)–C(9) and N(4)–C(27) bond distances in **1b** and **1c** [*ca.* 1.280 Å] are consistent with C=N bond character. No intermolecular contacts of note are apparent.

The FAB mass spectra of complexes **1b–d** show fragmentation peaks in each case corresponding to the loss of one or two halide groups from their respective molecular ions. In their IR spectra, the $\nu(C{=}N)_{imine}$ bands are seen at *ca.* 1590 cm^{-1} and shifted by *ca.* 40 cm^{-1} to lower wavenumber in comparison with the corresponding pro-ligand (Lx-H). The ^1H NMR spectrum of **1d** indicates that (as with **1a**[13]) in solution the metal centres occupy equivalent binding sites as exemplified by the presence of only one type of imino-methyl group (at δ 2.25). Complexes **1b** and **1c** were, however, insufficiently soluble in $CDCl_3$ to allow NMR characterisation. Interestingly, dissolution of **1a–1d** occurs readily in DMSO-d_6 with the resulting NMR spectra revealing a reduction in the symmetry, perhaps suggesting the coordination of DMSO at one metal centre. However, attempts at growing crystals suitable for a single crystal X-ray diffraction studies were unsuccessful; in the case of **1a** affording crystals of L1-H.[13]

(b) Syntheses of 2 and 3

Interaction of **1a** with two equivalents of NaOAc in the presence of $TlBF_4$ gave the diacetate-bridged salt $[(L1)Zn_2(\mu\text{-}OAc)_2](BF_4)$ (**2**), while with two equivalents of Nadbm (dbm = dibenzoylmethanato) the bis(dbm)-chelated salt $[(L1)Zn_2(dbm)_2](BF_4)$ (**3**) was obtained in good yield. Both **2** and **3** have been characterised by FAB mass spectrometry, IR spectroscopy and by ^1H NMR spectroscopy (see Experimental section). Both complexes have additionally been the subject of single crystal X-ray diffraction studies.

Crystals of **2** suitable for the X-ray determination were grown by slow evaporation of a hot acetonitrile solution containing the complex. Two independent cations (A and B) and two tetrafluoroborate anions are apparent in the asymmetric unit for **2** with some noteworthy differences evident between A and B (*vide infra*). A view of one of the independent cations (A) is depicted in Fig. 3; selected bond distances and angles for both A and B and the BF_4 anions are listed in Table 2. The following discussion is concerned with cation A while any variations between A and B will be highlighted. As with **1**, two zinc ions in **2** are bridged by a phenolate oxygen atom and chelated by two pyridyl-imine units from L1. In addition, a pair of *syn–syn* acetate groups bridge the metal centres to afford a $Zn(\mu\text{-}O_{phenolate})(\mu\text{-}OAc)_2Zn$ core. The five-coordinate geometries displayed by the metal centres can be best described as distorted square pyramidal [τ = 0.41 (Zn(1)), 0.35 (Zn(2))][15] with O(2) and O(4) defining the apical sites. Within L1, both pyridyl-imine units are nearly planar [tors.: N(1)–C(30)–C(31)–N(2) 8.32° and N(3)–C(15)–C(13)–N(4) 12.35°] but are notably tilted with respect to the central phenolate group [tors.: N(2)–C(24)–C(26)–C(25) 34.08°; N(3)–C(19)–N(20)–C(25) 34.79°]; this tilting is more uneven in cation B [tors.: N(2)–C(24)–C(26)–C(25) 41.64° *vs.* N(3)–C(19)–N(20)–C(25) 14.15°]. The two $Zn–O(1)_{phenolate}$ bond lengths are equivalent [at 2.017(3) Å] in cation A while a noticeable asymmetry is present in B [2.085(3) *vs.* 1.988(3) Å]. This flexibility in L1 also affects the intermetallic separations with the Zn · · · .Zn distance in B [3.161(3) Å] being marginally longer than in A [3.127(4) Å] but falling in the range found in other dizinc cations containing the $Zn(\mu\text{-}O_{phenolate})(\mu\text{-}OAc)_2Zn$ core.[16] Some variation is apparent in the four $Zn–O_{acetate}$ bond distances in A [*range*: 1.948(3)–2.003(3) Å] with a similar trend evident in B. The BF_4 anions occupy the cavities created by adjacent cations with the closest H · · · F contact being 2.445 Å.

Table 2 Selected bond distances (Å) and angles (°) for **2**

	Cation A	Cation B
Zn(1)–O(1)	2.017(3)	2.085(3)
Zn(1)–O(3)	1.948(3)	1.953(3)
Zn(1)–O(4)	1.991(3)	1.959(3)
Zn(1)–N(1)	2.124(3)	2.162(4)
Zn(1)–N(2)	2.068(4)	2.058(4)
Zn(2)–O(1)	2.017(3)	1.988(3)
Zn(2)–O(2)	2.003(3)	2.005(3)
Zn(2)–O(5)	1.960(3)	1.980(3)
Zn(2)–N(3)	2.079(3)	2.087(3)
Zn(2)–N(4)	2.109(4)	2.092(3)
Zn(1) · · · Zn(2)	3.127(4)	3.161(3)
C(31)–N(1)	1.267(5)	1.278(5)
C(13)–N(4)	1.270(5)	1.271(5)
B–F (anion)	1.283(8)–1.448(9)	1.303(8)–1.358(8)
O(1)–Zn(1)–N(1)	165.13(13)	162.80(13)
O(4)–Zn(1)–N(2)	99.25(14)	105.78(14)
O(3)–Zn(1)–O(4)	118.68(14)	114.97(14)
O(4)–Zn(1)–O(1)	95.79(12)	97.48(12)
O(1)–Zn(2)–N(4)	165.35(13)	162.20(13)
O(5)–Zn(2)–N(3)	144.01(14)	146.79(13)
O(2)–Zn(2)–O(5)	120.18(14)	109.55(13)
O(5)–Zn(2)–O(1)	94.71(13)	94.21(12)
Zn(1)–O(1)–Zn(2)	101.64(12)	101.76(13)

Suitable crystals of **3** for the X-ray determination were grown from chloroform by slow diffusion of hexane at room temperature. A perspective view of the cation in **3** is depicted in Fig. 4; selected bond distances and angles are listed in Table 3. The structure of **3** consists of a dizinc cation and a tetrafluoroborate anion with a crystallographic plane of symmetry present within the cationic unit which lies along the O(1)–C(1)–C(4) vector. Within the cationic unit the two zinc atoms are bound by L1 in a fashion similar to that seen in **1** and **2** with each zinc atom additionally

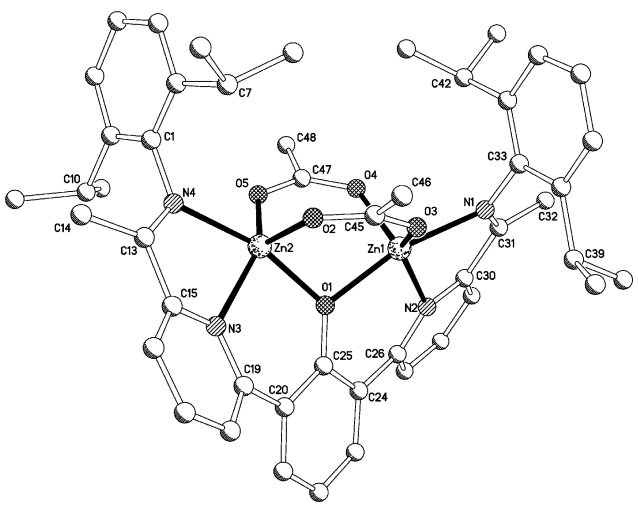

Fig. 3 Molecular structure of the cationic unit in **2** (cation A) with a partial atom labeling scheme; all hydrogen atoms have been omitted for clarity.

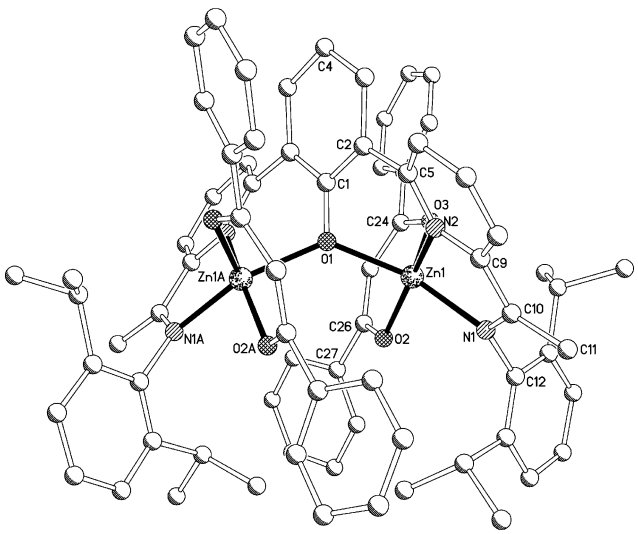

Fig. 4 Molecular structure of the cationic unit in **3** with a partial atom labeling scheme; all hydrogen atoms have been omitted for clarity.

Table 3 Selected bond distances (Å) and angles (°) for **3**

Zn(1)–O(1)	2.042(2)	Zn(1)–N(2)	2.099(5)
Zn(1)–O(2)	1.984(4)	Zn(1)···Zn(1A)	3.794(5)
Zn(1)–O(3)	1.968(4)	C(10)–N(1)	1.289(7)
Zn(1)–N(1)	2.085(5)	B–F (anion)	1.287(1)–1.468(10)
N(1)–Zn(1)–O(1)	144.96(17)	N(1)–Zn(1)–N(2)	76.7(2)
O(2)–Zn(1)–O(3)	93.85(17)	Zn(1)–O(1)–Zn(1A)	136.4(3)
O(1)–Zn(1)–N(1)	144.96(17)	O(2)–Zn(1)–N(2)	161.44(19)

Atoms with suffix A are generated by symmetry ($-x + 1, y, -z + 3/2$).

bound by a chelating dbm ligand so as to complete a distorted octahedral geometry [O(1)–Zn(1)–N(1) 144.96(17)°, O(2)–Zn(1)–N(2) 161.44(19)°] at each metal centre. As with **1** and **2**, the central phenolate group is tilted with respect to the pyridyl-imine planes [tors.: C(1)–C(2)–C(5)–N(2) 34.4°]. The absence of a second bridging ligand (*cf.*, **1** and **2**) results in the Zn–O(1)–Zn angle being more open [136.4(3)°] which is accompanied by a more elongated Zn···Zn separation [3.794(5) Å]. The BF_4 anions sit between adjacent cations with the closest contact [2.376 Å] being between a *para*-H on one of the 2,6-diisopropylphenyl groups and a BF_4 fluoride atom.

In the FAB mass spectra of **2** and **3** fragmentation peaks corresponding to the loss of BF_4 ions along with acetate or dibenzoylmethanato fragmentation from their respective molecular ions are apparent. The $\nu(C{=}N)_{imine}$ bands are unclear for both species in their IR spectra and are likely masked by stretches corresponding to bridging acetate (asymmetric stretch) or chelating dbm ligands in **2** and **3**, respectively. In their ^{1}H NMR spectra the imino-methyl groups (two per complex) are equivalent with singlet resonances visible at *ca.* δ 2.33; the CH_3CO_2 (**2**) or $CH(CPhCO)_2$ (**3**) protons also take the form of singlets at δ 1.93 and δ 5.79, respectively. In addition, the ^{19}F NMR spectra of **2** and **3** reveal singlets at *ca.* δ −153 consistent with the presence of the BF_4^- counter anions.

(c) Syntheses of 4 and 5

Given the ease of reactivity of **1a** towards acetate and dibenzoylmethanato, we decided to probe the reactions of **1a** with alkoxides and pyridonates. Thus, reaction of **1a** with TlOEt gave [(L1)Zn_2(μ-OH)Cl_2] (**4**) while with Tlhp (hp = 2-pyridonate), a mixture of **4** and [(L1)Zn_3(μ-hp)$_2Cl_3$] (**5**) were isolated in a 3 : 7 ratio (from ^{1}H NMR spectrum). Complexes **4** and **5** have been characterised by IR and ^{1}H NMR spectroscopy along with FAB mass spectrometry (see Experimental section). In addition, both complexes have also been the subject of single crystal X-ray diffraction studies.

Crystals of **4** suitable for the X-ray determination were grown from chloroform by slow diffusion of diethyl ether at room temperature. A view of **4** is shown in Fig. 5; selected bond distances and angles are listed in Table 4. The molecular structure of **4** resembles **1a**[13] with a μ-hydroxide ligand replacing the bridging chloride in **1a**. Inspection of the geometric parameter (τ)[15] reveals both zinc centres, as with **1a** and **2**, to adopt distorted square pyramidal geometries [τ = 0.06 (Zn(1)), 0.29 (Zn(2))] while the central phenolate group is also tilted unevenly with respect to the pyridyl-imine units [tors.: N(2)–C(19)–C(20)–C(25) 14.4°; C(25)–C(24)–C(26)–N(3) 37.4°] in L1. The effect of the presence of the bridging hydroxide is to reduce the Zn(1)–O(1)–Zn(2) angle [Zn(1)–O(1)–Zn(2) 95.30(12)° *vs.* 101.63(13)° (**1a**)[13]] while also compressing the Zn(1)···Zn(2) separation [3.069 Å *vs.* 3.209(4) Å (**1a**)[13]]; the range in intermetallic separations in complexes containing Zn(μ-$O_{phenolate}$)(μ-OH)Zn cores is 3.042–3.139 Å.[17] The bridging hydroxide [O(2)] is almost symmetrically disposed across the metal centres [Zn(1)–O(2) 1.998(3) Å *vs.* Zn(2)–O(2) 1.989(3) Å] while the phenolate bridge is more uneven [Zn(1)–O(1) 2.003(3) Å *vs.* Zn(2)–O(1) 2.148(3) Å]. No intermolecular contacts of note are present.

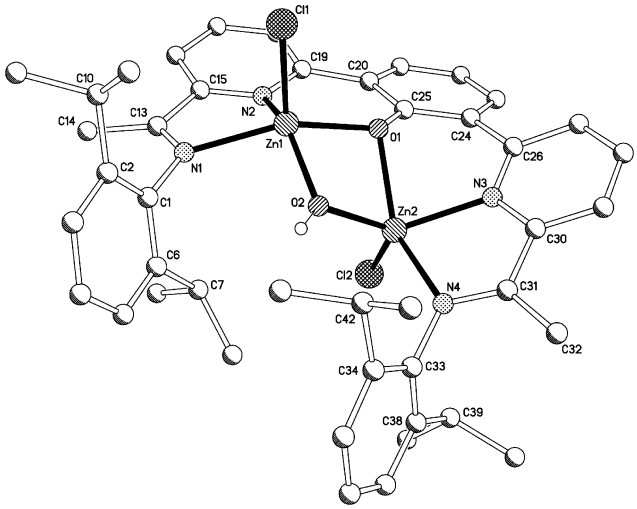

Fig. 5 Molecular structure of **4** with a partial atom labeling scheme; all hydrogen atoms, apart from H2, have been omitted for clarity.

Table 4 Selected bond distances (Å) and angles (°) for **4**

Zn(1)–O(1)	2.003(3)	Zn(2)–O(2)	1.989(3)
Zn(1)–O(2)	1.998(3)	Zn(2)–Cl(2)	2.214(2)
Zn(1)–Cl(1)	2.2547(17)	Zn(2)–N(3)	2.087(4)
Zn(1)–N(1)	2.145(4)	Zn(2)–N(4)	2.155(4)
Zn(1)–N(2)	2.134(4)	C(13)–N(1)	1.286(6)
Zn(1)...Zn(2)	3.069(4)	C(31)–N(4)	1.288(5)
Zn(2)–O(1)	2.148(3)		
N(1)–Zn(1)–O(1)	149.81(13)	N(3)–Zn(2)–O(2)	128.74(13)
N(2)–Zn(1)–O(2)	139.65(13)	Cl(2)–Zn(2)–O(2)	117.67(9)
O(1)–Zn(1)–O(2)	80.27(12)	O(1)–Zn(2)–O(2)	77.03(12)
Cl(1)–Zn(1)–O(2)	116.18(10)	Zn(1)–O(1)–Zn(2)	95.30(12)
N(4)–Zn(2)–O(1)	145.95(12)	Zn(1)–O(2)–Zn(2)	100.69(13)

Crystals of **5** suitable for the X-ray determination were grown from dichloromethane by slow diffusion of hexane at room temperature. A view of **5** is shown in Fig. 6; selected bond distances and angles are listed in Table 5. The structure of **5** is based on a

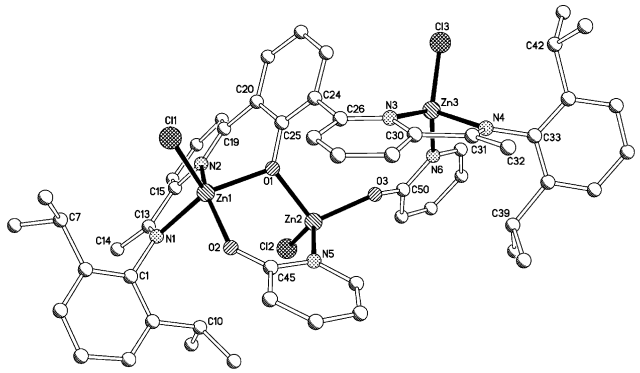

Fig. 6 Molecular structure of **5** with a partial atom labeling scheme; all hydrogen atoms apart from H1 have been omitted for clarity.

Table 5 Selected bond distances (Å) and angles (°) for **5**

Zn(1)–O(1)	2.014(5)	Zn(1) · · · Zn(2)	3.268(5)
Zn(1)–O(2)	2.008(6)	Zn(3)–Cl(3)	2.196(3)
Zn(1)–Cl(1)	2.268(2)	Zn(3)–N(3)	2.012(7)
Zn(1)–N(1)	2.131(7)	Zn(3)–N(4)	2.067(7)
Zn(1)–N(2)	2.149(7)	Zn(3)–N(6)	2.000(7)
Zn(2)–O(1)	2.004(5)	Zn(2) · · · Zn(3)	4.649(6)
Zn(2)–O(3)	1.939(6)	C(13)–N(1)	1.276(10)
Zn(2)–Cl(2)	2.217(3)	C(31)–N(4)	1.258(10)
Zn(2)–N(5)	1.965(8)		
N(1)–Zn(1)–O(1)	140.8(2)	N(5)–Zn(2)–Cl(2)	121.2(2)
N(2)–Zn(1)–O(2)	147.0(2)	Zn(1)–O(1)–Zn(2)	108.9(3)
Cl(1)–Zn(1)–O(1)	103.16(18)	N(3)–Zn(3)–Cl(3)	121.41(19)
Cl(1)–Zn(1)–O(2)	106.02(19)	N(3)–Zn(3)–N(4)	80.7(3)
N(5)–Zn(2)–O(1)	99.3(3)	N(3)–Zn(3)–N(6)	123.7(3)
N(5)–Zn(2)–O(3)	104.9(3)		

neutral trimetallic zinc complex in which L1 binds to all three zinc atoms with Zn(1) and Zn(2) 1,3-bridged by one pyridonate ligand and Zn(2) and Zn(3) by the other. In addition, each metal centre is bound by a terminal chloride ligand. As with **1a–4**, one of the zinc centres [Zn(1)] fills a tridentate *N*,*N*,*O*-cavity within L1 with the oxygen atom of the phenolate group additionally acting as a bridging ligand to Zn(2). Unlike **1a–4**, the pyridyl-imine unit in L1 no longer binds to Zn(2) but has twisted away [tors.: C(25)–C(24)–C(26)–N(3) 129.1°] so to act as a *N*,*N*-chelate to Zn(3). The result is that both distorted tetrahedral [Zn(2), Zn(3)] and square pyramidal geometries ($\tau = 0.1$)[15] are present within the complex. The pyridonate-bridged zinc atoms have considerably different intermetallic distances with the Zn(1) · · · Zn(2) distance [3.268(5) Å] being slightly longer than that seen in **1a**[13] while the Zn(2) · · · Zn(3) distance is significantly more elongated [4.649(6) Å]. Notably, the 1,3-bridging mode of the pyridonate ligands, while common place for other first row transition metals,[18] has not been reported for polyzinc complexes with crystallographically reported examples displaying a preference for the ligand to act as an *N*,*O*-chelate,[19] a 1,1-bridging ligand[20] or as a monodentate O-bound ligand.[21] No intermolecular contacts are apparent of note.

As with **1** the imino-methyl signals in the ^{1}H NMR spectrum of **4** are equivalent with a singlet evident at δ 2.26. The presence of four sharp doublets for the CH*Me*$_2$ protons (in a ratio of 6 : 6 : 6 : 6) in **4** suggests that rotation of both N-aryl groups and isopropyl substituents is severely restricted at room temperature. Interestingly, a similar observation in **1a** is only seen at low temperature;[13] it is tempting to ascribe this temperature difference to hydrogen bonding effects in **4**. The presence of the bridging hydroxide is supported by a weak band at 3480 cm^{-1} in the IR spectrum while a broad singlet is seen in its ^{1}H NMR spectrum at δ 3.5. The FAB mass spectrum for **4** shows fragmentation peaks corresponding to the loss of a hydroxide group from the molecular ion in **4**.

Despite repeated attempts at recrystallising **5**, the presence of complex **4** remained a constant side product and thus analytically pure samples of **5** could not be obtained. Nevertheless, the ^{1}H NMR spectrum showed, in addition to peaks for **4**, peaks consistent with the solid state structure with the inequivalent imino-methyl resonances visible at δ 2.30 and 2.31. In the FAB mass spectrum, a fragmentation peak corresponding to the loss of one pyridonate group from the molecular ion in **5** was evident.

The formation of a bridging hydroxide ligand in **4** during the reaction of **1a** with TlOEt was unexpected and the origin of the hydrolysis reaction is uncertain. It is noteworthy that Hillmyer *et al.* have also reported the difficulties in the reactions of related dizinc trichlorides with thallium ethoxides presumably in this case also forming hydroxide complexes.[8b] Indeed, the ready hydrolysis reactions of zinc halides have been reported elsewhere.[22] The presence of **4** as a significant by-product in the reaction of **1** with TlhpOH is likely due to the incomplete formation of TlhpOH (made *in-situ* from TlOEt and HhpOH) with the result that any unreacted TlOEt would undergo the hydrolysis reaction detailed above with L1-H. Notably, heating the mixture of **4** and **5** in air in acetonitrile did not lead to an increased ratio of **4** suggesting that **5** is hydrolytically stable under these conditions.

By analogy with the ethoxide-based dizinc catalysts reported by Tolman and Hillmyer,[8a,8b] it was envisioned that hydroxide **4** and the mixture of **4**/pyridonate **5** may also serve as catalysts for the ring opening of cyclic esters. Hence both were screened as catalysts for the ring-opening polymerisation of ε-caprolactone. Reactions were performed by mixing ε-caprolactone with a toluene solution of the initiator at a set temperature to provide an initial monomer concentration. Conversion to polycaprolactone was determined by ^{1}H NMR spectroscopy by removing aliquots at various intervals. Both **4** and **4**/**5** gave no evidence for any conversion after 72 h at room temperature. On running the reaction of **4** at 80 °C, trace conversion was observed after 72 h. On the other hand at 100 °C, 8% conversion could be achieved after 22 h while after 117 h a 55% conversion was noted. A similar reaction profile was observed for the mixture of **4**/**5** at 100 °C, albeit with slightly reduced levels of conversion.

It is uncertain why these systems display such low activities for ε-caprolactone polymerisation when compared to previously reported ethoxide-based dizinc systems,[8a,8b] but may be due to the relative nucleophilicity of a hydroxide/pyridonate nucleophile in **4**/**5** over an ethoxide (during the carbonyl attack step). Furthermore, the steric bulk of the aryl groups in **4** may also be impeding approach by an incoming molecule of ε-caprolactone.

3 Conclusions

In this study, we have shown that a family of chiral dizinc trichloride complexes of type **1** can be readily generated in

which the steric properties of the imino-aryl groups can be systematically varied. Derivatisation of **1a** by introducing a range of monoanionic ligands (*viz.* OAc, dbm, OH, hp) has been successfully undertaken leading to bimetallic (**2–4**) and trimetallic species (**5**) with intermetallic separations ranging from 3.069(4)–4.649(6) Å. Preliminary screening of **4** and **4/5** as initiators for the ring-opening polymerisation of ε-caprolactone reveals only modest activities/conversions.

4 Experimental

4.1 General

All reactions, unless otherwise stated, were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques or in a nitrogen purged glove box. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use.[23] The infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer on solid samples. The ESI (ElectroSpray) and the FAB (Fast atom bombardment) mass spectra were recorded using a micromass Quattra LC mass spectrometer and a Kratos Concept spectrometer with dichloromethane or NBA as the matrix, respectively. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX spectrometer (300 MHz) at ambient temperature unless otherwise stated; chemical shifts (δ) are referred to the residual protic solvent peaks and chemical shifts are in Hertz (Hz). Elemental analyses were performed at the Science Technical Support Unit, London Metropolitan University.

The reagents, 2,6-diisopropylaniline, 2,6-dimethylaniline, 2,4,6-trimethylaniline, 2,4-dimethylaniline, sodium acetate, thallium tetrafluoroborate, dibenzoylmethane, thallium ethoxide, 2-hydroxypyridine and zinc dichloride were purchased from Aldrich Chemical Co. and used without further purification; ε-caprolactone was distilled prior to use. The compounds, 2,6-{O=C(Me)C_5H_3N}$_2C_6H_3OH$[13] and L1-H[13] were prepared according to previously reported procedures. Nadbm was prepared by treating a methanolic solution of dibenzoylmethane (Hdbm) with an equimolar ratio of aqueous sodium hydroxide followed by drying of the product under reduced pressure. All other chemicals were obtained commercially and used without further purification.

4.2 Template synthesis of 1

(a) **1a**. An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with 2,6-{O=C(Me)C_5H_3N}$_2C_6H_3OH$ (0.300 g, 0.903 mmol), 2,6-diisopropylaniline (1.599 g, 9.027 mmol, 10 eq.), $ZnCl_2$ (0.271 g, 1.987 mmol, 2.2 eq.) and *n*-butanol (40 ml) and the contents stirred at 125 °C for 72 h. After cooling to room temperature, the suspension was concentrated to half volume and hexane introduced to complete the precipitation of the product. Following filtration and washing with hexane, the product was dried overnight under reduced pressure to afford [(L1)Zn_2(μ-Cl)Cl_2] (**1a**) as a yellow solid. Recrystallisation from acetonitrile gave **1a** as yellow blocks. Yield: 46% (0.368 g, 0.416 mmol). Compound **1a**: the spectroscopic data are as previously reported.[13]

(b) **1b**. Using the procedure described for **1a** with 2,6-{O=C(Me)C_5H_3N}$_2C_6H_3OH$ (0.300 g, 0.903 mmol), 2,6-dimethylaniline (1.094 g, 9.027 mmol, 10 eq.), $ZnCl_2$ (0.246 g, 1.805 mmol, 2 eq.) and *n*-butanol (40 ml) gave [(L2)Zn_2(μ-Cl)Cl_2] (**1b**) as yellow blocks. Yield: 45% (0.315 g, 0.401 mmol). Compound **1b**: ^{1}H NMR (300 MHz, $CDCl_3$): insoluble. IR (cm^{-1}): 1699 (w), 1634 (m), 1590 (s, ν(C=N)), 1567 (m), 1450 (s), 1413 (m), 1367 (m), 1260 (s), 1206 (s), 1110 (m), 1016 (m), 827 (m), 766 (s), 790 (s), 748 (s). MS (FAB): m/z 739 [M − Cl]$^+$. Anal. Calc. for $C_{36}H_{33}N_4OZn_2Cl_3$: C, 55.79; H, 4.26; N, 7.23. Found: C, 55.71; H, 4.22; N, 7.35%.

(c) **1c**. Using the procedure described for **1a** with 2,6-{O=C(Me)C_5H_3N}$_2C_6H_3OH$ (0.300 g, 0.903 mmol), 2,4,6-trimethylaniline (1.220 g, 9.027 mmol, 10 eq.), $ZnCl_2$ (0.246 g, 1.805 mmol, 2 eq.) and *n*-butanol (40 ml) gave [(L3)Zn_2(μ-Cl)Cl_2] (**1c**) as yellow blocks. Yield: 53% (0.384 g, 0.479 mmol). Compound **1c**: ^{1}H NMR (300 MHz, $CDCl_3$): insoluble. IR (cm^{-1}): 1635 (m), 1590 (s), 1568 (m), 1477 (m), 1454 (s), 1410 (m), 1366 (m), 1340 (w), 1253 (m), 1213 (s), 1184 (m), 1148 (w), 1111 (w), 1012 (m), 852 (s), 824 (m), 789 (s), 747 (s), 686 (w). MS (FAB): m/z 767 [M − Cl]$^+$. Anal. Calc. for $C_{38}H_{37}N_4OZn_2Cl_3$: C, 56.83; H, 4.61; N, 6.98. Found: C, 56.51; H, 4.22; N, 7.35%.

(d) **1d**. Using the procedure described for **1a** with 2,6-{O=C(Me)C_5H_3N}$_2C_6H_3OH$ (0.150 g, 0.451 mmol), 2,4-dimethylaniline (0.547 g, 4.513 mmol, 10 eq.), $ZnCl_2$ (0.135 g, 0.993 mmol, 2.2 eq.) and *n*-butanol (30 ml) gave [(L4)Zn_2(μ-Cl)Cl_2] (**1d**) as a yellow solid. Yield: 51% (0.178 g, 0.230 mmol). Compound **1d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03 (s, 6H, Ar–CH_3), 2.19 (s, 6H, Ar–CH_3), 2.25 (s, 6H, CH_3C=N), 6.85 (t, $^{3}J_{HH}$ 6.6 Hz, 1H, Phenolate-H_p), 6.9–7.0 (m, 6H, Ar–*H*), 7.66 (d, $^{3}J_{HH}$ = 6.6 Hz, 2H, Phenolate-H_o), 7.77 (d, $^{3}J_{HH}$ 7.8 Hz, 2H, Py-*H*), 7.9–8.1 (m, 4H, Py-*H*). IR (cm^{-1}): 1635 (m, ν(C=N)), 1591 (s), 1555 (m), 1494 (m), 1455 (s), 1369 (m), 1343 (m), 1308 (m), 1246 (m), 1220 (s), 1196 (m), 1148 (w), 1012 (m), 861 (m), 845 (s), 826 (m), 791 (s), 764 (s), 734 (m). MS (FAB): m/z 739 [M-Cl]$^+$. Anal. Calc. for $C_{36}H_{33}N_4OZn_2Cl_3$: C, 55.79; H, 4.26; N, 7.23. Found: C, 55.74; H, 4.24; N, 7.17%.

4.3 Synthesis of Lx–H

(a) **L2-H**. 2,6-{O=C(Me)C_5H_3N}$_2C_6H_3OH$ (0.500 g, 1.504 mmol) was suspended in 2,6-dimethylaniline (1.823 g, 15.044 mmol, 10 eq.) and stirred for 15 min at 160 °C until dissolution. A catalytic amount of formic acid was added, and the reaction mixture was stirred for an additional 30 min at this temperature. Following removal of the excess 2,6-dimethylaniline under reduced pressure, the resulting brown residue was stirred in ethanol before being cooled to −30 °C to afford a yellow precipitate. The precipitate was collected by filtration and washed with cold ethanol to afford 2,6-{(2,6-$Me_2C_6H_3$)N=C(Me)C_5H_3N}$_2C_6H_3OH$ (L2-H) as a yellow solid. Yield: 45% (0.361 g, 0.670 mmol). Compound L2-H: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.98 (s, 12H, Ar–CH_3), 2.19 (s, 6H, CH_3C=N), 6.88 (m, 2H, Ar–*H*), 7.0–7.09 (m, 5H, Ar–*H* and Phenol-*H*), 7.87 (t, $^{3}J_{HH}$ = 7.8, 2H, Py-*H*), 7.00 (d, $^{3}J_{HH}$ = 7.8, 2H, Phenol-*H*), 8.14 (d, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 0.9 Hz, 2H, Py-*H*), 8.26 (d, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 0.9 Hz, 2H, Py-*H*). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): 16.8 (*C*H_3C=N), 18.0 (*C*H_3Ar), 119.1 (CH), 119.4 (CH), 123.2 (CH), 123.7 (CH), 124.1, 125.4, 128.0 (CH), 130.5 (CH), 137.4 (CH), 148.6, 154.5, 155.7, 158.0, 166.4 (C=N). IR (cm^{-1}): 1638 (m), 1592 (m), 1567 (m), 1470 (m), 1450 (m), 1362 (m), 1267 (m), 1207 (m), 1170 (w), 1138 (w), 1112 (m), 825 (w),

815 (w), 783 (s), 762 (s), 741 (s), 691 (w). MS (ESI): *m/z* 539 [*M* + H]$^+$. Anal. Calc. for $C_{36}H_{34}N_4O$: C, 80.30; H, 6.32; N 10.41%. Found: C, 80.55; H, 6.48; N, 10.27%.

(b) **L3-H**. A similar procedure to that outlined for L2-H was employed using 2,6-{O=C(Me)C_5H_3N}$_2C_6H_3OH$ (0.500 g, 1.504 mmol) in 2,4,6-trimethylaniline (2.034 g, 15.044 mmol, 10 eq.) gave 2,6-{(2,4,6-$Me_3C_6H_2$)N=C(Me)C_5H_3N}$_2C_6H_3OH$ (L3-H) as a yellow solid. Yield: 49% (0.415 g, 0.732 mmol). Compound L3-H: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.94 (s, 12H, Ar–C*H*$_3$), 2.18 (s, 6H, Ar–C*H*$_3$), 2.23 (s, 6H, C*H*$_3$C=N), 6.83 (s, 4H, Ar–*H*), 7.04 (t, 1H, $^3J_{HH}$ = 7.8 Hz, Phenol-*H*), 7.87 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Py-*H*), 7.97 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Phenol-*H*), 8.13 (d, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 0.9 Hz, 2H, Py-*H*), 8.25 (d, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 0.9 Hz, 2H, Py-*H*). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): 16.8 (*C*H$_3$C=N), 17.9 (*C*H$_3$Ar), 20.8 (*C*H$_3$Ar), 119.1 (CH), 119.4 (CH), 123.6 (CH), 124.2, 125.3, 128.6 (CH), 130.5 (CH), 132.3, 137.4 (CH), 146.1, 154.6, 155.7, 158.0, 166.6 (C=N). IR (cm^{-1}): 1635 (m), 1567 (m), 1476 (w), 1449 (m), 1363 (m), 1264 (m), 1215 (m), 1138 (w), 1112 (w), 850 (m), 824 (w) and 783 (s), 742 (s). MS (ESI): *m/z* 567 [*M* + H]$^+$. Anal. Calc. for $C_{38}H_{38}N_4O$: C, 80.42; H, 6.71; N 9.89%. Found: C, 80.72; H, 6.76; N, 9.79%.

(c) **L4-H**. A similar procedure to that outlined for L2-H was employed using 2,6-{O=C(Me)C_5H_3N}$_2C_6H_3OH$ (0.200 g, 0.602 mmol) in 2,4-dimethylaniline (0.729 g, 6.018 mmol, 10 eq.) gave L4-H as a yellow solid. Yield: 40% (0.130 g, 0.241 mmol). Compound L4-H: ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.04 (s, 6H, Ar–C*H*$_3$)), 2.26 (s, 6H, Ar–C*H*$_3$), 2.30 (s, 6H, C*H*$_3$C=N), 6.52 (m, 2H, Ar–*H*), 6.93–7.04 (m, 5H, Ar–*H* and Phenol-*H*), 7.82–7.88 (m, 2H, Py-*H*), 7.97 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Phenol-*H*), 8.13 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Py-*H*), 8.19 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Py-*H*). IR (cm^{-1}): 1640 (m, *v*(C=N)), 1591 (m), 1564 (w), 1494 (m), 1448 (m), 1363 (w), 1262 (m), 1217 (w), 1079 (br), 786 (s), 745 (m). MS (ESI) (*m/z*): 539 [*M* + H]$^+$. Anal. Calc. for $C_{36}H_{34}N_4O$: C, 80.30; H, 6.32; N 10.41%. Found: C, 80.46; H, 6.49; N, 10.19%.

4.4 Synthesis of 1 from Lx–H

(a) **1b from L2-H**. An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with $ZnCl_2$ (0.127 g, 0.928 mmol) in *n*-butanol (30 ml) and the contents heated to 110 °C until the zinc salt had completely dissolved. L2-H (0.250 g, 0.464 mmol, 0.5 eq.) was added and the mixture stirred and heated to 110 °C overnight. After cooling to room temperature, the suspension was concentrated and washed several times with hexane to afford [(L2)Zn_2(μ-Cl)Cl_2] (**1b**) as a yellow solid. Yield: 85% (0.305 g, 0.394 mmol). Compound **1b**: the spectroscopic data were as described in section 4.2(b).

(b) **1c from L3-H**. Using a procedure based on that described for **1b** employing $ZnCl_2$ (0.120 g, 0.822 mmol) and L3-H (0.250 g, 0.441 mmol, 0.5 eq.) gave [(**L3**)Zn_2(μ-Cl)Cl_2] (**1c**) as a yellow solid. Yield: 78% (0.275 g, 0.343 mmol). Compound **1c**: the spectroscopic data were as described in section 4.2(c).

(c) **1d from L4-H**. Using a procedure based on that described for **1b** employing $ZnCl_2$ (0.319 g, 2.343 mmol) and L4-H (0.631 g, 1.171 mmol, 0.5 eq.) afforded [(L4)Zn_2(μ-Cl)Cl_2] (**1d**) as a yellow solid. Yield: 29% (0.262 g, 0.338 mmol). Compound **1d**: the spectroscopic data were as described in section 4.2(d).

4.5 Synthesis of 2

An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with **1a** (0.100 g, 0.113 mmol), NaOAc (0.019 g, 0.226 mmol, 2 eq.) and suspended in acetonitrile (8 ml) and stirred for 15 min at room temperature. $TlBF_4$ (0.049 g, 0.169 mmol, 1.5 eq.) was added and the reaction mixture allowed to stir for a further 24 h. The solution was filtered through Celite and concentrated under reduced pressure to give a yellow solid residue. The residue was crystallised from acetonitrile solution to afford [(L1)Zn_2(μ-OAc)$_2$](BF_4) (**2**) as yellow crystals. Yield: 45% (0.050 g, 0.051 mmol). Compound **2**: ^{1}H NMR (300 MHz, CD_3CN): δ 0.91 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 0.98 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.93 (s, 6H, C*H*$_3$CO$_2$), 2.36 (s, 6H, C*H*$_3$C=N), 2.69 (br, 4H, C*H*(CH$_3$)$_2$), 6.9–7.2 (m, 7H, Ar–*H* and Phenolate-*H*$_p$), 7.62 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Py-*H*), 7.8–7.9 (m, 2H, Py–*H*), 8.2–8.4 (m, 4H, Phenolate-*H*$_m$ and Py–*H*). ^{19}F NMR (283.5 MHz, $CDCl_3$): δ 152.36 (s, BF_4). IR (cm^{-1}): 2964 (w), 1636 (m), 1589 (s, *v*(COO)$_{asym}$ and *v*(C=N)), 1442 (s), 1408 (s, *v*(COO)$_{sym}$), 1369 (m), 1326 (w), 1255 (m), 1198 (m), 1048 (br, *v*(B–F)), 937 (m), 861 (m), 825 (m), 792 (s), 775(s) and 747 (s). MS (FAB): *m/z* 899 [*M* − BF_4]$^+$, 855 [*M* − MeCO − BF_4]$^+$. Anal. Calc. for $C_{48}H_{55}N_4O_5BF_4Zn_2$: C, 58.50; H, 5.59; N, 5.69. Found: C, 58.71; H, 5.62; N, 5.44%.

4.6 Synthesis of 3

An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. Complex **1a** (0.100 g, 0.113 mmol) and Nadbm (0.056 g, 0.226 mmol, 2 eq.) were introduced, dissolved in acetonitrile (8 ml) and stirred for 15 min at room temperature. $TlBF_4$ (0.049 g, 0.169 mmol, 1.5 eq.) was added to the reaction mixture and the contents allowed to stir for 72 h. Following filtration through Celite, the filtrate was concentrated under reduced pressure and the yellow solid residue dissolved in chloroform (10 ml) and layered with hexane (20 ml). After standing for three days [(L1)Zn_2(dbm)$_2$](BF_4) (**3**) was obtained as pale yellow blocks. Yield: 71% (0.105 g, 0.08 mmol). Compound **3**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.6–0.7 (m, 24H, CH(C*H*$_3$)$_2$), 2.29 (s, 6H, C*H*$_3$C=N), 2.61 (br, 4H, C*H*(CH$_3$)$_2$), 5.79 (s, 2H, C*H*(CPhCO)$_2$)), 6.7–7.5 (m, 29H, Ar–*H*, Py–*H* or Phenolate-*H*$_p$), 7.90 (m, 2H, Ar–*H*), 8.1–8.3 (m, 4H, Py-*H* or Phenolate-*H*$_m$). ^{19}F NMR (283.5 MHz, $CDCl_3$): δ 153.6 (s, BF_4). IR (cm^{-1}): 2965 (w), 1636 (w), 1592 (s), 1545 (s), 1519 (s), 1479 (m), 1452 (s), 1381 (s), 1303 (w), 1269 (m), 1198 (m), 1054 (br, *v*(B–F)), 937 (m), 852 (m), 827 (m), 792 (s), 754 (s) and 689 (s). MS (FAB): *m/z* 1226 [*M* − BF_4]$^+$, 1004 [*M* − dbm − BF_4]$^+$. Anal. Calc. for $C_{74}H_{71}N_4O_5BF_4Zn_2$: C, 67.65; H, 5.41; N, 4.27. Found: C, 67.89; H, 5.30; N, 4.19%.

4.7 Synthesis of 4

An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with **1a** (0.100 g, 0.110 mmol) and dissolved in dichloromethane (5 ml) before being cooled to 0 °C. A solution of TlOEt (29 mg, 8.2 μl, 0.110 mmol, 1 eq.) in dichloromethane (5 ml) in a second Schlenk flask was cannular filtered into the flask containing **1a** to give an instantaneous formation of a creamy precipitate. The reaction mixture was stirred at room temperature for a further

Table 6 Crystallographic and data processing parameters for **1b**, **1c**, **2**, **3**, **4** and **5**[a]

Complex	**1b**	**1c**[b]	**2**	**3**	**4**	**5**
Formula	$C_{36}H_{33}N_4OZn_2Cl_3\cdot 2.5CH_3CN$	$C_{38}H_{37}N_4OZn_2Cl_3\cdot 2CH_3CN$	$C_{48}H_{55}BF_4N_4O_5Zn_2\cdot 0.5CH_3CN\cdot 0.25H_2O$	$C_{37}H_{35.5}B_{0.5}F_2N_2O_{2.5}Zn\cdot 2CHCl_3$	$C_{44}H_{50}N_4O_2Zn_2Cl_2\cdot CHCl_3$	$C_{54}H_{57}Cl_3N_6O_3Zn_3\cdot 4CH_2Cl_2$
M	877.39	884.91	1010.54	895.69	987.89	1480.22
Crystal size/mm^3	0.36 × 0.32 × 0.06	0.33 × 0.19 × 0.07	0.31 × 0.26 × 0.13	0.20 × 0.12 × 0.09	0.28 × 0.19 × 0.09	0.27 × 0.12 × 0.09
Temperature/K	150	150	150	150	150	150
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$\bar{P}1$	$P2(1)$	$\bar{P}1$	$C2/c$	$\bar{P}1$	$\bar{P}1$
a/Å	11.756(4)	11.894(12)	15.005(3)	16.694(5)	12.406(10)	14.552(5)
b/Å	13.837(5)	25.95(2)	16.307(3)	31.326(9)	13.866(11)	15.446(5)
c/Å	25.758(10)	13.804(14)	22.415(4)	16.280(5)	14.110(12)	16.558(6)
α/°	96.318(6)	90	79.668(3)	90	81.701(15)	115.106(5)
β/°	90.532(7)	102.102(18)	85.727(3)	99.124(7)	76.356(15)	94.580(6)
γ/°	101.770(7)	90	66.039(3)	90	75.449(16)	102.681(5)
U/Å^3	4075(3)	4166(7)	4930.6(14)	8406(4)	2274(3)	3253.7(19)
Z	4	4	4	8	2	2
D_c/Mg m^{-3}	1.430	1.411	1.361	1.415	1.443	1.511
$F(000)$	1804	1824	2102	3664	1020	1512
μ(Mo–K$_\alpha$)(mm^{-1})	1.415	1.384	1.038	1.011	1.390	1.596
Reflections collected	29375	32596	38847	30280	16513	23469
Independent reflections	14208	16235	19140	7414	7944	11343
R_{int}	0.0681	0.0666	0.0510	0.1789	0.0534	0.1090
Restraints/parameters	0/841	1/1003	0/1214	0/427	0/497	0/632
Final R indices	$R1 = 0.0661$	$R1 = 0.0548$	$R1 = 0.0601$	$R1 = 0.0778$	$R1 = 0.0553$	$R1 = 0.0758$
($I > 2\sigma(I)$)	$wR2 = 0.1530$	$wR2 = 0.0815$	$wR2 = 0.1291$	$wR2 = 0.1521$	$wR2 = 0.1132$	$wR2 = 0.1565$
All data	$R1 = 0.0924$	$R1 = 0.0920$	$R1 = 0.0987$	$R1 = 0.1779$	$R1 = 0.0812$	$R1 = 0.1720$
	$wR2 = 0.1617$	$wR2 = 0.0909$	$wR2 = 0.1426$	$wR2 = 0.1823$	$wR2 = 0.1206$	$wR2 = 0.1810$
Goodness of fit on F^2 (all data)	0.932	0.865	0.971	0.816	0.938	0.781

[a] Data in common: graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å; $R_1 = \Sigma \| F_o \| - | F_c \| / \Sigma | F_o |$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2]$, $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$, where a is a constant adjusted by the program; goodness of fit $= [\Sigma (F_o^2 - F_c^2) 2/(n-p)]^{1/2}$ where n is the number of reflections and p the number of parameters; [b] Flack parameter = 0.523(12).

12 h. Additional dichloromethane (10 ml) was added and the mixture cannular filtered to give a pale yellow filtrate. The filtrate was concentrated under reduced pressure and the solid residue taken up in chloroform (10 ml) and layered with diethyl ether (30 ml). After standing for three days [(L1)Zn_2(μ-OH)Cl_2] (**4**) was obtained as pale yellow blocks. Yield 86% (0.084 g, 0.100 mmol). Compound **4**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.63 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH(CH_3)$_2$), 0.79 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH(CH_3)$_2$)), 0.99 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(CH_3)$_2$)), 1.18 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH(CH_3)$_2$), 2.26 (s, 6H, CH_3C=N), 2.81 (sept, $^3J_{HH}$ = 6.4 Hz, 2H, CH(CH$_3$)$_2$), 3.01 (sept, $^3J_{HH}$ = 6.7 Hz, 2H, CH(CH$_3$)$_2$), 3.50 (s, br, 1H, O-*H*), 6.72 (t, $^3J_{HH}$ = 7.9 Hz, 1H, Phenolate-H_p), 6.93 (t, $^3J_{HH}$ = 4.7 Hz, 2H, Ar-*H*), 7.12 (m, 4H, Ar-*H*), 7.71 (m, 4H, Ar-*H*, Py-*H*), 7.98 (m, 4H, Ph-*H*, Py-*H*). IR (cm^{-1}): 3480 (w, br, *ν*(OH)), 2964 (m), 1634 (w), 1589 (m, *ν*(C=N)), 1547 (w), 1456 (m), 1406 (w), 1383 (w), 1366 (m), 1325 (w), 1258 (s), 1193 (m), 1087 (s), 1015 (s), 935 (w), 865 (m), 794 (s), 688 (m). MS (FAB): *m*/*z* 851 [*M* − OH]$^+$. Anal. Calc. for $C_{44}H_{50}N_4O_2Cl_2Zn_2.CHCl_3$: C, 54.72; H, 5.16; N, 5.67. Found: C, 54.55; H, 5.29; N, 5.23%.

4.8 Synthesis of 4 and 5

An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with 2-hydroxypyridine (0.011 g, 0.11 mmol) and dissolved in acetonitrile (10 ml). TlOEt (8.2 μl, 0.11 mmol) was introduced into the flask to give an instantaneous formation of a creamy precipitate and the suspension stirred for 15 min. Compound **1a** (0.100 g, 0.11 mmol) was added and the reaction mixture stirred at room temperature for a further 12 h. The volatiles were removed under reduced pressure and the residue taken up in dichloromethane (30 ml). Following cannular filtration, the filtrate was concentrated to half volume and layered with hexane (ratio of CH_2Cl_2 to hexane = 1 : 3). After standing for one week, yellow crystals of both **4** and [(L1)Zn_3(μ-hp)$_2$$Cl_3$] (**5**) in a 3 : 7 ratio (by ^{1}H NMR) could be obtained. Combined yield 65%. Compound **4**: the spectroscopic data were as described in section 4.7. Compound **5**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.38 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH(CH_3)$_2$), 0.79 (m, 3H, CH(CH_3)$_2$)), 0.90 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$)), 1.00 (m, 3H, CH(CH_3)$_2$), 1.10 (m, 3H, CH(CH_3)$_2$), 1.34 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(CH_3)$_2$)), 2.30 (s, 3H, CH_3C=N), 2.31 (s, 3H, CH_3C=N), 2.60 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, CH(CH$_3$)$_2$), 2.93 (sept, $^3J_{HH}$ = 6.7 Hz, 1H, CH(CH$_3$)$_2$), 3.04 (m, 1H, CH(CH$_3$)$_2$), 3.28 (sept, $^3J_{HH}$ = 6.7 Hz, 1H, CH(CH$_3$)$_2$), 5.90 (t, $^3J_{HH}$ = 5.8 Hz, 1H, pyridonate-*H*), 6.17 (d, $^3J_{HH}$ = 8.7 Hz, 1H, pyridonate-*H*), 6.26 (t, $^3J_{HH}$ = 6.3 Hz, 1H, pyridonate-*H*), 6.7–8.1 (m, 19H, phenolate-*H*, Py-*H*, Ar-*H*, pyridonate-*H*), 8.73 (dd, $^3J_{HH}$ = 6.5 Hz, $^3J_{HH}$ = 2.6, 1H, pyridonate-*H*). MS (FAB): *m*/*z* 909 [*M* − 2 Cl − Zn − hp]$^+$.

4.9 Solution ε-CL polymerisation procedure

An oven dried 100 ml Schlenk vessel equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The vessel was charged with the catalyst (0.02 mmol, 1 eq.) and dissolved in toluene (5 mL). Into this solution was added freshly distilled ε-caprolactone (50 eq.) and the polymerisation reaction mixture commenced by lowering the reaction vessel into an oil bath at set temperature. After stirring for an appropriate time, an aliquot (*ca.* 100 μl) was withdrawn, quenched with a drop of pentane and dried under reduced pressure at room temperature. Conversion was determined by observing the ^{1}H NMR resonances of the polymer and monomer by dissolving in $CDCl_3$.

4.10 Crystallographic studies

Data collection for **1b**, **1c**, **2**, **3**, **4** and **5** was carried out on a Bruker APEX 2000 CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Details of the data collection, refinement and crystal data are listed in Table 6. The data were corrected for Lorentz and polarization effects and empirical absorption corrections applied. Structure solution by direct methods and structure refinement on F^2 employed SHELXTL version 6.10.[24] Hydrogen atoms were included in calculated positions (C–H = 0.96 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5 U_{eq}(C) for methyl H atoms and 1.2 U_{eq}(C) for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters. In the case of **3**, the BF_4 anion was disordered over a two-fold axis. For **1b**, **2**, **4** and **5**, the SQUEEZE option in PLATON[25] was used to remove the disorder solvent molecules.

CCDC reference numbers 651128–651133.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709385c

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