New structural motifs in Lithium and Zinc calix[4]arene chemistry

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Electronic Supporting Information

General Experimental Details

All chemicals were sourced commercially and used without further purification. Dry solvents were prepared via distillation over sodium, and were handled under a dry nitrogen atmosphere. Infrared spectra were recorded on a Perkin Elmer Spectrum BX. Elemental analysis was performed by Stephen Boyer, London Metropolitan University.

Synthetic procedures

Preparation of 25,27-bis(methoxycarboxlic acid)-26,28-dihydroxycalix[4]arene (LH_2)

The calix[4]arene diester, 25,27-bis(methoxycarbonylethoxy)-26,28-dihydroxycalix[4]arene was prepared using the method reported by Shinkai and Iwamoto[1]. Saponification of the calix[4]arene diester using KOH in ethanol/water and recrystallisation from methanol/water gave the diacid **L**H_2.

Preparation of Li_2(calix[4]arene(OH)$_2$(OCH_2CO_2)$_2$) (1)

Ligand **L**H_2 (0.61g, 0.81 mmol) and Li_2CO_3 (0.06g, 0.77 mmol) were dissolved in refluxing ethanol (40 ml). After 2 hours the solution was cooled to room temperature and $ZnCl_2$ (0.1g, 0.77 mmol) was added. The solution was stirred for 30 mins and then filtered, giving a light pink solution from which crystals of suitable size for single crystal diffraction were grown by slow evaporation of the solvent. Elem. Anal. calcd for $C_{32}H_{26}Li_2O_8$,0.3H_2O: C, 68.83: H, 4.81; found: C, 69.12: H, 4.78 IR/cm^{-1} (KBr): 3340(b) 3184 (b), 2962(s) 2930(s) 2863(s), 1784(s) 1751(s) 1734 (s), 1629 (s) 1579 (s) 1537 (s), 1267(s) 1261 (s). ^{1}H NMR (DMSOd_6, 400 MHz, 273 K): δ = 7.07 (overlapping m, 4H, aryl*H*), 7.01 (overlapping m, 4H, aryl*H*), 6.69 (t, 2H, $^3J_{HH}$ 7.60 Hz, aryl*H*,), 6.47 (t, 2H, $^3J_{HH}$ 7.60 Hz, aryl*H*), 4.26 (d, 4H, $^2J_{HH}$ 18 Hz, *endo*-CH_2), 3.31 (d, 4H, $^2J_{HH}$ 18 Hz, *exo*-CH_2): ^{7}Li NMR (DMSOd_6, 400 MHz, 273K) δ = 17.08; ^{13}C NMR (DMSOd_6, 75MHz, 273 K): δ = 154.5 (CH_2CO_2), 134.51, 134.26, 129.26, 129.19. 128.88, 128.77, 128.62, 119.21 (all aryl*C*), 79.42 (OCH_2), 31.40 (ArCH_2Ar).

Preparation of Li_2(calix[4]arene(OH)$_2$(OCH_2CO_2)$_2$(C_2H_6O)$_2$) (2)

To a solution of ligand **L**H_2 (0.6g, 1.1mmol) in dry THF (30ml), was added ^{t}BuLi (1.2 ml, 1.6M in pentane) at −78 °C. The solution was stirred and allowed to warm to room temperature. Following evaporation of the THF, the grey/blue solid was extracted with dry ethanol (40 ml) giving a brightly coloured red solution from which crystals suitable for X-ray diffraction were grown over the course of 3 days. Elem. Anal. calcd for $C_{32}H_{26}Li_2O_8$,2C_2H_6O,2H_2O: C,63.53; H, 6.22; found C, 63.30; H, 6.37. IR/cm^{-1} (KBr): 3349(b) 3313(b), 2958(s), 2922(s), 2854(s), 1679(s), 1632(s), 1261(s), 1205(s); MS (MALDI, *m/z*) 1663.6 $[C_{33}H_{28}O_7Li_2]^+_{n=3}$, 2215.7 $[C_{33}H_{28}O_7Li_2]^+_{n=4}$, 2768.9 $[C_{33}H_{28}O_7Li_2]^+_{n=5}$. ^{1}H NMR (DMSO$d_6$, 400 MHz, 273 K): δ =

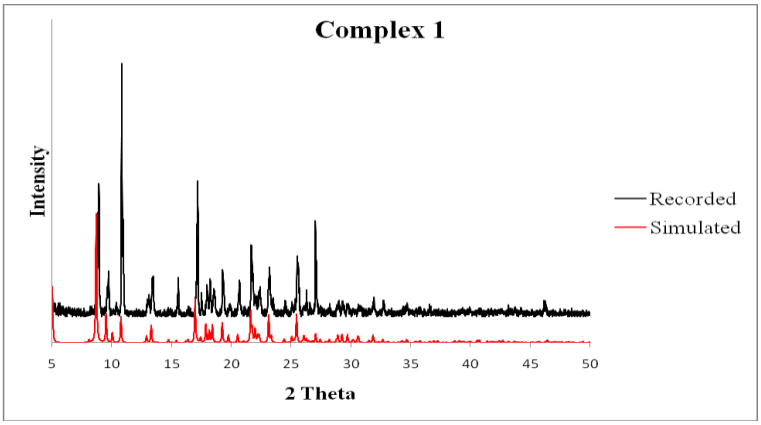
[1] S. Shinkai, K. Iwamoto, *J.Org. Chem.* **1992**, 57, 7066-7073

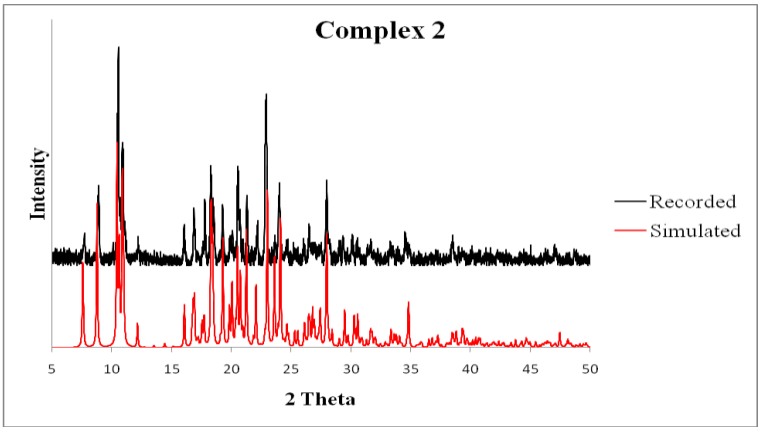
7.12 (d, 4H, $^{2}J_{HH}$ 7.40 Hz. aryl*H*), 7.05 (d, 4H, $^{2}J_{HH}$ 7.56 Hz, aryl*H*), 6.77 (t, 2H, $^{3}J_{HH}$ 7.56 Hz, aryl*H*), 6.58 (t, 2H, $^{3}J_{HH}$ 7.57 Hz, aryl*H*)), 4.39 (s, 4H, OCH_2), 4.21 (d, 4H, $^{2}J_{HH}$ 12.0 Hz, *endo*-CH_2), 3,42 (d, 4H, $^{2}J_{HH}$ 12 Hz, *exo*-CH_2), 1.05 (t, 3H, $^{3}J_{HH}$ 7.00 Hz, CH_3CH$_2$OH): ^{7}Li NMR (DMSO d_6, 400 MHz, 273K): δ = 1.97; ^{13}C NMR (DMSOd_6, 75MHz, 273 K): δ = 170.07 (CH$_2$*C*O$_2$), 151.96, 151.75, 133.71, 128.88, 128.54, 127.80, 125.06, 119.35 (all aryl*C*), 75.68 (O*C*H$_2$), 30.54 (Ar*C*H$_2$Ar).

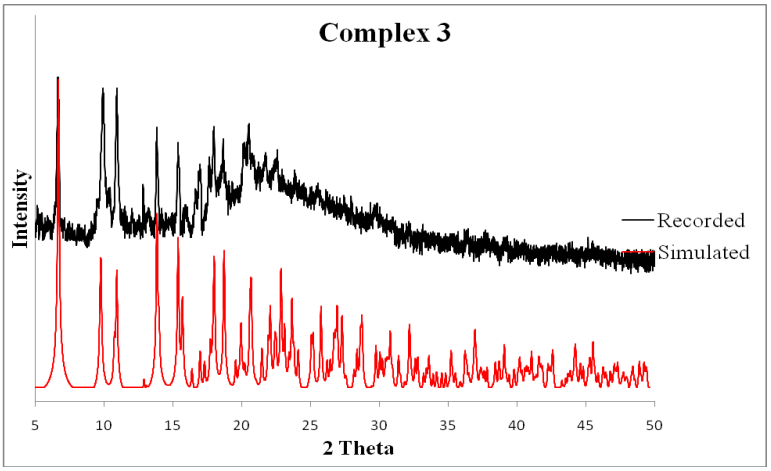
Preparation of [Zn(calix[4]arene(OH)$_2$(OCH$_2$CO$_2$)$_2$(DMF)(H$_2$O)]n (3)

Ligand **L**H$_2$ (0.16 g, 0.25 mmol) and Zn(OAc)$_2$ (0.05 g, 0.25 mmol) were dissolved in a DMF/ethanol/water (12:3:1 ml) mixture in a glass vial. The vial was sealed, heated to 85 ^{o}C for 4 days and then cooled at a rate of 2 ^{o}C to room temperature, yielding purple fine needles. Elem. Anal. calcd for $C_{32}H_{28}NO_9Zn$,1.5C_3H_7NO: C, 59.97; H, 5.24; N, 2.87; found: C, 60.23; H, 5.24; N, 2.88; IR/cm^{-1} (KBr): 3368(b), 2726(s), 2670(s), 1654(s), 1628(s), 1589(s), 1410(s), 1304(s), 1254(s), 1221(s), 1195(s), 1156(s), 1091(s) 1068(s), 1041(s), 967(b), 930(s), 910(s), 821.7(s), 760(s), 744(s), 721(s), 690/9s/0, 665(s); ^{1}H NMR (DMSO d_6, 400 MHz, 273 K): δ = 8.02 (s, 1H, C*H*O), 7.05 (d, 8H, $^{2}J_{HH}$ 7.36 Hz, aryl*H*), 6.78 (t, 2H, $^{3}J_{HH}$ 7.43 Hz, aryl*H*), 6.53 (t, 2H, $^{3}J_{HH}$ 7.30 Hz, aryl*H*), 4.52 (overlapping m, 6H, *endo*-CH_2, OCH_2), 3.33 (overlapping m, 56H, *exo*-CH_2, H_2O,) 2.95 (s, 3H, CH_3), 2.80 (s, 3H, CH_3). Attempts to obtain ^{13}C NMR spectroscopic data on this complex were thwarted by poor solubility (even in hot dmso$_{d6}$, the complex quickly drops out of solution).

Powder XRD patterns

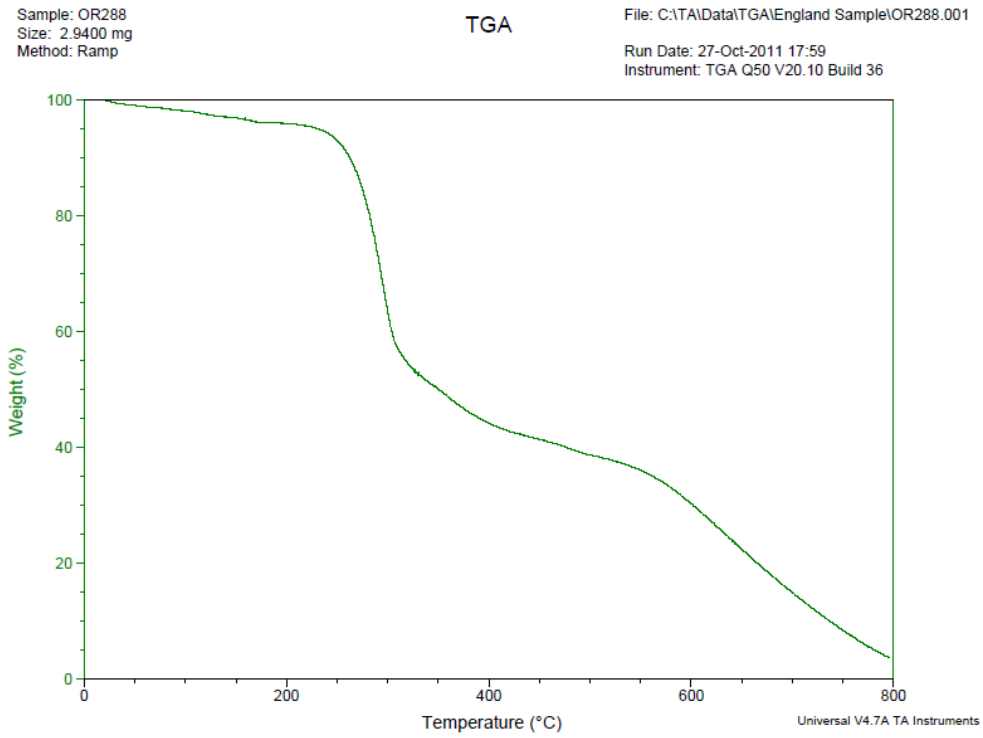




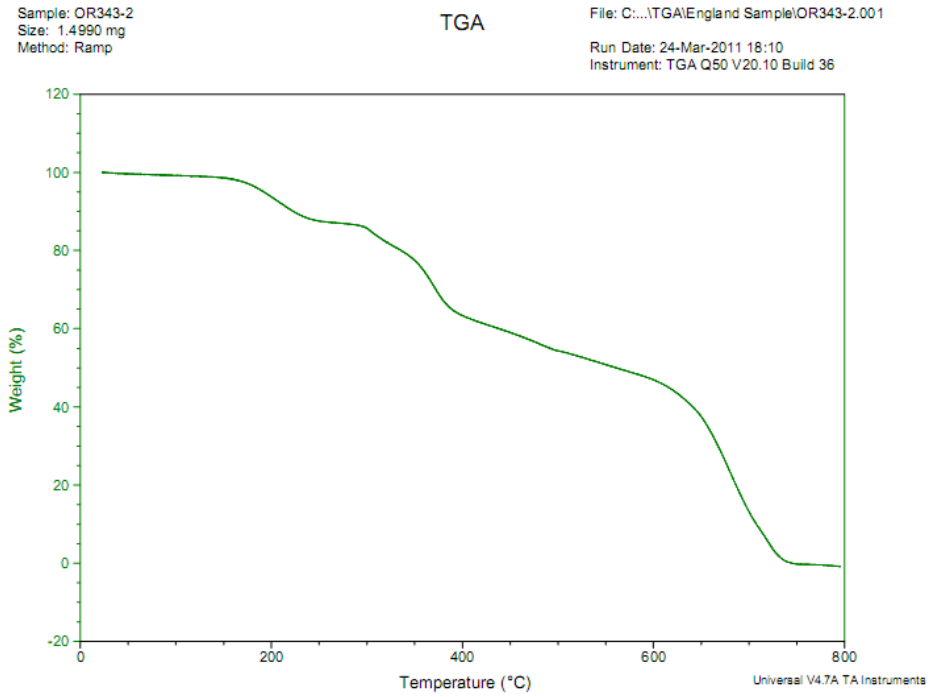


TGA

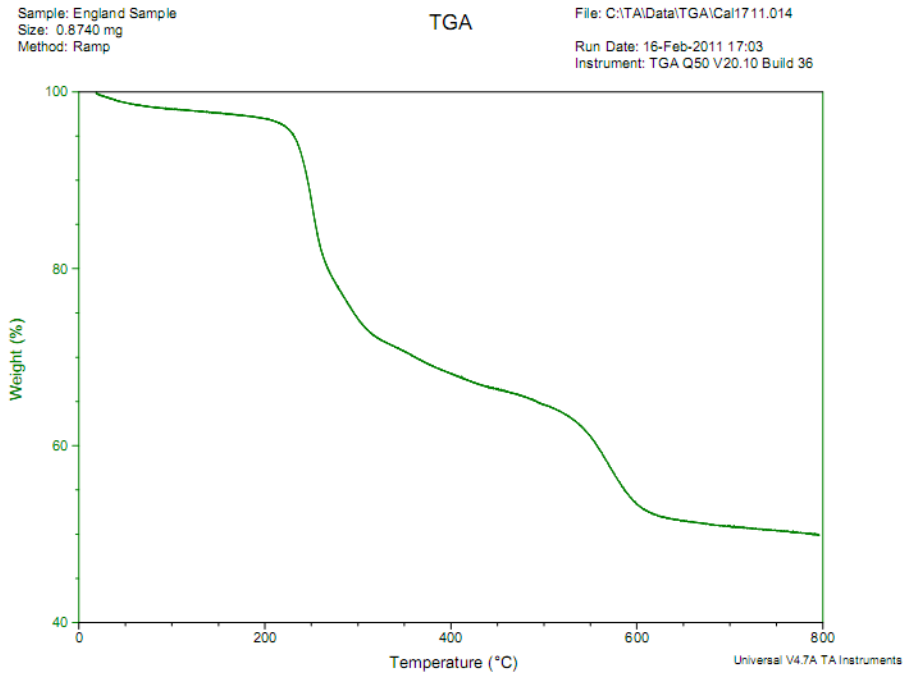
Complex 1



Complex 2



Complex 3



Crystal structure analyses

Crystal data for the three compounds are reported in a footnote in the main MS and in tables below (with dimensions about the metal centres and in the hydrogen bonds).

Crystals of compounds **1-3** were mounted in oil on glass fibres and fixed in a cold nitrogen stream. For compounds **1** and **3**, diffraction data were recorded on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-Kα radiation and graphite monochromator, and were processed using the CrysAlisPro-CCD and -RED (1) programs. Data for a crystal of **2** were measured on a Bruker-Nonius APEX II diffractometer with confocal mirrors and CCD detector (at the National Crystallographic Service, University of Southampton), and processed with the COLLECT (2) and DENZO (3) programs. The structures of the three samples were determined by the direct methods routines in the SHELXS program (4A) and refined by full-matrix least-squares methods, on F^2's, in SHELXL (4B). Compounds **2** and **3** refined smoothly, with the non-hydrogen atoms refined anisotropically. Except for the phenolic and ethanol hydrogen atoms involved in hydrogen bonds in compound **2**, which were refined freely, all hydrogen atoms were included in idealised positions and their Uiso values were set to ride on the Ueq values of the parent carbon atoms.

In compound **1**, there is gross disorder in the two carboxylate groups; several atoms in the regions of both these groups were included with partial occupancy and were refined isotropically. The non-hydrogen atoms of rest of the calixarene unit were well resolved and refined with anisotropic thermal parameters. The solvent channel showed diffuse electron density; three centres were refined as partially occupied oxygen atoms, but without full resolution. The hydroxyl hydrogen atoms and the hydrogen atoms of the methylene groups of C(201) and C(401) were located in difference maps and were refined freely; all remaining hydrogen atoms were included in idealised positions and their Uiso values were set to ride on the Ueq values of the parent carbon atoms.

Scattering factors for neutral atoms were taken from reference (5). Computer programs used in this analysis have been noted above, and were run through WinGX (6) on a Dell Precision 380 PC at the University of East Anglia.

References

(1) Programs CrysAlisPro, Oxford Diffraction Ltd., Abingdon, UK (2010).

(2) COLLECT data collection software, R. W. W. Hooft, Nonius B.V., (1998).

(3) Z. Otwinowski and W. Minor, 'Processing of X-ray diffraction data collected in oscillation mode', *Macromolecular Crystallography*, Pt A, (1997) **276,** 307-326.

(4) G. M. Sheldrick, SHELX-97 – Programs for crystal structure determination (SHELXS) and refinement (SHELXL), *Acta Cryst.* (2008) A**64**, 112-122.

(5) *'International Tables for X-ray Crystallography'*, Kluwer Academic Publishers, Dordrecht (1992). Vol. C, pp. 500, 219 and 193.

(6) L. J. Farrugia, *J. Appl. Cryst.*, (1999) **32**, 837-838 .

Compound 1.

Crystal and structure refinement data for
$[Li_2\text{-}\{calix\text{-}4\text{-}arene\text{-}(OH)_2,\text{-}(OCH_2COO)_2\}].solvent$

Elemental formula	C32 H26 Li2 O8
Formula weight	552.4
Crystal system	Trigonal
Space group	R-3 (no. 148)
Unit cell dimensions	a = 35.2552(11) Å α = 90 ° b = 35.2552(11) Å β = 90 ° c = 11.7244(3) Å γ = 120 °
Volume	12620.2(6) $Å^3$
No. of formula units, Z	18
Calculated density	1.308 Mg/m^3
F(000)	5184
Absorption coefficient	0.093 mm^{-1}
Temperature	140(1) K
Wavelength	0.71073 Å
Crystal colour, shape	pink hexagonal prism
Crystal size	0.37 x 0.26 x 0.23 mm
Crystal mounting	on a glass fibre, in oil, fixed in cold N_2 stream
On the diffractometer:	
Theta range for data collection	3.5 to 23.0 °
Limiting indices	-38<=h<=38, -38<=k<=38, -12<=l<=12
Completeness to theta = 23.0	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.071 and 0.845
Reflections collected (not including absences)	49096
No. of unique reflections	3890 [R(int) for equivalents = 0.065]
No. of 'observed' reflections ($I > 2\sigma_I$)	2675
Structure determined by:	direct methods, in SHELXS

Refinement:	Full-matrix least-squares on F^2, in SHELXL
Data / restraints / parameters	3890 / 0 / 428
Goodness-of-fit on F^2	0.990
Final R indices ('observed' data)	R_1 = 0.057, wR_2 = 0.159
Final R indices (all data)	R_1 = 0.086, wR_2 = 0.170
Reflections weighted: $w = [\sigma^2(Fo^2)+(0.1164P)^2]^{-1}$ where $P=(Fo^2+2Fc^2)/3$	
Largest diff. peak and hole	0.35 and -0.33 e.Å^{-3}
Location of largest difference peak	near O(208)

Table 1.1 Selected molecular dimensions. Bond lengths are in Ångstroms, angles in degrees. E.s.ds are in parentheses.

About the lithium atoms

Li(1)...Li(2[a])	3.440(13)	O(204)-Li(2)	1.988(14)
Li(1)-O(203[a])	2.02(2)	Li(2)-O(210[b])	2.08(4)
Li(1)-O(208[a])	2.017(17)	Li(2)-O(405[c])	1.887(16)
O(404)-Li(1)	1.981(15)	Li(2)-O(408[c])	1.938(19)
O(406)-Li(1)	2.19(4)		
O(404)-Li(1)-O(203[a])	102.3(8)	O(405[c])-Li(2)-O(204)	113.1(7)
O(404)-Li(1)-O(208[a])	93.8(7)	O(408[c])-Li(2)-O(204)	98.4(7)
O(203[a])-Li(1)-O(406)	131.8(12)	O(405[c])-Li(2)-O(210[b])	96.0(13)
O(208[a])-Li(1)-O(406)	120.8(11)	O(204)-Li(2)-O(210[b])	90.0(11)

Symmetry transformations used to generate equivalent atoms:
a : -y, x-y, z
b : y, -x+y, 1-z
c : -x+y, -x, z
d : x-y, x, 1-z
e : -x, -y, 1-z

Table 1.2 Hydrogen bonds, in Ångstroms and degrees.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3)...O(2)	1.02(7)	1.73(7)	2.734(3)	167(6)
O(1)-H(1A)...O(4)	0.88(8)	1.95(8)	2.771(3)	155(7)
O(1)-H(1B)...O(2)	1.15(10)	1.60(10)	2.735(3)	168(8)

Table 1.3 Shortest Lithium…Lithium distances, in Ångstroms.

Li(1)...Li(2[a])	-y,+x-y,+z	3.440(13)	in basic trimer
Li(2)...Li(1[c])	-x+y,-x,+z	3.440(12)	in basic trimer
Li(2)...Li(2[b])	y,-x+y,-z+1	3.899(11)	in neighbouring trimer, I
Li(2)...Li(2[d])	x-y,+x,-z+1	3.899(10)	in neighbouring trimer, I
Li(1)...Li(1[f])	y,-x+y,-z+2	4.228(16)	in neighbouring trimer, II
Li(1)...Li(1[g])	x-y,+x,-z+2	4.228(13)	in neighbouring trimer, II
Li(1)...Li(2[c])	-x+y,-x,+z	4.750(11)	in basic trimer
Li(2)...Li(1[a])	-y,+x-y,+z	4.750(13)	in basic trimer
Li(1)...Li(1[a])	-y,+x-y,+z	4.794(12)	in basic trimer
Li(1)...Li(1[c])	-x+y,-x,+z	4.794(17)	in basic trimer
Li(2)...Li(2[a])	-y,+x-y,+z	4.954(12)	in basic trimer
Li(2)...Li(2[c])	-x+y,-x,+z	4.954(14)	in basic trimer

Compound 2

Crystal data and structure refinement for Compound **2**.

Elemental formula	C34 H32 Li2 O9
Formula weight	598.48
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.3639(7) Å α = 87.429(4) ° b = 11.7721(5) Å β = 78.483(3) ° c = 11.8355(8) Å γ = 83.793(4) °
Volume	1406.22(15) $Å^3$
Z, Calculated density	2, 1.413 Mg/m^3
F(000)	628
Absorption coefficient	0.101 mm^{-1}
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal colour, shape	pink plates
Crystal size	0.09 x 0.04 x 0.01 mm
Crystal mounting:	on a glass fibre, in oil, fixed in cold N_2 stream
On the diffractometer:	
Theta range for data collection	2.92 to 22.50 °
Limiting indices	-11<=h<=11, -12<=k<=12, -12<=l<=12
Completeness to theta = 22.50	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.650089
Reflections collected (not including absenses)	16007
No. of unique reflections	3662 [R(int) for equivalents = 0.081]
No. of 'observed' reflections ($I > 2\sigma_I$)	2285
Structure determined by:	direct methods, in SHELXS
Refinement:	Full-matrix least-squares on F^2, in SHELXL
Data / restraints / parameters	3662 / 0 / 418
Goodness-of-fit on F^2	1.066

Final R indices ('observed' data) R_1 = 0.079, wR_2 = 0.167

Final R indices (all data) R_1 = 0.141, wR_2 = 0.192

Reflections weighted:
$w = [\sigma^2(Fo^2)+(0.0625P)^2+2.8747P]^{-1}$ where $P=(Fo^2+2Fc^2)/3$

Largest diff. peak and hole 0.28 and -0.33 e.Å^{-3}

Table 2.1 Selected molecular dimensions. Bond lengths are in Ångstroms, angles in degrees. E.s.ds are in parentheses.

About the lithium atoms

Li(1)-O(104)	1.932(11)	Li(2)-O(11)	2.274(12)
Li(1)-O(314)	1.992(10)	Li(2)-O(31)	2.098(12)
Li(1)-O(213)#1	1.877(11)	Li(2)-O(104)	1.932(11)
Li(1)-O(41)	1.962(12)	Li(2)-O(314)	2.011(12)
Li(1)…Li(2)	2.717(15)	Li(2)-H(11)	2.33(8)
Li(2)-O(1)	1.952(11)	Li(2)-H(31)	2.26(9)
O(213)#1-Li(1)-O(104)	115.6(5)	O(1)-Li(2)-O(314)	163.3(7)
O(213)#1-Li(1)-O(41)	115.1(5)	O(104)-Li(2)-O(31)	134.4(6)
O(104)-Li(1)-O(41)	102.1(5)	O(1)-Li(2)-O(31)	93.7(5)
O(213)#1-Li(1)-O(314)	127.2(6)	O(314)-Li(2)-O(31)	102.3(5)
O(104)-Li(1)-O(314)	91.0(4)	O(104)-Li(2)-O(11)	134.2(6)
O(41)-Li(1)-O(314)	101.0(5)	O(1)-Li(2)-O(11)	84.5(4)
O(104)-Li(2)-O(1)	81.6(4)	O(314)-Li(2)-O(11)	90.7(5)
O(104)-Li(2)-O(314)	90.4(5)	O(31)-Li(2)-O(11)	89.7(4)

Table 2.2 Hydrogen bonds, in Ångstroms and degrees.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(11)-H(11)...O(21)	1.04(9)	1.69(9)	2.697(5)	162(7)
O(11)-H(11)...O(314)	1.04(9)	2.52(8)	3.055(5)	111(5)
O(31)-H(31)...O(21)	0.97(10)	1.72(10)	2.665(5)	163(8)
O(41)-H(41)...O(103)#2	1.09(9)	1.59(9)	2.633(6)	158(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z #2 -x+2,-y,-z

Compound 3

Crystal data and structure refinement for Compound **3**.

Elemental formula	C35 H35 N O10 Zn
Formula weight	695.01
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 9.9928(5) Å α = 90 ° b = 17.3371(11) Å β = 90 ° c = 17.7642(9) Å γ = 90 °
Volume	3077.6(3) $Å^3$
Z, Calculated density	4, 1.500 Mg/m^3
F(000)	1448
Absorption coefficient	0.862 mm^{-1}
Temperature	140(1) K
Wavelength	0.71073 Å
Crystal colour, shape	purple needles
Crystal size	0.17 x 0.03 x 0.02 mm
Crystal mounting:	on a glass fibre, in oil, fixed in cold N_2 stream
On the diffractometer:	
Theta range for data collection	3.64 to 25.00 °
Limiting indices	-11<=h<=11, -20<=k<=20, -21<=l<=21
Completeness to theta = 25.00	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.91681
Reflections collected (not including absenses)	40585
No. of unique reflections	5399 [R(int) for equivalents = 0.199]
No. of 'observed' reflections ($I > 2\sigma_I$)	3606
Structure determined by:	direct methods, in SHELXS
Refinement:	Full-matrix least-squares on F^2, in SHELXL
Data / restraints / parameters	5399 / 0 / 427
Goodness-of-fit on F^2	1.019

Final R indices ('observed' data)	R_1 = 0.076, wR_2 = 0.113
Final R indices (all data)	R_1 = 0.123, wR2 = 0.127
Reflections weighted: w = $[\sigma^2(Fo^2)+(0.0353P)^2]^{-1}$ where $P=(Fo^2+2Fc^2)/3$	
Absolute structure parameter	-0.04(2)
Largest diff. peak and hole	0.83 and -0.56 e.Å^{-3}

Table 3.1 Selected molecular dimensions. Bond lengths are in Ångstroms, angles in degrees. E.s.ds are in parentheses.

About the zinc atom			
Zn(1)-O(41)	2.049(6)	Zn(1)-O(114)#1	1.996(5)
Zn(1)-O(51)	2.050(4)	Zn(1)-O(314)#2	2.043(4)
Zn(1)-O(313)	2.057(4)		
O(41)-Zn(1)-O(51)	116.4(2)	O(314)#2-Zn(1)-O(41)	89.6(2)
O(41)-Zn(1)-O(313)	85.2(2)	O(114)#1-Zn(1)-O(51)	110.8(2)
O(51)-Zn(1)-O(313)	80.36(16)	O(314)#2-Zn(1)-O(51)	85.43(18)
O(114)#1-Zn(1)-O(314)#2	105.1(2)	O(114)#1-Zn(1)-O(313)	92.1(2)
O(114)#1-Zn(1)-O(41)	131.44(19)	O(314)#2-Zn(1)-O(313)	160.78(18)

Symmetry transformations used to generate equivalent atoms:
#1 x-1/2,-y-1/2,-z #2 x+1/2,-y-1/2,-z

Table 3.2 Hydrogen bonds, in Ångstroms and degrees.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(51)-H(51)...O(21)	0.82	2.08	2.897(6)	174.1
O(1)-H(1)...O(11)	0.82	2.14	2.918(6)	158.0
O(21)-H(21)...O(31)	0.82	1.99	2.704(6)	145.6
O(21)-H(21)...O(313)	0.82	2.65	3.154(6)	120.9