Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Chiral Alkaline-Earth Metal Complexes Having M-Se Direct Bond (M = Mg, Ca, Sr, Ba): Syntheses, Structures and ε-Caprolactone Polymerisation

Ravi K. Kottalanka,[a] Adimulam Harinath,[a] and Tarun K. Panda*[a]

[a]*Department of Chemistry, Indian Institute of Technology Hyderabad, Ordnance Factory Estate, Yeddumailaram 502205, Telangana, India. Fax: + 91(40) 2301 6032; Tel: + 91(40) 2301 6036; E-mail: tpanda@iith.ac.in*

List of Content:

1. Table TS1. Crystallographic data and structure refinement parameters for complexes **1a,b, 4a,b-8a,b.**

Crystal	**1a**	**1b**	**4a**	**4b**	**5a**	**5b**
CCDC No.	1053400	1053401	1053402	1053403	1053404	1053405
Empirical formula	$C_{20}H_{20}NPSe$	$C_{20}H_{20}NPSe$	$C_{48}H_{54}CaN_2O_2P_2Se_2$	$C_{48}H_{54}CaN_2O_2P_2Se_2$	$C_{48}H_{54}N_2O_2P_2Se_2Sr$	$C_{48}H_{54}N_2O_2P_2Se_2Sr$
Formula weight	384.30	384.30	950.87	950.87	998.41	998.41
T (K)	293(2)	293(2)	150(2)	150(2)	150(2)	150(2)
λ (Å)	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\,1$	$P\,1$	$P\,2_1$	$P\,2_1$	$P\,2_1$	$P\,2_1$
a (Å)	6.0159(11)	6.0127(12)	13.0607(5)	13.0797(10)	12.5000(7)	12.4934(6)
b (Å)	9.3867(17)	9.368(3)	14.5382(5)	14.5246(8)	14.6217(4)	14.6187(7)
c (Å)	9.5866(17)	9.581(3)	13.6308(6)	13.6284(14)	13.9074(8)	13.9134(6)
α (°)	106.872(16)	106.91(3)	90	90	90	90
β (°)	107.869(16)	107.98(2)	118.032(5)	117.984(11)	115.038(7)	115.041(5)
γ (°)	103.345(15)	103.26(2)	90	90	90	90
V (Å^3)	461.65(14)	459.9(2)	2284.57(15)	2286.4(3)	2303.0(2)	2302.25(19)
Z	1	1	2	2	2	2
D_{calc} g cm^{-3}	1.382	1.388	1.382	1.381	1.440	1.439
μ (mm^{-1})	3.545	3.558	3.971	3.968	4.391	4.393
F (000)	196	196	980	980	1016	1014
Theta range for data collection	5.26 to 70.94 deg.	5.27 to 71.98 deg.	3.67 to 70.76 deg.	4.77 to 70.73 deg.	3.51 to 70.58 deg.	3.51 to 70.63 deg.
Limiting indices	-7<=h<=7 -11<=k<=8 -11<=l<=11	-7<=h<=6 -11<=k<=11 -11<=l<=11	-14<=h<=15 -9<=k<=17 -16<=l<=16	-11<=h<=15 -17<=k<=10 -16<=l<=15	-14<=h<=15 -17<=k<=17 -17<=l<=16	-15<=h<=14 -13<=k<=17 -16<=l<=16
Reflections collected / unique	3019 / 2114 [R(int) = 0.0216]	3475 / 2382 [R(int) = 0.0218]	9628 / 6006 [R(int) = 0.0310]	6267 / 4638 [R(int) = 0.0342]	10051 / 6833 [R(int) = 0.0397]	11230 / 6302 [R(int) = 0.0424]
Completeness to theta = 71.25	96.6 % (70.94)	95.2 % (71.98)	97.9 % (70.76)	93.8 % (70.73)	97.8 % (70.58)	98.2 % (70.63)
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	1.00000 and 0.25106	1.00000 and 0.78826	1.00000 and 0.62045	1.00000 and 0.64464	1.00000 and 0.71299	1.00000 and 0.52179
Refinement method	Full-matrix	Full-matrix least-	Full-matrix least-	Full-matrix least-	Full-matrix least-	Full-matrix least-

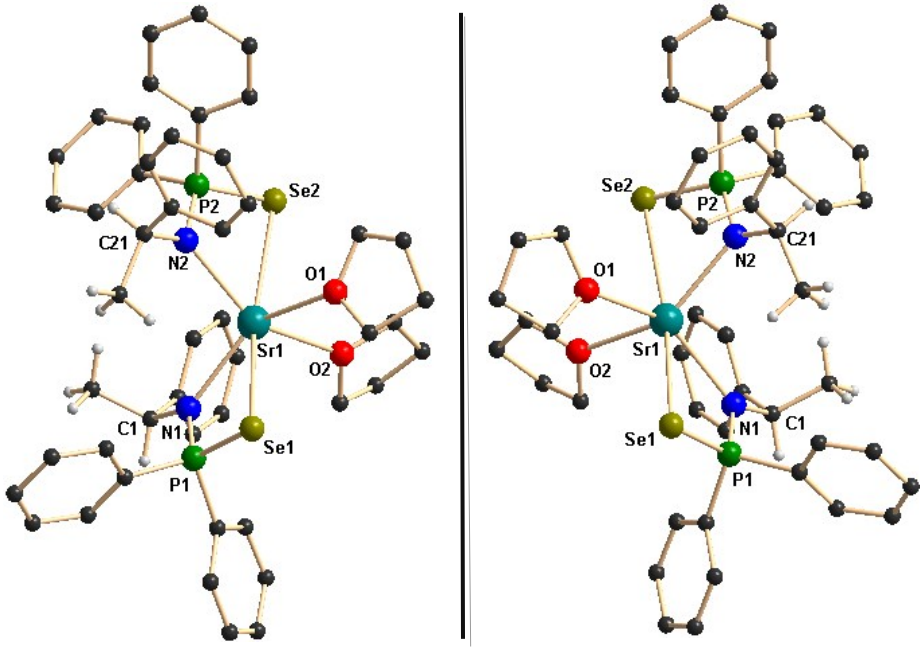
	least-squares on F^2	squares on F^2	squares on F^2	squares on F^2	squares on F^2	squares on F^2
Data / restraints / parameters	2114 / 3 / 210	2382 / 3 / 211	6006 / 1 / 517	4638 / 1 / 517	6833 / 1 / 517	6302 / 1 / 517
Goodness-of-fit on F^2	1.086	1.015	1.025	1.047	1.049	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0544, wR2 = 0.1402	R1 = 0.0542, wR2 = 0.1610	R1 = 0.0342, wR2 = 0.0874	R1 = 0.0424, wR2 = 0.1104	R1 = 0.0602, wR2 = 0.1622	R1 = 0.0402, wR2 = 0.0979
R indices (all data)	R1 = 0.0547, wR2 = 0.1417	R1 = 0.0552, wR2 = 0.1657	R1 = 0.0359, wR2 = 0.0895	R1 = 0.0455, wR2 = 0.1146	R1 = 0.0650, wR2 = 0.1697	R1 = 0.0464, wR2 = 0.1032
Absolute structure parameter	0.00(5)	0.01(5)	0.002(13)	-0.05(3)	0.00(3)	0.00(2)
Largest diff. peak and hole	0.885 and -0.394 $e.A^{-3}$	0.618 and -0.735 $e.A^{-3}$	0.455 and -0.607 $e.A^{-3}$	0.473 and -0.761 $e.A^{-3}$	1.680 and -0.805 $e.A^{-3}$	0.722 and -0.756 $e.A^{-3}$

Table 1. Crystallographic data and structure refinement parameters for complexes **1a,b, 4a,b-8a,b. (contd.)**

Crystal	**6a**	**6b**	**7a**	**7b**	**8a**	**8b**
CCDC No.	1053406	1053407	1053408	1053409	1053410	1053411
Empirical formula	$C_{48}H_{54}BaN_2O_2P_2Se_2$	$C_{48}H_{54}BaN_2O_2P_2Se_2$	$C_{20}H_{23}BNP$	$C_{20}H_{23}BNP$	$C_{48}H_{60}B_2BaN_2O_2P_2$	$C_{48}H_{60}B_2BaN_2O_2P_2$
Formula weight	1048.12	1048.12	319.17	319.17	917.87	917.87
T (K)	150(2)	150(2)	293(2)	293(2)	150(2)	150(2)
λ (Å)	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\,2_1$	$P\,2_1$	$P\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1$	$P\,2_1$
a (Å)	12.5451(2)	12.5571(3)	11.3581(10)	8.8785(2)	13.1696(9)	13.1465(5)
b (Å)	14.6496(3)	14.6478(3)	6.1729(5)	18.0839(4)	14.8039(4)	14.7929(3)
c (Å)	14.0905(2)	14.0913(4)	13.3347(12)	23.6013(6)	13.7579(9)	13.7413(7)
α (°)	90	90	90	90	90	90
β (°)	115.323(2)	115.305(3)	90.752(8)	90	117.394(9)	117.316(5)
γ (°)	90	90	90	90	90	90

V (Å^3)	2340.73(7)	2343.16(10)	934.85(14)	3789.38(15)	2381.5(2)	2374.34(16)
Z	2	2	2	8	2	2
D_{calc} g cm^{-3}	1.487	1.486	1.134	1.119	1.280	1.284
μ (mm^{-1})	9.319	9.309	1.264	1.247	7.403	7.425
F (000)	1052	1052	340	1360	948	948
Theta range for data collection	3.47 to 70.86 deg.	3.47 to 71.12 deg.	3.31 to 70.69 deg.	3.08 to 70.72 deg.	3.62 to 70.75 deg.	3.62 to 70.78 deg.
Limiting indices	-14<=h<=15 -14<=k<=17 -16<=l<=17	-13<=h<=15 -12<=k<=17 -16<=l<=17	-13<=h<=13 -7<=k<=7 -16<=l<=13	-9<=h<=10 -18<=k<=21 -28<=l<=26	-16<=h<=12 -16<=k<=18 -10<=l<=16	-16<=h<=15, -10<=k<=17, -15<=l<=16
Reflections collected / unique	9480 / 6551 [R(int) = 0.0284]	10629 / 6444 [R(int) = 0.0436]	3685 / 2609 [R(int) = 0.0280]	10266 / 5991 [R(int) = 0.0257]	10805 / 7370 [R(int) = 0.0310]	11397 / 6453 [R(int) = 0.0320]
Completeness to theta = 71.25	98.2 % (70.86)	98.1 % (71/12)	97.7 %	98.0 % (70.72)	98.1 % (70.75)	97.5 %
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	1.00000 and 0.39804	1.00000 and 0.31944	1.00000 and 0.86951	1.00000 and 0.66265	1.00000 and 0.66652	1.00000 and 0.51058
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6551 / 1 / 519	6444 / 1 / 516	2609 / 1 / 211	5991 / 0 / 420	7370 / 1 / 540	6453 / 1 / 541
Goodness-of-fit on F^2	1.031	1.061	1.044	1.034	1.004	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.1042	R1 = 0.0538, wR2 = 0.1402	R1 = 0.0478, wR2 = 0.1179	R1 = 0.0418, wR2 = 0.1102	R1 = 0.0357, wR2 = 0.0905	R_1 = 0.0333, wR_2 = 0.0843
R indices (all data)	R1 = 0.0394, wR2 = 0.1047	R1 = 0.0543, wR2 = 0.1412	R1 = 0.0573, wR2 = 0.1285	R1 = 0.0456, wR2 = 0.1169	R1 = 0.0650, wR2 = 0.1697	R1 = 0.0464, wR2 = 0.1032
Absolute structure parameter	-0.009(3)	-0.004(4)	0.00(4)	0.000(19)	-0.021(4)	-0.019(4)
Largest diff. peak and hole	1.081 and -1.064 e.A^{-3}	1.568 and -1.383 e.A^{-3}	0.140 and -0.297 e.A^{-3}	0.381 and -0.530 e.A^{-3}	1.680 and -0.805 e.A^{-3}	0.722 and -0.756 e.A^{-3}

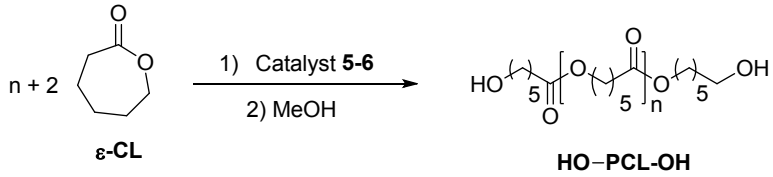
2. Figure S1. Solid state structures of calcium complexes **5a** and **5b**. Hydrogen atoms are omitted for clarity except methyl and methine hydrogen atoms.



5a (***R***-isomer) **Mirror** **5b** (***S***-isomer)

3. Typical polymerization procedure:

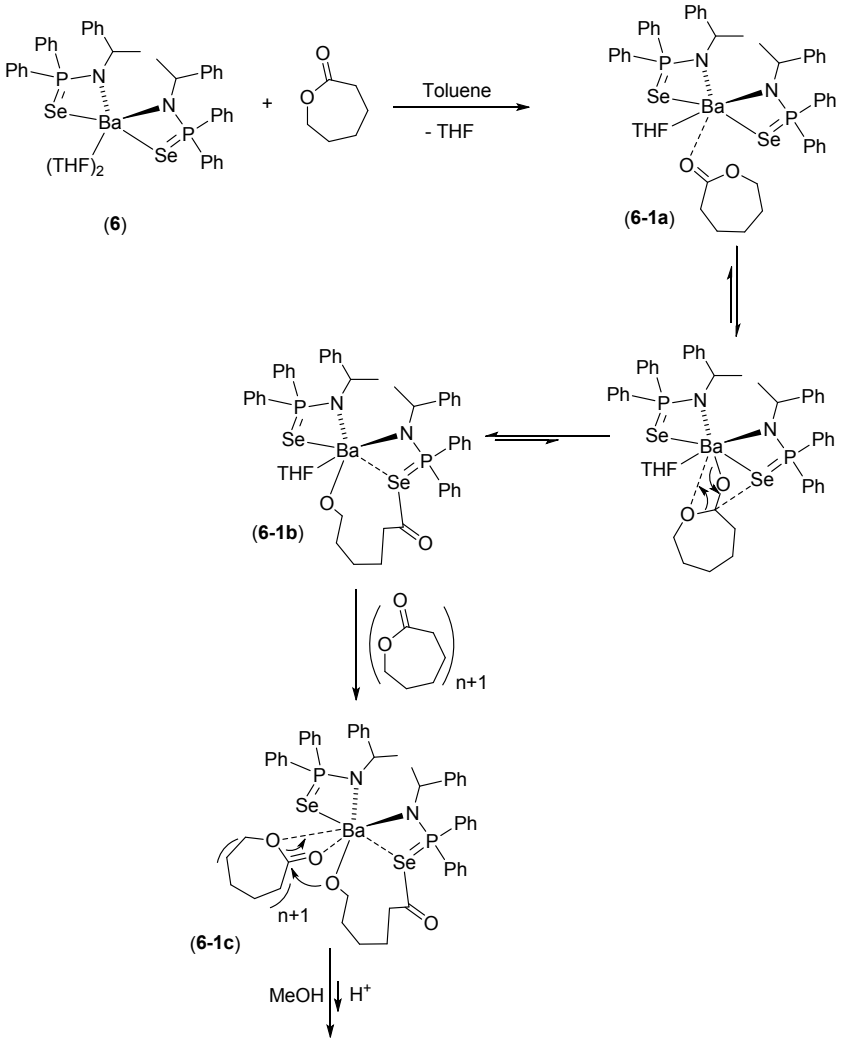
In a glove box under argon atmosphere, the catalyst was dissolved in the appropriate amount (1.0 ml) of dry toluene. ε-caprolactone in 1.0 mL of toluene was then added under vigorous stirring. The reaction mixture was stirred at room temperature for 5–20 minutes, after which the reaction mixture was quenched by addition of a small amount of (1.0 ml) methanol and then added acidified methanol little excess. The polymer was precipitated in excess methanol and it was filtered and dried under vacuum. The final polymer was then analysed by NMR and GPC.



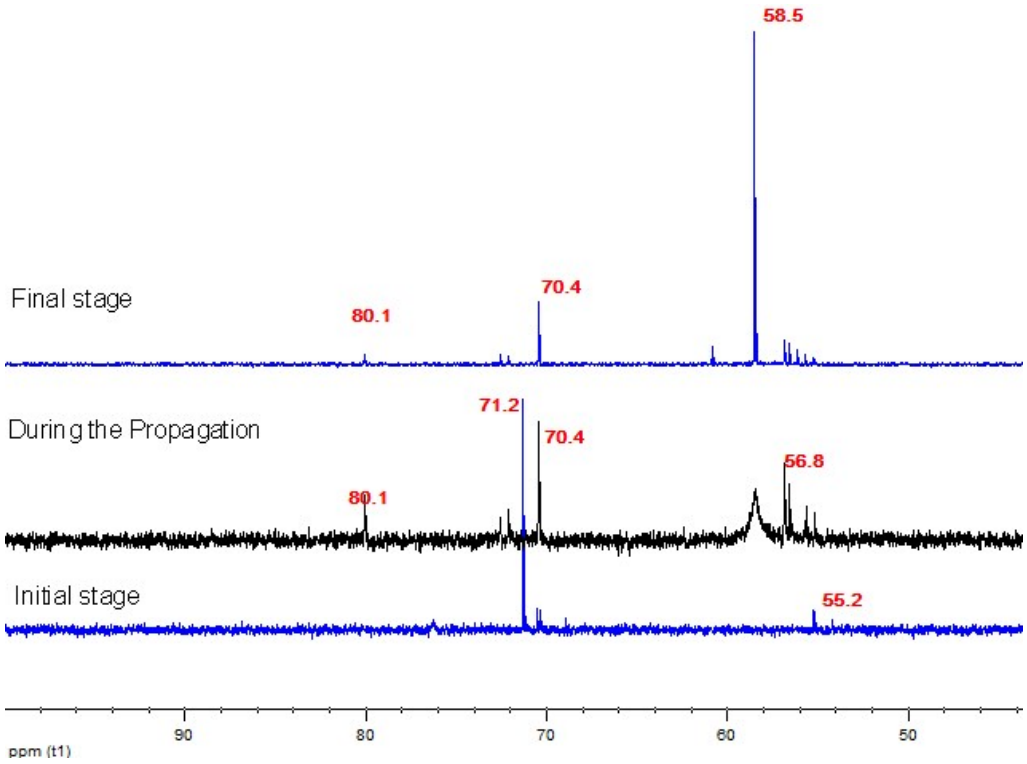
4. Pluasible machanism for ring-opening polymerisation of ε-Caprolactone initiated by chiral barium complex [Ba{N(*R*-*CHMePh)P(Se)Ph_2}$_2$($THF)_2$].

The plausible mechanism of the ROP of CL initiated by enantiomeric pure chiral strontium and barium complexes **5a** or **5b** and **6a** or **6b** was depicted in the Scheme below. First we studied by NMR spectroscopy with equimolar reaction of [{$(THF)_2$Ba{Ph_2P(Se)N(*R*-*CHMePh}$_2$] (**6a**) with ε-CL in C_6D_6, which though Lewis base exchange, gave [{$(THF)_2$Ba{Ph_2P(Se)N(*R*-*CHMePh}$_2$(ε-CL)] (**6-1a**). Although (6-1a) could not be isolated since it rapidly evolved towards the formation of (6-1b) (vide infra), it could be characterized in situ by its ^{1}H NMR and ^{31}P{^{1}H} NMR spectra. We have identified two peaks in the ^{31}P{^{1}H} NMR spectra, one is at δ 80.1 ppm and another is at δ 70.4 ppm. The former peak is indicating the formation new selenium-carbon bond during the ring opening of the ε-CL initiated by Ba complex (**6a** or **6b**). The intermediate complex (6-1b) which is generated in the initiation step further undergoes insertion of ε-CL through a coordination-insertion type mechanism to form the active polymer chain

[{Ba{$Ph_2P(Se)N(R$-*CHMePh}$_2$-{$O(CH_2)_5C(O)\}_{n+1}O$-$(CH_2)_5C(O)\}$] (**6-1c**). Subsequent addition of acidified methanol to (**6-1c**) results in hydrolysis of the Ba-O bond at one end and cleavage of Se-C bond at other end and finally capped by -OH group.



5. ^{31}P {^{1}H} NMR spectral study in C_6D_6 during the ring—opening polymerisation of ε-caprolactone initiated by chiral barium complex [Ba{N(*R*-*CHMePh)P(Se)Ph$_2$}$_2$(THF)$_2$].



6. ^{1}H NMR in $CDCl_3$ of poly(ε-Caprolactone).