

Structural Characterization of a Tetrametallic Diamine-bis(phenolate) Complex of Lithium and Synthesis of a Related Bismuth Complex

Marcus W. Drover,^a Jennifer N. Murphy,^a Jenna C. Flogeras,^a Céline M. Schneider,^{a,b}
Louise N. Dawe,^{a,c} and Francesca M. Kerton^{*a}

- a Department of Chemistry, Memorial University of Newfoundland
St. John's, Newfoundland, Canada A1B 3X7
- b NMR Laboratory, C-CART, Memorial University of Newfoundland, St. John's, NL, A1B
3X7, Canada
- c C-CART X-ray Diffraction Laboratory, Memorial University of Newfoundland, St. John's,
Newfoundland, Canada A1B 3X7; Current address, Department of Chemistry, Wilfrid
Laurier University, Science Building, 75 University Ave. W., Waterloo, Ontario, Canada
N2L 3C5
- * Author to whom correspondence should be addressed. Tel: +1-709-864-8089, Fax: +1-709-
864-3702, E-mail: fkerton@mun.ca

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Abstract

A novel lithium complex was prepared from the reaction of 1,4-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)imidazolidine $\text{H}_2[\text{O}_2\text{N}_2]^{\text{BuBuIm}}$ (L1H₂) with *n*-butyllithium to provide the corresponding tetralithium amine-bis(phenolate) complex $\{\text{Li}_2[\text{L1}]\}_2 \cdot 4\text{THF}$, **1**. Variable temperature ⁷Li NMR revealed that this complex is labile in solution, dissociating at elevated temperatures to afford two dilithium entities. Additionally, ⁷Li MAS NMR was performed on **1** to provide information regarding the lithium coordination environment in the bulk solid-state. The reactivity of **1** was assessed in the ring-expansion polymerization of ϵ -caprolactone (ϵ -CL), which was first order in ϵ -CL with an activation energy of 50.9 kJmol⁻¹. Reaction of **1** and a related Li complex (formed *in situ*) with BiCl₃ afforded hydrolytically unstable bismuth phenolate species, as evidenced by the isolation and structural characterization of $[\text{Bi}_4(\text{Cl})_3(\mu\text{-Cl})(\mu\text{-O})(\text{O})_2\{\text{O}_2\text{N}_2\}^{\text{BuBuPip}}]_2$, **2**, where $[\text{O}_2\text{N}_2]^{\text{BuBuPip}}$ is the homopiperazine-containing analog of L1.

Keywords: Lithium / N, O ligands / Coordination compounds / NMR studies / Bismuth

1. Introduction

Amine-phenolate ligands have been used to form complexes with metals from around the periodic table for a diverse range of applications from biomimetic modelling to catalysis.[1] The ease by which these ligands are modified gives rise to a myriad of potential ligand donor systems to stabilize both electron rich and electron poor metal centres. They have been widely studied with *s*-, *d*- and *f*-block metals but *p*-block compounds are less well represented than analogs from the left hand side of the periodic table. In order to prepare many of these complexes, lithium adducts must be prepared first, which can then be reacted with a metal halide to give the desired product through a salt metathesis reaction.

Over the years, several amine-bis(phenolate) complexes of lithium have been structurally characterized.[2-4] One of the first, which we reported in 2006, showed that in the presence of 1,4-dioxane, two isomeric amine-bis(phenolate) ligands could yield structurally different lithium complexes namely a polymeric complex or a tetralithium species with 1,4-dioxane acting as the bridging group.[2] In many cases, when a bridging ether is not present, the compounds contain two chelating ligands around a tetra-lithiated core and adopt an elongated ladder-like conformation as described by Clegg *et al.* in 2008.[4] Typically, two Li atoms are nominally 5-coordinate, resulting from two bridging oxygen atoms, two nitrogen atoms, and an *ipso*-C from an adjacent benzene ring. This motif is a standard structural feature of many lithium-containing compounds. In the work of Huang and Chen, solid-state structure analysis revealed a tetra-lithium complex, which adopted a boat-like conformation, flanked on each side by an amine-bis(phenol) ligand.[3] More recently, Kozak and co-workers have reported the synthesis of analogous ladder compounds using diamine-bis(phenol) ligands bearing THF pendant arms,[5] and showed that tridentate amine-bis(phenolate) adopt ladder-like structures in the solid-state.[6] They also employed ^6Li and ^7Li NMR spectroscopy in solution and the solid-state to gain insight into similarities and differences in the number of Li environments for both phases.[6] However, they were unable to model their solid-state NMR data to obtain quadrupolar-coupling parameters.

Many lithium compounds of phenolate ligands have found application as initiators in ring-opening polymerization (ROP) reactions of cyclic esters including lactide and ϵ -caprolactone (ϵ -CL).[3, 6-11] In most cases, reactions can proceed in the absence of a co-initiator (alcohol) to yield cyclic polymers or in the presence of alcohol to yield linear polyesters. In some cases, reactions clearly proceed via an activated monomer mechanism,[11] whereas in other cases the mechanism is less clear but in the absence of alcohol they likely proceed via a conventional coordination-insertion process.

Given the rigid, heterocycle-containing backbone of the ligands used in the current study (Figure 1), we thought they might be well-suited for coordination with a large p -block metal ion. In particular, bismuth(III) salts have been widely implemented in organic synthesis (including: Mukaiyama-aldol,[12, 13] Michael addition, [12] acylation reactions,[14] and formation and deprotection of acetals[15]) and therefore, we thought that amine-phenolate bismuth complexes may show interesting catalytic behaviour. Despite the known catalytic activity of bismuth salts, well-characterized coordination compounds of bismuth are limited in comparison with many transition metals and light s/p -block elements. The lack of structural data has prevented extensive studies of the catalytic features and reactivity of many metallorganic bismuth compounds. This may be because the synthesis of metallorganic bismuth compounds is often plagued by the formation of multimetallic oxygen-bridged clusters.[16-20] This typically results from the facile hydrolysis or oxidation of the bismuth-containing metal precursor, affording complex aggregates with Bi_xO_y central cores. Although cluster formation in bismuth-containing materials is common, there are examples where this phenomenon has been successfully avoided by employing an amine-phenol ligand.[21] Specifically, amine-tris(phenol) ligands were implemented as scaffolds in the synthesis of mononuclear compounds of bismuth and antimony. With bismuth, this led to the formation of an arene bridged inverted-sandwich complex.

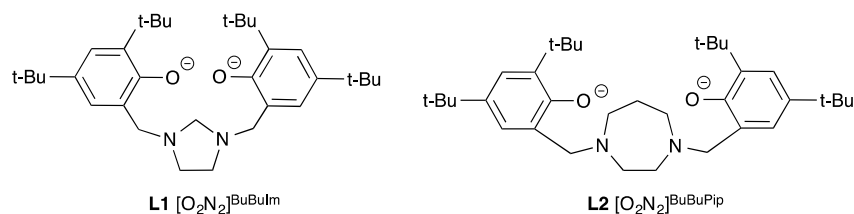


Figure 1. Amine-bis(phenolate) ligands used in this study.

2. Experimental

2.1 General and Instrumental Considerations

The proligands, $\text{H}_2[\text{O}_2\text{N}_2]^{\text{BuBuIm}}$ and $\text{H}_2[\text{O}_2\text{N}_2]^{\text{BuBuPip}}$, were prepared in water following literature procedures.[22, 23] All other manipulations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or a glovebox. *n*-Butyllithium (1.6 M in hexanes) and BiCl_3 were purchased from Alfa-Aesar and used without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc., purified and dried before use.

MALDI-TOF mass spectrometry was performed on an Applied Biosystems 4800 MALDI TOF/TOF Analyzer equipped with a reflectron, delayed ion extraction and high performance nitrogen laser (200 Hz operating at 355 nm). Anthracene was used as the matrix.[24, 25] Elemental analyses were performed at Guelph Chemical Laboratories, Guelph, ON, Canada. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^7\text{Li}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 25 °C (unless otherwise stated) and were referenced internally using the residual ^1H and ^{13}C resonances of the solvent. ^{13}C resonances were assigned on the basis of DEPT and 2D-NMR experiments. $^7\text{Li}\{^1\text{H}\}$ NMR spectra were referenced externally to saturated solutions of LiCl. For solid-state NMR experiments, samples were finely ground and packed into a 4 mm zirconium oxide rotor. $^7\text{Li}\{^1\text{H}\}$ SSNMR ($\nu_0(^7\text{Li}) = 98.2$ MHz) spectra were recorded on a Bruker Avance 600 MHz spectrometer at 25 °C. $^7\text{Li}\{^1\text{H}\}$ spectra were collected using a solid-state MAS $^1\text{H}/\text{X}$ probe. For MAS experiments, spectra at three different spinning rates, ranging between 2.5 and 15 kHz, were acquired. The magic angle was adjusted using KBr. A single 3 μs pulse was employed to excite the central and satellite transitions (CT and ST); 5 s recycle delays were used. The spectral widths were 400 kHz and 3958 complex data points were acquired. Isotropic chemical shifts are reported with respect to LiCl, whose $^7\text{Li}\{^1\text{H}\}$ spectrum was recorded and used as an external referencing standard. Analytical simulations of $^7\text{Li}\{^1\text{H}\}$ SSNMR spectra were performed using DMFit.

2.2 Crystal Structure Determination

Single crystals of suitable dimensions were used for data collection. Methods of crystal growth are outlined in the synthetic procedures below. Crystals of **1** and **2** were mounted on low temperature diffraction loops. All measurements were made on a Rigaku Saturn70 CCD diffractometer using graphite monochromated Mo-K α radiation, equipped with a SHINE optic.

For all structures, H-atoms were introduced in calculated positions and refined on a riding model while all non-hydrogen atoms were refined anisotropically. In the structure of **1**, the carbon atoms of one THF group, and one lattice solvent toluene molecule were disordered over two positions (C38-C41: C38A-C41A with refined occupancies 0.464(17): 0.536(17) and C42-C48: C42A-C48A with refined occupancy 0.42(2): 0.58(2).) Distance and rigid bond restraints were applied to both disorder groups. In the structure of **2**, a disordered toluene molecule was treated with similar anisotropic displacement restraints and the corresponding H-atoms were omitted from the model, but included in the formula for the calculation of intensive properties.

Structural illustrations were created using Mercury software, which is available free of charge from <http://www.ccdc.cam.ac.uk/products/mercury/>. Crystallographic and structure refinement data of compounds **1** and **2**, and their CCDC reference numbers are given in Table 1.

2.3 Synthesis of Compounds

2.3.1 Synthesis of 1. $\text{H}_2[\text{O}_2\text{N}_2]^{\text{BuBuIm}}$ (2.01 g, 3.94 mmol) was dissolved in THF (30.0 mL) and cooled to $-78\text{ }^\circ\text{C}$. *n*-Butyllithium (1.6 M, 5.4 mL, 8.7 mmol) was slowly added to give a cloudy, yellow solution which was warmed to room temperature and allowed to react for an additional 72 h. After this period, volatiles were removed under reduced pressure to afford an off-white powder (2.35 g, 98%). Clear, colorless crystals suitable for X-ray diffraction were obtained via slow evaporation of a solution of **1** in a 1:1 toluene:pentane solution (at $-35\text{ }^\circ\text{C}$) under an inert atmosphere. ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 7.59 (d, ArH, 2H, $^4J = 2.5$ Hz); 7.49 (d, ArH, 2H, $^4J = 2.5$ Hz); 7.07 (overlapping multiplet, ArH, 4H); 4.71 (d, CH, 2H, $^2J = 11.2$ Hz); 4.66 (d, CH, 2H, $^2J = 11.3$ Hz); 4.38 (d, CH, 2H, $^2J = 11.0$ Hz); 4.09 (d, CH, 2H, $^2J = 5.8$ Hz); 3.26 (m, CH_2 , THF, 22H); 2.84 (t, CH_2 ; imid ring, 4H, $^3J = 11.9$ Hz); 2.55 (m, CH_2 , imid ring, 4H); 2.15 (m, CH_2 , imid ring, 4H); 1.73 (s, $\text{C}(\text{CH}_3)_3$, 18H); 1.57 (s, $\text{C}(\text{CH}_3)_3$, 18H); 1.51 (s, $\text{C}(\text{CH}_3)_3$, 18H); 1.45 (s, $\text{C}(\text{CH}_3)_3$, 18H); 1.17 (m, CH_2 , THF, 22H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, C_6D_6 , 298 K): δ 165.3 (ArCOH); 164.9 (ArCOH); 137.0 (ArC(CH₃)₃); 136.7 (ArC(CH₃)₃); 133.8 (ArC(CH₃)₃); 133.73 (ArC(CH₃)₃); 126.9 (ArCH); 126.2 (ArCH); 125.7 (ArCH); 125.1 (ArCH); 124.4 (ArCCH₂N); 124.0 (ArCCH₂N); 78.52 (ArCCH₂N), 78.48 (ArCCH₂N), 68.4 (CH_2 : THF); 61.7 (NCHN); 61.1 (NCHN); 52.5 (NCH₂CH₂N); 50.6 (NCH₂CH₂N); 36.0 (ArC(CH₃)₃); 35.9 (ArC(CH₃)₃); 34.5 (ArC(CH₃)₃); 34.4 (ArC(CH₃)₃); 32.9 (ArC(CH₃)₃); 32.8 (ArC(CH₃)₃); 31.3 (ArC(CH₃)₃); 31.1 (ArC(CH₃)₃); 25.6 (CH_2 : THF). $^7\text{Li}\{^1\text{H}\}$ NMR (49.6 MHz, C_7D_8 , 193 K): δ 1.90, $\omega_{1/2} = 51.5$ Hz (Li1); 1.55, $\omega_{1/2} = 20.6$ Hz (Li2); 0.70, $\omega_{1/2} = 44.3$ Hz (Li3); 0.23, $\omega_{1/2} =$

20.6 Hz. Anal. Calcd. for $C_{78}H_{124}Li_4N_4O_7$ C 74.49, H 9.94, N 4.46. Found: C 74.77 H 10.25 N 4.52. MS (MALDI-TOF) m/z (% , ion): 1047.9 (18, $Li_4[L1]_2^+$); 1040.9 (8, $[Li_4[L1]_2-Li]^+$)

2.3.2 Synthesis of Bismuth Complexes. To a slurry of **1** (2.05 g, 3.92 mmol) in 15.0 mL THF, was added dropwise (via cannula) to a suspension of $BiCl_3$ (1.24 g, 3.94 mmol) in 15.0 mL THF at -78 °C. After 30 min, the resulting yellow solution was allowed to warm to room temperature, resulting in an orange solution. After 24 h, volatiles were removed under reduced pressure to afford an orange powder. The resulting solid was then extracted with toluene (20.0 mL) and filtered through Celite. Subsequent solvent removal gave a pale, orange solid (1.01 g, 40%, assuming product was $Bi[O_2N_2]^{BuBuIm}Cl$). Attempts to grow crystals were unsuccessful.

In a similar fashion, attempts were made to prepare $Bi[O_2N_2]^{BuBuPip}Cl$: $Li_2[O_2N_2]^{BuBuPip}$ (1.86 mmol) was prepared *in situ* in THF (15 mL). To this solution was added dropwise (via cannula) to a suspension of $BiCl_3$ (0.57 g, 1.86 mmol) in THF (15 mL) at -78 °C. The reaction was allowed to proceed as above. Solvent removal gave a pale, orange solid (0.48 g, 33%). Yellow crystals were obtained via slow evaporation of a solution of $Bi[O_2N_2]^{BuBuPip}Cl$ in a 1:1 toluene:pentane solution (at -35 °C) under an inert atmosphere. These crystals rapidly decomposed at $T > -35$ °C. This material was partially characterized as follows: Anal. Calcd. for $C_{35}H_{54}BiClN_2O_2$ C 53.95, H 6.98, N 3.59. Found: C 54.12, H 6.71, N 3.30. MS (MALDI-TOF) m/z (% , ion): 778.4 (4, $Bi[L2]Cl^+$); 743.4 (100, $Bi[L2]^+$). This compound decomposed in NMR solvents. Reaction of $Bi[O_2N_2]^{BuBuPip}Cl$ with adventitious moisture provided a pale, yellow solid **2** (0.11 g, 9%), with the formula, $Bi_4(\mu-Cl)(\mu-O)_2[L2]_2(Cl)_3$. **2** was characterized by single-crystal X-ray diffraction, elemental microanalysis, solid-state NMR (it was insoluble in NMR solvents) and MS. $^{13}C\{^1H\}$ NMR (150.8 MHz, SS, 298 K): δ 155.8(ArCO); 140.8 (ArC(CH₃)₃); 136.1 (ArC(CH₃)₃); 124.6 (ArCH); 75.5 (ArCH₂N); 58.0 (CH₂; homopip. ring); 53.9 (CH₂; homopip. ring); 34.3 (ArC(CH₃)₃); 32.0 (ArC(CH₃)₃). Anal. Calcd. for $C_{70}H_{108}Bi_4Cl_4N_4O_6$ C 40.43, H 5.24, N 2.69. Found: C 40.17, H 5.12, N 2.89. MS (MALDI-TOF) m/z (% , ion): 778.4 (7, $Bi[L2]Cl^+$); 743.4 (100, $Bi[L2]^+$).

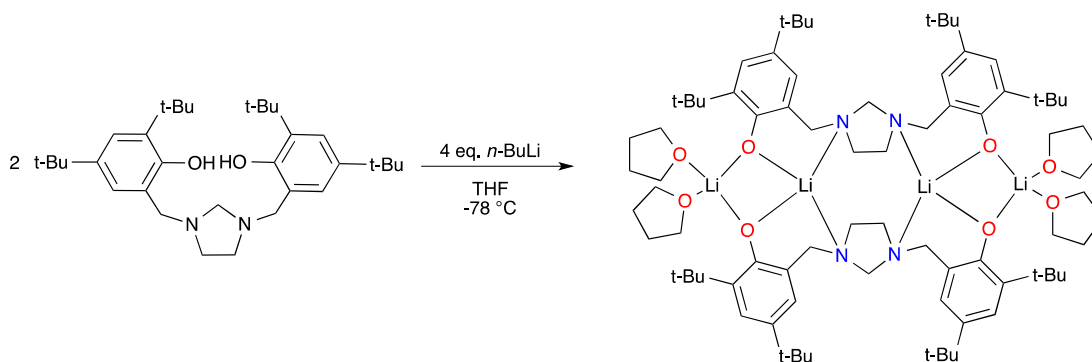
2.3.3 Typical Polymerization Procedure. Reaction mixtures were prepared in a glove box and subsequent operations were performed using standard Schlenk techniques. A sealable Schlenk flask equipped with a stir bar was charged with a solution of **1** (73.6 mg) in 2.0 mL toluene. A second Schlenk flask was charged with a toluene (2.0 mL) solution of ϵ -caprolactone (0.401 g, 3.54 mmol, 50 equiv). The two flasks were then attached to a Schlenk line and temperature

equilibration was ensured in both Schlenk flasks by stirring the solutions for 10 minutes in a temperature controlled oil bath. The complex solution was transferred to the rapidly stirring monomer solution and polymerization times were measured from that point. At given time intervals, aliquots of the reaction mixture were removed *via* pipette for determining monomer conversion by ^1H NMR spectroscopy. The reaction was quenched with methanol once near-quantitative conversion had been obtained. GPC data were collected on a Viscotek GPCMax System equipped with a Refractive Index Detector (Phenogel 5 μ linear/mixed bed 300 \AA ~ 4.60 mm column in series with a Phenogel 5 μ , 100 \AA , 300 \AA ~ 4.60 mm column). Samples were run in chloroform at a concentration of 1 mg mL $^{-1}$ at 35 $^\circ\text{C}$. The instrument was calibrated against polystyrene standards (Viscotek) to determine the molecular weights (M_n^{GPC} and M_w) and the polydispersity index (M_w/M_n or D) of the polymers. The M_n value was calculated according to $M_n = 0.56M_n^{\text{GPC}}$.

3. Results and Discussion

3.1 Molecular Structure of **1**

The tetradentate ligand $\text{H}_2[\text{O}_2\text{N}_2]^{\text{BuBuIm}}$ (**L1H₂**) was prepared from 2,4-di-*tert*-butylphenol, ethylenediamine and three equiv. formaldehyde.[22] The ligand was dried, recrystallized and then reacted with *n*-butyllithium in THF, Scheme 1. This afforded $\{\text{Li}_2[\text{L1}]\}_2 \cdot 4\text{THF}$, **1**, in near quantitative yield.



Scheme 1. Synthesis of complex **1**.

The ^1H NMR resonances for $\text{H}_2[\text{L1}]$ appear as sharp, well-defined peaks which are easily assignable to each of their methyl (CH_3), methylene (CH_2) and methine (CH) protons. Upon

reaction to yield **1**, the resonances of L1 change significantly. In solution, H₂[L1] exhibits free rotation about its C_{Ar}-CH₂-N_{imid} bonds, resulting in chemically equivalent, isochronous methylene protons and a single resonance at 3.35 ppm. However, once lithiated, these protons become chemically inequivalent and non-isochronous, resulting in diastereotopicity. This gives rise to four sets of doublets each of integration two. This downfield shift and change in multiplicity is well known for other amine-phenolate systems, and is characteristic of ligand metalation.[2-5, 7] Coupling constants (²J) for the diastereotopic protons of **1** are in close agreement to those reported by others for related ligand systems.[5]

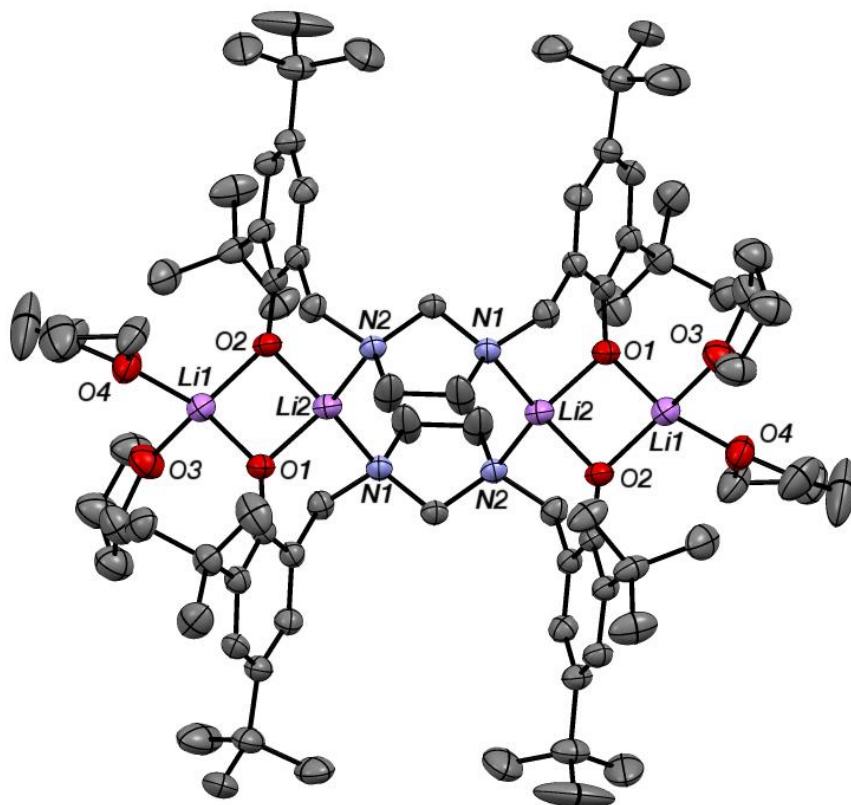


Figure 2. Molecular structure diagram of **1**. Thermal ellipsoids shown at 50% probability and H-atoms removed for clarity.

Table 1. Crystallographic and Structure Refinement Data for **1** and **2**.

	1	2
CCDC	1403400	1403401
Empirical formula	C ₉₆ H ₁₄₈ Li ₄ N ₄ O ₈	C _{108.5} H ₁₅₂ Bi ₄ Cl ₄ N ₄ O ₆
Formula weight	1514.01	2586.15
Temperature/K	163(2)	163(2)
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c
a/Å	11.5812(18)	15.141(4)
b/Å	17.424(3)	21.244(5)
c/Å	23.613(4)	32.957(8)
α/°	90.00	90.00
β/°	101.386(7)	96.526(3)
γ/°	90.00	90.00
Volume/Å ³	4671.1(13)	10532(5)
Z	2	4
ρ _{calc} /cm ³	1.076	1.631
μ/mm ⁻¹	0.066	6.806
F(000)	1656.0	5116.0
Crystal size/mm ³	0.38 × 0.35 × 0.34	0.12 × 0.11 × 0.06
Radiation	MoKα (λ = 0.71075)	MoKα (λ = 0.71075)
2Θ range for data collection/°	5.98 to 53	5.16 to 53
Index ranges	-14 ≤ h ≤ 14, -20 ≤ k ≤ 21, -29 ≤ l ≤ 29	-19 ≤ h ≤ 19, -26 ≤ k ≤ 26, -41 ≤ l ≤ 41
Reflections collected	42399	110405
Independent reflections	9668 [R _{int} = 0.0442]	21788 [R _{int} = 0.0883]
Data/restraints/parameters	9668/62/620	21788/24/1182
Goodness-of-fit on F ²	1.039	1.166
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0666, wR ₂ = 0.1802	R ₁ = 0.0616, wR ₂ = 0.1198
Final R indexes [all data]	R ₁ = 0.0894, wR ₂ = 0.1945	R ₁ = 0.0749, wR ₂ = 0.1270
Largest diff. peak/hole / e Å ⁻³	0.42/-0.30	2.26/-1.87

Table 2. Selected Bond Lengths [\AA] and Angles [$^\circ$] for **1**.

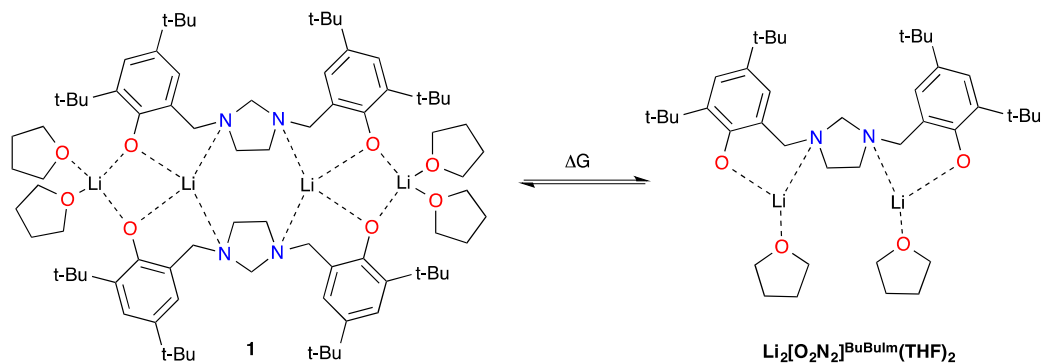
Li1–O1	1.938(4)	C38–O4–Li1	126.2(6)	C1–O1–Li1	123.5(2)
Li1–O2	1.901(4)	C41–O4–Li1	125.2(7)	C1–O1–Li2	122.8(2)
Li1–O3	2.076(4)	C7–N1–Li2	96.4(1)	Li1–O1–Li2	83.9(2)
Li1–O4	1.994(4)	C8–N1–Li2	106.0(2)	C17–O2–Li1	133.9(2)
Li2–O1	1.903(4)	C17–O2–Li2	120.0(2)	C10–N1–Li2	126.8(2)
Li2–O2	1.917(4)	Li1–O2–Li2	84.5(2)	C9–N2–Li2	106.5(2)
Li2–N1	2.096(4)	C34–O3–Li1	120.7(2)	C10–N2–Li2	128.1(2)
Li2–N2	2.095(4)	C37–O3–Li1	131.6(2)	C11–N2–Li2	94.4(2)

Crystals suitable for single crystal X-ray diffraction were grown by slow evaporation of a 1:1 toluene:pentane solution of **1** under an inert atmosphere at -35°C . The structure of **1** is shown in Figure 2. It is ladder-like in nature and is comprised of four Li atoms, capped by two amine-bis(phenolate) ligands. At its core, **1** consists of a 6-membered metallacycle, with two adjacent rhombic or “daisy-chain” Li_2O_2 units. For **1**, each Li centre is tetracoordinate; Li(1) is bound by two bridging phenolate-O atoms and two THFs, while Li(2) is bound by the tertiary amine of the imidazolidine backbone from two different ligands (N1 and N2) and the bridging phenolate-O donor atoms. Bond lengths around the Li atoms are provided in Table 2. The Li–O_{Ar} bond distances are in the range 1.901(4) to 1.938(4) \AA , which is similar to those observed by others for related complexes.[3-6] Although **1** is novel we note that, during their studies on lanthanide coordination chemistry, Shen and co-workers reported the synthesis of a tetrasodium complex of L1,[26] which is structurally very similar to **1**.

3.2 NMR studies of **1**

From crystallography, the molecular structure of **1** is highly symmetric and if this was maintained in solution, one might expect to see only one type of phenolate environment (i.e. one pair of *t*-Bu environments). In practice, two ligand groups are observed and this is likely due to twisting along the backbone of the ligand. Two sets of aromatic protons, *t*-Bu, and imidazolidine resonances are all seen in C_6D_6 at 298 K. The presence of two types of ligand environment suggests that this tetra-lithium complex does not dissociate upon dissolution in C_7D_8 or C_6D_6 . Another possibility, if conditions were serendipitous, would be the presence of a Li₄ and Li₂

equilibrium mixture with a ratio of 1:2 to yield resonances of the correct integration in the spectrum. As described below, this is not the case. To the best of our knowledge, this system represents one of the few lithium bis(phenolate) structures that does not disaggregate in solution at room temperature. This observation prompted variable-temperature ^1H and $^7\text{Li}\{^1\text{H}\}$ NMR studies (Figure 3 and supplementary data). At 193 K, four distinct Li environments are evident for **1** (δ 1.90, $\omega_{1/2} = 51.5$ Hz (Li1); 1.55, $\omega_{1/2} = 20.6$ Hz (Li2); 0.70, $\omega_{1/2} = 44.3$ Hz (Li3); 0.23, $\omega_{1/2} = 20.6$ Hz (Li4)). These signals coalesce to one Li environment (δ 1.07, $\omega_{1/2} = 48.0$ Hz) at 373 K. Each of the $^7\text{Li}\{^1\text{H}\}$ NMR spectra acquired were reproducible and afforded chemical shifts and peak widths identical to those obtained in previous runs. This eliminates the possibility of sample decomposition at high temperature or differences between samples of **1**. The shifts are consistent with those reported for other Li-based phenolates, indicating multiple unique environments around the Li atoms in each case.[3, 6] This observation suggests that for samples in solution, **1** contains ligands arranged in a slightly different formal arrangement (e.g. twisted) to those in the crystalline sample (which would give rise to two ^7Li environments if maintained in solution). It should also be noted that four different ^7Li environments are also seen in solid-state NMR spectra obtained on powdered samples of **1** (supplementary data).



Scheme 2. Proposed tetralithium-dilithium equilibrium for **1**

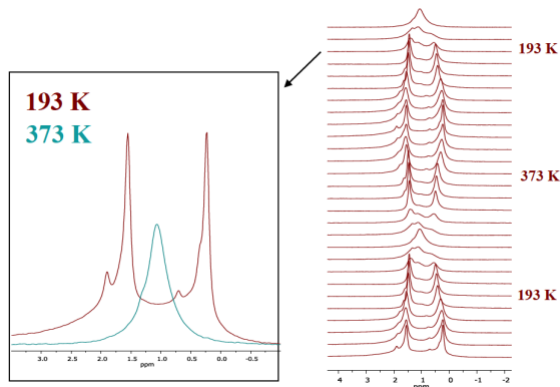


Figure 3. Variable temperature ${}^7\text{Li}\{^1\text{H}\}$ NMR spectra of **1** in C_7D_8

The rate of exchange of ${}^7\text{Li}$ nuclei can be extrapolated from the ${}^7\text{Li}\{^1\text{H}\}$ NMR data (equation 1), and we propose that this Li-Li exchange is facilitated via the postulated dilithium species at high temperature. In modelling our spectral data, 193 K, the freezing point of C_7D_8 , was taken as the point at which the rate of exchange was smallest. Similarly, intermediate exchange points (219 - 363 K; extensive peak overlap) and the coalescence point (373 K; single, sharp peak) were also modelled using exchange rate constants.

$$\Delta G = -RT \ln \left(\frac{k_{exc} h}{k_B T} \right) = \Delta H - T \Delta S \quad (1)$$

This analysis allowed the determination of the enthalpy, entropy and Gibbs free energy (at 298 K) associated with the Li-exchange process ($\Delta H = 4.80 \text{ kJmol}^{-1}$, $\Delta S = 185.6 \text{ Jmol}^{-1}\text{K}^{-1}$ and $\Delta G = -53.5 \text{ kJmol}^{-1}$) (Figure 4). These data are in good agreement with previous studies in the literature. Jackman and Smith studied Li-exchange in the following three systems: 4-bromophenolate in THF ($\Delta G = -28.9 \text{ kJmol}^{-1}$), 3,5-dimethylphenolate in pyridine ($\Delta G = -46.0 \text{ kJmol}^{-1}$) and 2-isopropylphenolate in THF ($\Delta G = -52.9 \text{ kJmol}^{-1}$).^[27] For these molecules, similar to the results reported herein, temperature-dependant Li_4/Li_2 equilibria were proposed in order to explain the exchange phenomena. It is not surprising that our data are most similar to the 2-isopropylphenolate complexes, as both this and **1** contain ortho substituents on the phenolate group, which would strongly influence the exchange process.

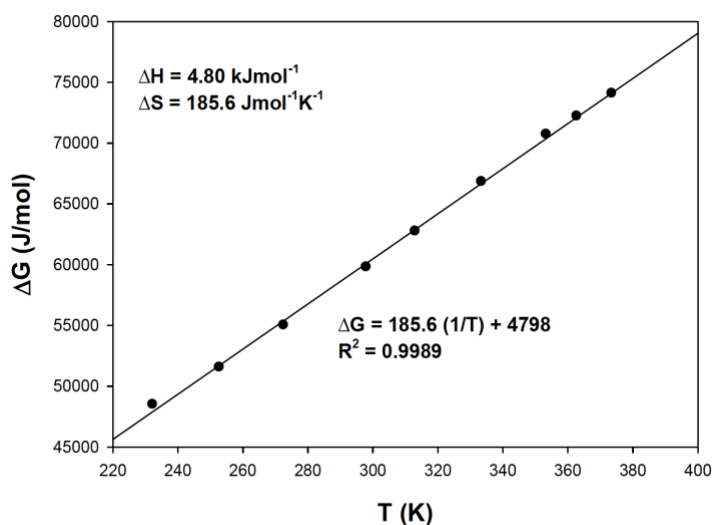


Figure 4. Gibbs free energy of Li-Li exchange (ΔG) for **1**

3.4 Reactivity studies of **1**

3.4.1 Ring-opening polymerization of ϵ -caprolactone using **1**

In the field of ring-opening polymerization (ROP) of cyclic esters, Li-based initiators have advantages of being easily accessible, stable on storage and non-toxic in the quantities required of initiators. Huang and Chen reported lithium complexes bearing dianionic amine-bis(phenolate) ligands for the controlled ROP of L-lactide.[3] Each of these tetra-lithiated complexes provided the corresponding polymer in the absence or presence of benzyl alcohol co-initiator (30-70% yield after 30 min at 25.6 °C). Using a dilithium amine-bis(phenolate) complex as an initiator in ROP of *rac*-lactide, Dean *et al.* achieved 86-91% conversion in 60-120 min at 26 °C in the absence of co-initiator to yield low molecular weight polymers with broad dispersity (2.5-4.1).[6] We have also published a related article dealing with the polymerization of ϵ -caprolactone (ϵ -CL), initiated by lithium piperazinyl amine-phenolate complexes,[10] which we proposed to proceed via a coordination-insertion mechanism, which is consistent with results reported by others.[3, 8, 28-30] However, it should also be noted that lithium phenolate complexes can also perform ROP reactions via an activated monomer mechanism.[11]

ROP of ϵ -CL was performed using **1** as a homogeneous catalyst, in the absence of a co-initiator. A [ϵ -CL]:[Li] ratio of 50:1 was used, and the solvent employed was toluene. These are

similar reaction parameters to those we have used previously.[10] ^1H NMR spectroscopy was used to follow the reaction, with aliquots being extracted at appropriate intervals and % conversion values calculated. After 2.5 h, 95% conversion was obtained. Similar conversion levels of 97% and 100% were obtained in our previous studies using trimetallic amine-phenolate complexes $\{\text{Li}[\text{ONN}]^{\text{RR}'}\}_3$ [$\text{R} = \text{Me}$, $\text{R}' = t\text{-Bu}$ and $\text{R} = \text{R}' = t\text{-Am}$] at 25 °C, after 30 and 40 min.[10] The longer reaction time required (under identical conditions) for **1** to achieve similar conversions may reflect the tendency of this complex to maintain its aggregated state in solution, as observed in the NMR studies reported above. NMR analyses of the resulting polymers show that they contain the expected polycaprolactone methylene signals at 1.39, 1.64, 2.32 and 4.07 ppm in CDCl_3 at 298 K, and are consistent with those previously reported.[10, 31] No signals could be assigned to polymer end groups (e.g. CH_2OH at 3.65 ppm), suggesting that the polymers obtained were cyclic polycaprolactone. $^{13}\text{C}\{^1\text{H}\}$ also confirmed the absence of a CH_2OH peak. The molecular weight of the polymer was $19\,000\text{ g mol}^{-1}$, which is significantly higher than the theoretically expected value based on the initial $[\varepsilon\text{-CL}]:[\text{Li}]$ ratio and this discrepancy is likely due to transesterification reactions occurring. The dispersity of the polymer was 1.62, which also suggests that the reaction was not well-controlled and that side reactions occurred.

In order to gain a better understanding of these reactions, a series of reactions were conducted at varying temperatures; 25, 40, 60 and 80 °C and semilogarithmic plots of the form, $\ln[\text{CL}]_0/[\text{CL}]_t$ vs. time (min) were constructed (Figure 5). These graphs are linear in nature suggesting a first order dependence on monomer concentration. Subsequent thermodynamic analysis employed the Arrhenius equation to illustrate the effect of a change in temperature on the rate of reaction ($R^2=0.9285$). This plot gave $E_a = 50.94\text{ kJmol}^{-1}$ and a pre-exponential factor, A of $6.42 \times 10^5\text{ min}^{-1}$. This activation energy is a little lower than those we reported for trimetallic lithium amine-phenolate catalysts ($56.8\text{-}67.2\text{ kJmol}^{-1}$) in the absence of a co-initiator.[10]

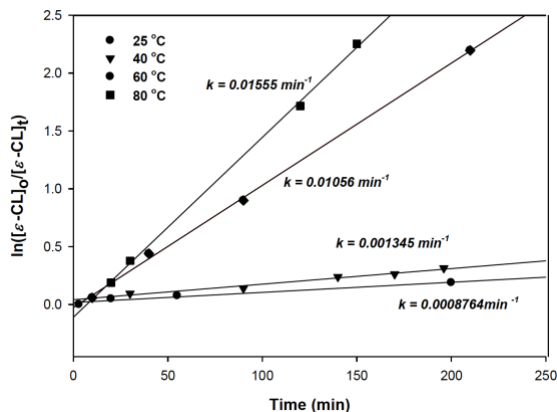
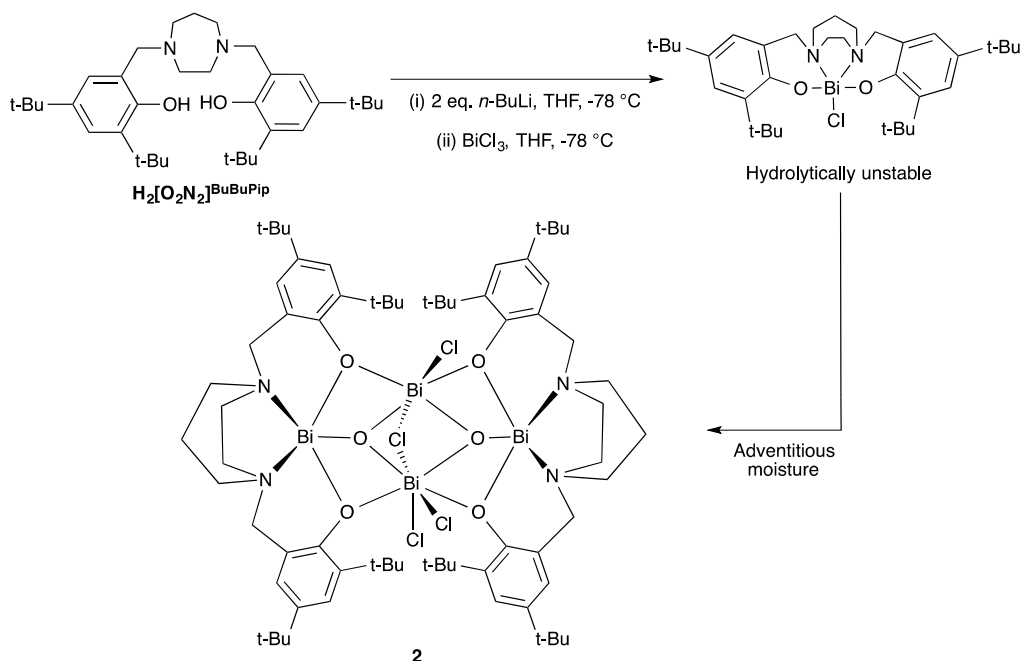


Figure 5. Semilogarithmic plot for the ring-expansion polymerization of ϵ -caprolactone initiated by **1**

3.4.2 Using **1** and $\text{Li}_2[\text{O}_2\text{N}_2]^{\text{BuBuPip}}$ as a ligand transfer reagent

In our group, we are interested in the synthesis of *p*-block coordination compounds for use as catalysts in transformations of carbon dioxide. Others have shown that bismuth is a promising metal in this regard.[32, 33] Given the similar ionic radius of Bi^{3+} with the lanthanides, which have already been studied with this type of ligand,[26] we attempted to prepare a bismuth complex using **1** as the ligand transfer reagent. Upon stirring **1** or a closely related Li complex (where the imidazoline unit has been replaced by a homopiperazine group) with BiCl_3 in THF, a colour change occurs and pale orange solids could be isolated (Scheme 3). Elemental analysis of these powders was in agreement with the formulations $\text{Bi}[\text{O}_2\text{N}_2]^{\text{BuBuIm}}\text{Cl}$ and $\text{Bi}[\text{O}_2\text{N}_2]^{\text{BuBuPip}}\text{Cl}$. Mass spectrometric analysis of $\text{Bi}[\text{O}_2\text{N}_2]^{\text{BuBuPip}}\text{Cl}$ also indicated that the ligand had been successfully transferred to bismuth. However, attempts to obtain NMR spectra of these complexes was thwarted due to their instability in common deuterated solvents at room temperature. During attempts to recrystallize these species, we were able to isolate yellow crystals of **2**, which we propose forms *via* reaction with water. The formation of such bismuth oxo-clusters is a well-known phenomenon in the coordination chemistry of bismuth, as discussed below. Mass spectrometric data for **2** was nearly identical to that of the orange powder in that the highest mass ions observed matched a formulation of $\text{Bi}[\text{O}_2\text{N}_2]^{\text{BuBuPip}}\text{Cl}$.



Scheme 3. Synthesis of complex **2**.

3.4.2.1 Molecular Structure of **2**

The structure of **2** ($\text{Bi}_4(\mu_2\text{-Cl})(\mu_3\text{-O})_2[\text{L}2]_2(\text{Cl})_3$) is shown in Figure 6, with selected bond distances and angles in Table 3. This compound is a tetrametallic Bi-containing, oxo-bridged cluster consisting of two diamine-bis(phenolate) ligands. Two bridging oxide moieties, O(5) and O(6) do not belong to the ligand framework, but instead are likely to have originated from adventitious moisture, as previously observed by others.[17] The oxo-cluster reported herein consists of two 5-coordinate, one 6-coordinate, and one 7-coordinate bismuth(III). Both Bi(1) and Bi(3) possess highly distorted square-based pyramidal geometries, while Bi(2) and Bi(3) possess irregular trigonal prismatic and face-capped octahedral geometries, respectively. This coordination framework results in seven fused rings, five of which arise from linking $\text{Bi}_2(\mu\text{-O})_2$ units and two from conjoining $\text{Bi}_2(\mu\text{-O})_2$ and $\text{Bi}_2(\mu\text{-Cl})$ units. Overall, this compound features a $\text{Bi}_4\text{O}_2(\text{OAr})_4$ core. This structural motif is quite common among Bi-containing clusters, in particular of those containing oxygen-containing bridges.[16-18, 20, 34-37] Indeed, **2** does not achieve complete planarity, remaining buckled or pinched in a “boat-like” conformation (Figure 7). This results from a bridging chloride ligand, which tethers the molecule together via a Bi(2)-Cl(3)-Bi(3) bridge. Similar Bi-Cl-Bi bridge bonds have been reported elsewhere, and are

summarized in Table 4. In most cases, one Bi-Cl interaction is shorter than the other with ranges of 2.746(4)-2.9325(13) Å for the shorter one and 2.763(3)-3.076(2) Å for the longer. A correlation with the coordination number of bismuth can also be seen with a longer Bi-Cl bond consistent with a greater Bi coordination number. In compound **2**, Bi(3) is 6-coordinate and has a Bi-Cl_{bridge} distance of 2.783(2) Å compared to Bi(2) which is 7-coordinate, with a bridging distance of 3.076(2) Å. The Bi-O_{Ar} distances in **2** range from 2.29 to 2.37 Å and are comparable with other bismuth aryloxide systems.[20, 21, 36, 38] The geometries about the μ_3 -O atoms are also very similar to Bi-compounds reported elsewhere.[19] The sum of the Bi-O μ -Bi angles around μ_3 -O atoms in **2** are 332.87 ° (μ_3 -O(6)) and 330.12 ° (μ_3 -O(5)). These oxo-ligands are very closely trigonal planar in structure, suggesting involvement of the oxygen lone pair in bonding to Bi. Distant toluene molecules were found to reside in empty spaces made by the coordinated ligands, but did not interact with any of the four Bi. Although the Bi₄(O)₂(OAr)₄ core is not planar, a single plane consisting of Bi(1)-Bi(4) is present. As a result, least squares plane analysis was performed on **2** with Bi(1)-Bi(4) defining the plane of interest. Bi(1)-Bi(4) were found to be coplanar with an average mean of 0.0594 Å. All atom-plane distances are in good agreement (0.633 – 0.730 Å). Atoms O(1), O(2), O(3) and O(4) coordinate above the plane with atom-plane distances ranging from 0.633 – 0.730 Å and O(5) and O(6) coordinate below the plane with atom-plane distances of 0.691 and 0.725 Å respectively (Figure 7(a)).

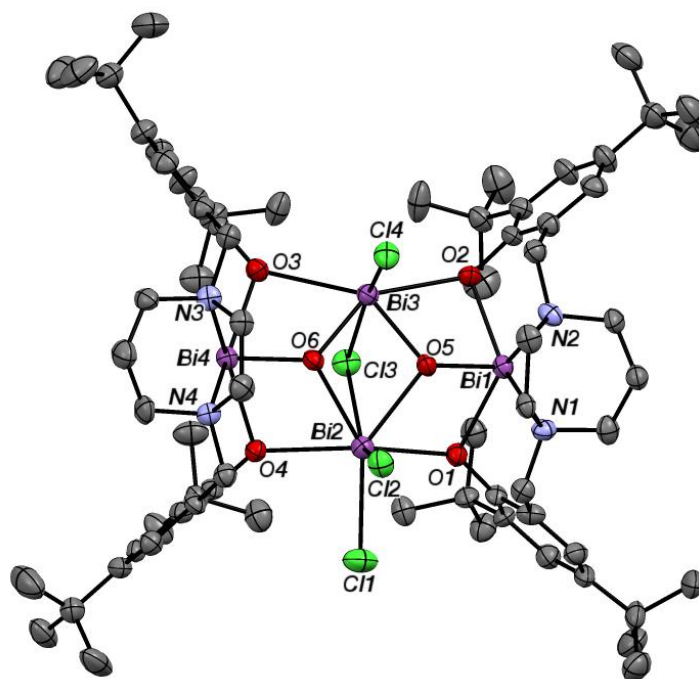


Figure 6. Molecular structure diagram of **2**. Thermal ellipsoids shown at 50% probability and H-atoms removed for clarity.

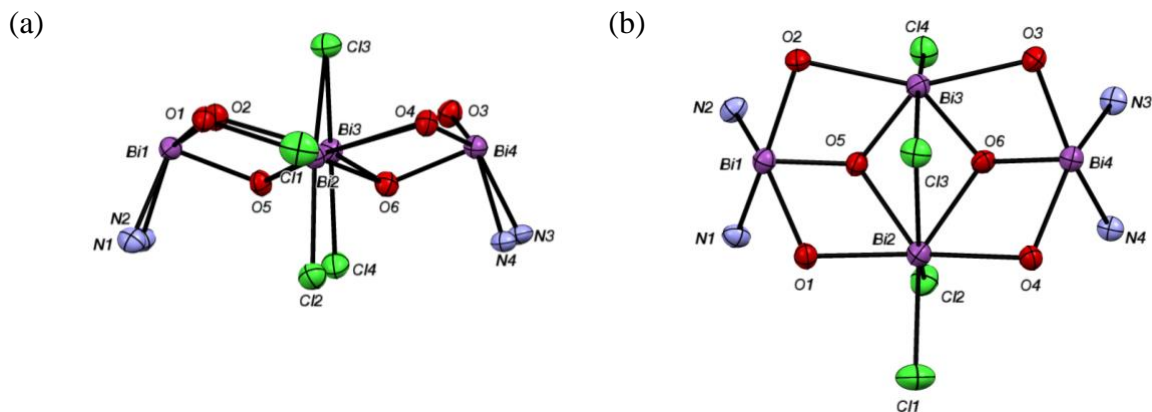


Figure 7. (a) Side View and (b) Top View for the $\text{Bi}_4(\text{O})_2(\text{OAr})_4(\text{NR}_2)_4$ core structure of compound **2**. Ellipsoids are shown at the 50% probability level.

Table 3. Selected bond lengths [\AA] and angles [$^\circ$] for **2**.

Bi1–O1	2.366(4)	Bi2–O1	2.482(5)	Bi3–O5	2.175(5)
Bi1–O2	2.294(5)	Bi2–O4	2.509(5)	Bi3–O6	2.164(5)
Bi1–O5	2.060(5)	Bi2–O5	2.461(4)	Bi4–O3	2.294(6)
Bi1–N1	2.491(7)	Bi2–O6	2.489(4)	Bi4–O4	2.364(5)
Bi1–N2	2.450(6)	Bi3–Cl3	2.783(2)	Bi4–O6	2.061(5)
Bi2–Cl1	2.642(3)	Bi3–Cl4	2.606(2)	Bi4–N3	2.474(6)
Bi2–Cl2	2.570(2)	Bi3–O2	2.654(6)	Bi4–N4	2.483(7)
Bi2–Cl3	3.016(2)	Bi3–O3	2.660(6)		
O1–Bi1–O2	126.7(2)	O3–Bi4–N4	143.3(2)	Bi3–O6–Bi4	117.5(2)
O1–Bi1–O5	74.5(2)	O4–Bi4–O6	76.7(2)	Cl4–Bi3–O2	100.4(1)
O1–Bi1–N1	79.4(2)	O4–Bi4–N3	143.0(2)	Cl4–Bi3–O3	102.1(1)
O1–Bi1–N2	142.3(2)	O4–Bi4–N4	78.9(2)	Cl4–Bi3–O5	89.1(1)
O2–Bi1–O5	78.3(2)	O6–Bi4–N3	90.0(2)	Cl4–Bi3–O6	88.3(1)
O2–Bi1–N1	144.8(2)	O6–Bi4–N4	88.2(2)	Cl3–Bi3–Cl4	165.61(7)
O2–Bi1–N2	81.3(2)	N3–Bi4–N4	66.1(2)	Cl3–Bi3–O2	85.1(1)
O5–Bi1–N1	88.9(2)	Bi2–Cl3–Bi3	75.61(5)	Cl3–Bi3–O3	81.0(1)
O5–Bi1–N2	90.1(2)	Bi1–O1–Bi2	104.1(2)	Cl3–Bi3–O5	80.4(1)
N1–Bi1–N2	65.9(2)	Bi1–O1–C1	109.9(4)	Cl3–Bi3–O6	79.7(1)
Cl1–Bi2–Cl2	86.69(8)	Bi2–O1–C1	138.5(4)	O3–Bi4–O4	129.2(2)
Cl1–Bi2–Cl3	125.94(7)	Bi1–O2–Bi3	93.8(2)	O3–Bi4–O6	78.4(2)
Cl1–Bi2–O1	85.0(1)	Bi1–O2–C19	114.7(5)	O2–Bi3–O5	68.7(2)
Cl1–Bi2–O4	86.5(1)	Bi3–O2–C19	144.0(5)	O2–Bi3–O6	143.7(2)
Cl1–Bi2–O5	143.4(1)	Bi3–O3–Bi4	93.4(2)	O3–Bi3–O5	142.9(2)
Cl1–Bi2–O6	146.6(1)	Bi3–O3–C36	141.8(5)	O3–Bi3–O6	68.9(2)
Cl2–Bi2–Cl3	147.36(7)	Bi4–O3–C36	116.3(5)	O5–Bi3–O6	76.3(2)
Cl2–Bi2–O1	107.4(1)	Bi2–O4–Bi4	102.5(2)	O3–Bi4–N3	79.7(2)
Cl2–Bi2–O4	105.8(1)	Bi2–O4–C54	138.4(5)	O2–Bi3–O3	140.7(2)
Cl2–Bi2–O5	81.7(1)	Bi4–O4–C54	111.3(5)	O1–Bi2–O4	145.1(2)
Cl2–Bi2–O6	81.7(1)	Bi1–O5–Bi2	115.2(2)	O1–Bi2–O5	65.9(2)
Cl3–Bi2–O1	78.8(1)	Bi1–O5–Bi3	117.5(2)	O1–Bi2–O6	128.5(2)
Cl3–Bi2–O4	79.1(1)	Bi2–O5–Bi3	100.1(2)	O4–Bi2–O5	130.0(2)
Cl3–Bi2–O5	71.6(1)	Bi2–O6–Bi3	99.6(2)	O4–Bi2–O6	66.9(2)
Cl3–Bi2–O6	70.4(1)	Bi2–O6–Bi4	113.0(2)	O5–Bi2–O6	65.5(2)

Table 4. Comparison of Bi-Cl_{bridge} bond lengths in **2** with others reported to date.

Compound	Bi-Cl _{bridge} (Å), Bi coordination no.		ref.
2 , Bi ₄ (μ-Cl)(μ-O) ₂ [L 2] ₂ (Cl) ₃	2.783(2), 6	3.076(2), 7	this work
[TmBiCl(μ-Cl)] ₂	2.807(5), 6	3.009(5), 6	[39]
Bu ^t Calix-8(BiCl) ₄ (LiCl) ₆ (DME) ₆ (THF) ₃	2.8421(11), 6	3.0266(12), 6	[35]
[NMe ₄] ₂ [Bi ₂ (2,6-OC ₆ H ₃ Me ₂) ₆ (μ-Cl) ₂]	2.9325(13), 6	3.0020(12), 5	[40]
Mo(OMe) ₅ (CH ₃ CN)Bi ₂ Cl ₇	2.859(1), 4	3.074(13), 4	[41]
[Ph ₂ BiCl] _∞	2.746(4), 5	2.763(3), 5	[42]
[{(Me ₃ Si) ₂ CHBiCl ₂ }•Et ₂ O] _∞	2.729(4), 5	2.852(4), 5	[43]

4. Conclusions

In summary, **1** a tetrametallic Li complex and **2** a tetrametallic Bi cluster have been prepared and structurally characterized. **1** was also extensively studied *via* variable temperature solution and solid state ⁷Li{¹H} NMR spectroscopy, which revealed solution-phase dynamics and increased asymmetry in bulk samples of **1** compared with the sample used for single-crystal X-ray diffraction analysis. Interestingly, MALDI-TOF MS supports the presence of a Li₄ moiety in the gas phase. Together, the data obtained on **1** infer a strong tendency to remain tetrametallic over bimetallic in all states of matter. Due to the reluctance of **1** to dissociate, it shows comparatively low reactivity towards ROP of ε-CL but is reactive in the absence of co-initiator and kinetic data for this ring expansion polymerization were obtained. Use of lithium amine-phenolate complexes including **1** to prepare molecular bismuth compounds was thwarted by the moisture-sensitive nature of the resulting products. However, a bismuth-oxo cluster complex **2** was structurally characterized, which has bonding parameters similar to related examples in the literature.

Appendix A. Supplementary data

Variable temperature ¹H NMR spectra, ⁷Li{¹H} solid-state NMR data and mass spectrometric data for **1** and associated discussion. CCDC 1403400 and 1403401 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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