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Communication

A Hybrid Lithium Oxalate−Phosphinate Salt

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The novel organophosphorus-containing lithium salt Li(THF)[$(C_2O_4)B(O_2PPh_2)_2$] (**1**; THF = tetrahydrofuran) was synthesized and characterized using a variety of spectroscopic techniques. An X-ray structural analysis on crystals of **1** grown from THF reveals a dimeric structure $[Li(THF)(C_2O_4)B(O_2PPh_2)_2]_2\cdot THF$, whereby the two units of **1** are bridged via P−O···Li interactions. Compound **1** displays high air and water stability and is also thermally robust, properties needed of electrolytes for their possible use as electrolytes and/or additives in lithium-ion battery applications.

Since their commercial inception about 2 decades ago, lithium-ion batteries have become the power sources of choice for mobile comunication devices, portable computers, and power tools.[1] Attention has most recently been focused on their potential use for vehicular applications, spurned by the ever-rising demand for clean transportation energy.[2,3] However, safety concerns and cycle life continue to delay widespread introduction of this promising technology into this fast-growing industrial segment. Among the major hurdles to be overcome is the danger associated with the flammability of the organic solvents. Not surprisingly, efforts are being devoted toward the development of flame-retardant additives aimed at protecting systems and consumers during catastrophic failure or abuse.[4]

We have thus initiated efforts to rationally design new flame-retardant ions (FRIONs) that retain and/or enhance the operational needs of a lithium-ion salt in terms of optimal charge storage transport and solid electrolyte interface (SEI) attributes. While $LiPF_6$ has been one of the most employed salts for lithium-ion batteries, one of the most intriguing new salts contains boron−carboxylic acid fragments. Initially disclosed in a German patent,[5] lithium bis(oxalato)borate (LiBOB) has garnered much attention as a lithium salt for electrolytes.[6] Recently, Lucht and co-workers reported a hybrid lithium tetrafluorooxalatophosphate derivative that has displayed characteristics similar to that of the parent $LiPF_6$ compound.[7] One component of our design is similarly built around the lithium oxalato subunit. The other design component centers on organophosphorus compounds, containing P=O bonds, which have been shown to be excellent flame retardants in the polymer industry.[8] Furthermore, phosphorus compounds have been shown to be more environmentally benign compared to their halogenated analogues.[9]

In this Communication, we report the synthesis and characterization of a possible FRION, Li(THF)[$(C_2O_4)B(O_2PPh_2)_2$] (**1**; THF = tetrahydrofuran). Compound **1** exhibits excellent water and air stability as well as stability to a wide range of solvents including propylene carbonate at elevated temperatures for several days. The initial synthesis of **1** involved the solid-state reaction of diphenylphosphinic acid, oxalic acid, and boric acid in the presence of lithium hydroxide (Scheme 1, route A). While conversions of up to 50% to **1** could be achieved (as estimated by ^{31}P NMR spectroscopy, δ 20.9 ppm), much diphenylphosphinic acid, as well as an additional compound $Li(THF)(Ph_2PO_2H)(O_2PPh_2)$ (**2**) in ca. 10% (δ 20.3 ppm), remained. Compound **2** was predominantly formed when an additional 3 equiv of lithium hydroxide was added to the reaction mixture. Compound **2** was isolated as the sole product (79%) after a 2:1:1:2 mixture of diphenylphosphinic acid, boric acid, oxalic acid, and excess lithium hydroxide in toluene was refluxed and water was removed using a Dean−Stark trap apparatus. The identity of **2** was rigorously assigned by ^{1}H, ^{31}P, and ^{13}C NMR, elemental analysis, and the results of a single-crystal

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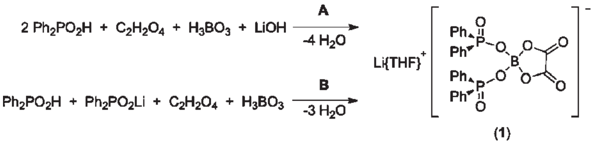
Scheme 1



(1)

X-ray diffraction study on a crystal of **2** (see the Supporting Information). Solution-phase routes to **1** were examined, including reactions that utilized anhydrous conditions and/or other boron reagents such as BCl_3, but these provided no notable improvements. Complicating the isolation of compound **1** was the fact that **1**, in the presence of other reaction products and reactants, decomposes to yield diphenylphosphinic acid. The conditions that provide access to limited quantities of pure **1** involve the solid-state reaction of boric acid, diphenylphosphinic acid, oxalic acid, and lithium diphenylphosphinide (Scheme 1, route B). Complete consumption of diphenylphosphinic acid was observed under these conditions (^{31}P NMR spectroscopy), and a 3:1 ratio of **1**:**2** was produced. Compound **1** was isolated by extraction of the reaction products with THF, followed by recrystallization by layering of a THF solution with pentane to give **1** in 19% yield as colorless, hygroscopic crystals (Scheme 1, route B). The ^1H NMR spectrum of **1** displayed upfield shifts for the aromatic resonances as well as spectral signatures for THF. The ^{11}B and ^{31}P NMR spectra displayed single resonances at 7.99 and 20.9 ppm, respectively. Because of the nature of ^1H and ^{31}P NMR resonances, it was postulated that both phosphinic acid moieties were in similar chemical environments in solution. The melting point of **1** had a range of 161−166 °C, most likely because of the slow loss of THF (vide infra).

Crystals of **1** grown from THF were analyzed by X-ray diffraction, and the results are presented in Figure 1. The overall solid-state structure of **1** is that of a dimer associated by P−O···Li interactions (Figure 1, lower) that also contains additional noncoordinated THF in the lattice. The lithium atoms are tetrahedrally coordinated by four oxygen atoms from three different phosphinic acid molecules and a coordinated THF molecule. The boron atoms also adopt a tetrahedral geometry comprised of four oxygen atoms from two different phosphinic acid molecules and a κ^2-*O*,*O*-oxalato substituent (Figure 1, upper). The B−O bond distances varied from 1.438(1) to 1.492(1) Å. The P1−O1 and P1−O3 bond distances, 1.550(1) and 1.491(1) Å, respectively, are similar to the bonds observed for diphenylphosphinic acid[10] rather than those for lithium diphenylphosphinide.[11] Moreover, the P2−O2 and P2−O4 bond distances are very similar to those for P1−O1 and P1−O3. The ^{31}P NMR resonances for these phosphorus atoms are not distinct in solution, despite differences in their environments in the solid state.

In order to assess the thermal stability of **1**, a thermogravimetric analysis (TGA) study was undertaken (Figure 2). The first thermal event occurred at 94.5 °C and corresponded to a mass loss of two THF molecules. A subsequent mass loss at the second thermal event occurred at 155.4 °C and could be attributed to a loss of 2 equiv of carbon dioxide, a possible decomposition product from oxalic acid. The next two thermal events occurred at 179.2 and 249.5 °C with mass losses associated with respectively another equiv of THF and 2 equiv of carbon dioxide. Previous work with LiBOB has demonstrated improved performance compared to $LiPF_6$, which has been linked to the ability of LiBOB to generate better SEIs. Furthermore, a 0.015 M solution of **1** in propylene carbonate was heated at 70 °C for 2 weeks in a sealed NMR tube and monitored periodically via ^{31}P NMR spectroscopy. No visible decomposition was discernible after 1 week.

In summary, a FRION candidate has been successfully synthesized and characterized. Further electrochemical and flammability testing of **1** are currently being undertaken.

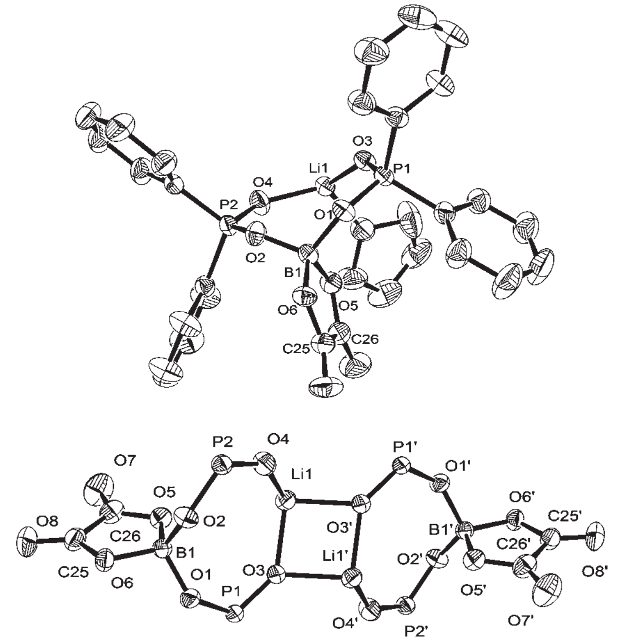


Figure 1. ORTEP diagrams of $[\mathbf{1}]_2\cdot 2THF$ showing monomeric (upper figure; THF and hydrogen atoms omitted for clarity) and dimeric association (lower figure; hydrogen atoms, phenyl rings, and THF omitted for clarity). Selected bond lengths (Å) and angles (deg): Li1−O3, 1.940(1); Li1−O3′, 1.960(1); Li1−O4, 1.856(1); P1−O1, 1.550(1); P1−O3, 1.491(1); P2−O2, 1.556(1); P2−O4, 1.481(1); B1−O1, 1.450(1); B1−O2, 1.438(1); B1−O5, 1.492(1); B1−O6, 1.484(1); O3−Li1−O4, 111.6(2); O3′−Li1−O4, 107.6(2); O1−P1−O3, 115.5(1); O2−P2−O4, 117.0(1); O1−B1−O2, 110.3(1); O5−B1−O6, 104.6(1).

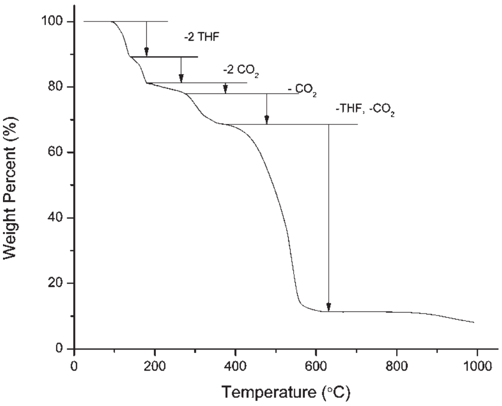


Figure 2. TGA on solid **1**.

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Supporting Information Available: Experimental details and crystal data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.