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Reprint of Structural characterization of a tetrametallic diamine-bis(phenolate) complex of lithium and synthesis of a related bismuth complex [☆]

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ABSTRACT

A novel lithium complex was prepared from the reaction of 1,4-bis(2-hydroxy-3,5-di-*tert*-butyl-benzyl)imidazolidine $H_2[O_2N_2]^{BuBuIm}$ (L1H$_2$) with *n*-butyllithium to provide the corresponding tetralithium amine-bis(phenolate) complex $\{Li_2[L1]\}_2{\cdot}4THF$, **1**. Variable temperature ^{7}Li NMR revealed that this complex is labile in solution, dissociating at elevated temperatures to afford two dilithium entities. Additionally, ^{7}Li 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 BiCl$_3$ afforded hydrolytically unstable bismuth phenolate species, as evidenced by the isolation and structural characterization of $[Bi_4(Cl)_3(\mu\text{-}Cl)(\mu\text{-}O)(O)_2\{[O_2N_2]^{BuBuPip}\}_2]$, **2**, where $[O_2N_2]^{BuBuPip}$ is the homopiperazine-containing analog of L1.

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 ^{6}Li and ^{7}Li NMR spectroscopy in solution and the solid-state to gain insight into similarities and differences in the number of Li

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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 (Fig. 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.

2. Experimental

2.1. General and instrumental considerations

The proligands, $H_2[O_2N_2]^{BuBuIm}$ and $H_2[O_2N_2]^{BuBuPip}$, 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, $^{13}C\{^1H\}$ and $^7Li\{^1H\}$ 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. $^7Li\{^1H\}$ 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. $^7Li\{^1H\}$ SSNMR ($\upsilon_0(^7Li)$ = 98.2 MHz) spectra were recorded on a Bruker Avance 600 MHz spectrometer at 25 °C. $^7Li\{^1H\}$ spectra were collected using a solid-state MAS ^1H/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 $^7Li\{^1H\}$ spectrum was recorded and used as an external referencing standard. Analytical simulations of $^7Li\{^1H\}$ 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 Kα 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

$H_2[O_2N_2]^{BuBuIm}$ (2.01 g, 3.94 mmol) was dissolved in THF (30.0 mL) and cooled to −78 °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 °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, $C(CH_3)_3$, 18H); 1.57 (s, $C(CH_3)_3$, 18H); 1.51 (s, $C(CH_3)_3$, 18H); 1.45 (s, $C(CH_3)_3$, 18H); 1.17 (m, CH_2, THF, 22H). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 298 K): δ 165.3 (Ar*C*OH); 164.9 (Ar*C*OH); 137.0 (Ar*C*$(CH_3)_3$); 136.7 (Ar*C*$(CH_3)_3$); 133.8 (Ar*C*$(CH_3)_3$); 133.73 (Ar*C*$(CH_3)_3$); 126.9 (Ar*C*H); 126.2 (Ar*C*H); 125.7 (Ar*C*H); 125.1 (Ar*C*H); 124.4 (Ar*C*CH_2N); 124.0 (Ar*C*CH_2N); 78.52 (ArC*C*H_2N), 78.48 (ArC*C*H_2N), 68.4 (*C*H_2: THF); 61.7 (N*C*HN); 61.1 (N*C*HN); 52.5 (N*C*H_2CH_2N); 50.6 (N*C*H_2CH_2N); 36.0 (Ar*C*$(CH_3)_3$); 35.9 (Ar*C*$(CH_3)_3$); 34.5 (Ar*C*$(CH_3)_3$); 34.4 (Ar*C*$(CH_3)_3$); 32.9 (ArC(*C*$H_3)_3$); 32.8 (ArC(*C*$H_3)_3$); 31.3 (ArC(*C*$H_3)_3$); 31.1 (ArC(*C*$H_3)_3$); 25.6 (*C*H_2: