

Cite this: *Dalton Trans.*, 2015, **44**, 7048Homoleptic borates and aluminates containing the difluorophosphato ligand – $[M(O_2PF_2)_x]^{y-}$ – synthesis and characterization†Christoph Schulz,^a Philipp Eiden,^a Petra Klose,^a Andreas Ermantraut,^a Michael Schmidt,^b Arnd Garsuch^b and Ingo Krossing^{*a}

Weakly coordinating anions (WCAs) with the difluorophosphato ligand (O_2PF_2) were the target of this study. Initial experiments were conducted towards the preparation of homoleptic aluminates of the well-studied $[Al(OR)_4]^-$ -type. The preparation of the initial target structure $Li[Al(O_2PF_2)_4]$ failed due to the remaining Lewis acidic character of the central aluminum atom. Instead, the formation of $Li_3[Al(O_2PF_2)_6]$ and $Al(O_2PF_2)_3$ was observed with hexacoordinate aluminum atoms and verified by NMR, IR and X-ray crystallography. A possible mechanism towards these compounds was postulated in the solvent induced dismutation of the tetracoordinate $Li[Al(O_2PF_2)_4]$. A singly charged WCA was realized by the exchange of the central aluminum atom for boron. The $[B(O_2PF_2)_4]^-$ anion was prepared starting from $BH_3 \cdot S(CH_3)_2$ and boron tribromide leading to the protic room temperature Ionic Liquid (IL) $[H(S(CH_3)_2)][B(O_2PF_2)_4]$ and the neat liquid Brønsted acid $H[B(O_2PF_2)_4]$, respectively, representing a significantly improved synthesis with regard to the first experiments of Dove *et al.* The basicity of the $[B(O_2PF_2)_4]^-$ anion and its WCA quality were investigated on the basis of the IR-spectroscopic NH-scale and the salt $[H(N(Oct)_3)][B(O_2PF_2)_4]$ that places it better than all oxanions and close to the carboranate based WCAs. A pathway to the solvent free pure $Li[B(O_2PF_2)_4]$ salt was established on a multi-gram scale with excellent purities enabling electrochemical applications (verified by NMR, IR, X-ray crystallography and cyclovoltammetry).

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Introduction

The preparation of stable salts of reactive cations imposes special requirements upon the respective anions, such as low nucleophilicity and basicity. A decrease in the electrostatic interactions of the respective ions is achieved in the design of complex anions with a large surface area leading to a delocalization of the negative charge. Thereby, the otherwise stronger cation–anion interactions are transformed into multiple weak interactions,^{2,3} determining the nomenclature of this substance class as “weakly coordinating anions”, or WCAs. Other desirable properties of any type of WCA include stability against electrophilic attack, oxidation and/or reduction.

Ongoing research on WCAs is devoted to the development of novel WCAs by using sterically demanding, often partially fluorinated ligands. Other approaches towards new classes of anions have been developed in the use of polyhedral boranates $[B_nH_n]^{2-}$ ($n = 10, 12$)⁴ or carboranates $[HCB_nH_n]^-$ ($n = 9, 11$)⁵ and their halogenated derivatives.⁶

Working with weakly coordinating anions (WCAs)^{2,3,7} of the type $[M^{III}(OR^F)_4]^-$ ($M^{III} = B, Al, OR^F = \text{fluorinated alkoxide}$)⁸ and $[M^V(OR^F)_6]^-$ (ref. 9) ($M^V = Nb, Ta$) led to an expertise in our group with respect to the stabilization of weakly bound complexes,¹⁰ highly reactive cations,¹¹ as well as the induction of high conductivities in low polarity media.¹² The numerous possibilities of an exchange of the uninegative ligand OR^F with a more general definition of R^F as the electronegative fluorinated residue allows for the construction of a large variety of WCAs comprising amongst others the teflatometallates $[M(OTeF_5)_n]^-$ ($n = 4, M = B$;¹³ $n = 6, M = As$,¹⁴ Sb ,^{15,16} Bi ,¹⁴ Nb ^{15,17}), as well as the trifluorosulfonatometallates $[M(OSO_2R^F)_n]^-$.¹⁸

This article is devoted to the chemistry of the uninegative difluorophosphato ligand (O_2PF_2) starting from difluorophosphoric acid and its derivatives. Simple inorganic $[O_2PF_2]^-$ salts (K^+, Cs^+ ;¹⁹ $Li^+, Na^+, Rb^+, [NH_4]^+$ (ref. 20)) are known.

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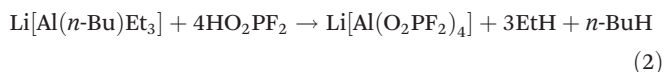
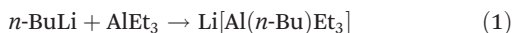
†Electronic supplementary information (ESI) available: Full experimental details, the discussed 1D- and 2D-NMR spectra, as well as IR spectra of the reactions are deposited. The complete crystal structure data including the CCSD deposition numbers are displayed. CCDC 1033591 and 1033599. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00469a

Structures containing difluorophosphate display a structural variety and different coordination modes. The expected simple ionic form with two almost equal P–O bonds is supplemented by a structure type with covalent bonding to one O atom of the ligand, leading to a monofunctional OP(O)F₂ group with a clear distinction of the two P–O bonds in the molecule, *i.e.* in the compounds P₂O₃F₂,²¹ (H₃C)₃Si(O₂PF₂)₂²² and Xe(O₂PF₂)₂.²³ A third structural type, in which the anion acts as a bridging ligand between two metal atoms, is realized in the compounds Cl₂Ti(O₂PF₂)₂,²⁴ [(H₃C)₂Ga(O₂PF₂)₂]₂,^{25,26} [(H₃C)₂Al(O₂PF₂)₃]₂^{25,26} and R₂Sn(O₂PF₂)₂.²⁷ In 1984, Dove *et al.* reported the existence of (difluorophosphato)borates in NMR tube experiments, delivering first spectroscopic evidence for the existence of [B(O₂PF₂)₄][−] and [FB(O₂PF₂)₃][−] anions in solution in equilibrium with other species.¹

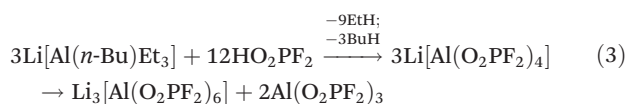
Results and discussion

Synthesis of Li₃[Al(O₂PF₂)₆] and Al(O₂PF₂)₃

A tetracoordinate aluminate – [Al(OP(O)F₂)₄][−] – was sought for by protolysis of the intermediately formed organometallic aluminate Li[Al(*n*-Bu)Et₃]²⁸ with difluorophosphoric acid (eqn (1) and (2)).



A colorless powder, slightly soluble in diethyl ether, dimethyl carbonate and acetonitrile was obtained. In disagreement to the sought Al-coordination number of four, the ²⁷Al-NMR spectrum in dimethyl carbonate showed a signal at δ = −18.1 ppm in the chemical shift range of sixfold coordinated aluminum. A doublet signal in the ¹⁹F-NMR spectrum at δ = −86.2 ppm and a triplet signal in the ³¹P-NMR spectrum at δ = −17.7 ppm, each with a coupling constant of ¹J_{FP} = 927 Hz, confirmed the sole existence of difluorophosphato ligands for the coordination of the aluminum. Crystallization of the product in diethyl ether at −20 °C led to colorless crystals, which were measured at 110 K. The structure was determined as ether solvated lithium hexakis-(difluorophosphato)-aluminate [Li(Et₂O)]₃[Al(O₂PF₂)₆]. The coordination of aluminum by six difluorophosphato ligands corresponded with the NMR spectroscopic results. Three oxygen atoms of the difluorophosphato ligands and one additional solvent molecule diethyl ether each coordinate the lithium cation. With these findings, the reaction scheme had to be modified according to eqn (3) towards the formation of a product mixture comprising Li₃[Al(O₂PF₂)₆] and the Lewis acid Al(O₂PF₂)₃.



Alterations in the reaction scheme regarding reactants and stoichiometries showed no success concerning the preparation

of Li₃[Al(O₂PF₂)₆] without the Lewis acid as a byproduct and therefore were abandoned.

Synthesis of Al(O₂PF₂)₃. In the earlier work mentioned, the IR spectroscopically characterized Lewis acid Al(O₂PF₂)₃²⁹ was considered a powerful building unit on the way to heteroleptic anions [XAl(O₂PF₂)₃][−]. Thus, synthetic access to this compound was worked out and found in the equimolar reaction of triethylaluminum with difluorophosphoric acid in pentane.



The compound was obtained as a colorless powder insoluble in organic solvents, therefore MAS-NMR and IR-/Raman-spectroscopy were used to determine the structure. Formation of a uniform aluminum species was proven by the ²⁷Al-MAS-NMR spectrum, which showed a signal at the chemical shift of δ = −16.2 ppm indicating a sixfold coordinated aluminum. ³¹P-MAS-NMR spectroscopy displayed the existence of two inequivalent difluorophosphates at δ = −29.0 ppm and −37.0 ppm, which suggested a coordination of the aluminum in two different ways. Vibrational spectroscopy delivered further structural indications. Monofunctional bonding of the difluorophosphates should lead to the fixation of a P–O single bond which results in a terminal formal P=O double bond and therefore a growing difference in the vibrational frequencies of the PO₂ stretching frequencies. Deviating from this, the very low difference of 94 cm^{−1} in Al(O₂PF₂)₃ (*cf.* Δν̄ = 183 cm^{−1} in [EMIm][O₂PF₂]³⁰ (EMIM = 1-ethyl-3-methylimidazolium)) indicated a bifunctional coordination of the difluorophosphate groups, which led to similar PO bonds and therefore close vibrational frequencies. As a conclusion of the different spectroscopic measurements, a polymeric structure of the Lewis acid was postulated, containing bridging and η²-chelating ligands (Fig. 1).

Further verification of this assignment was obtained by the calculated IR-spectra of a cyclic trimer (Al(O₂PF₂)₃)₃, constituting a compromise between computational cost and accuracy on the structural level, as it possesses all the aforementioned difluorophosphate coordination modes, while still being manageable with quantum chemical methods. The experimental spectrum is in fair agreement with the calculation and is shown in the ESI.† Due to the sixfold coordination of

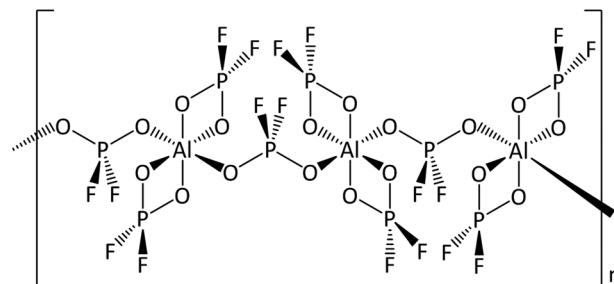


Fig. 1 Proposed polymeric structure of Al(O₂PF₂)₃.

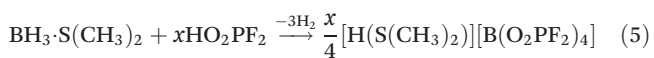


aluminum, the Lewis acidity of this compound and its suitability as a building block for heteroleptic aluminates are diminished leading to the abandoning of this approach.

From attempts to prepare the Lewis acid $\text{B}(\text{O}_2\text{PF}_2)_3$ to the successful syntheses of borates $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$

The poor solubilities of these aluminates motivated us to turn towards boron based systems. The smaller boron atom should allow the reduction of the coordination number from six in aluminum to four, which should lead to lighter anions with lower charge and thus increased solubilities in organic solvents.

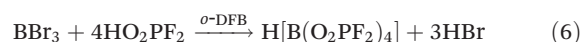
From $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$. With the prospect of obtaining a powerful building block on the way towards unsymmetrical borate anions, the preparation of the Lewis acid $\text{B}(\text{O}_2\text{PF}_2)_3$ was attempted from $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$ and difluorophosphoric acid in varying stoichiometries. However, the targeted Lewis acid remained absent. In the mixture, dimethyl sulfide was protonated causing a loss of its ability to coordinate and thereby stabilize the Lewis acidic boron species. The sole boron-containing compound yielded in the reactions according to eqn (5) was the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion.



The optimized synthesis of the homoleptic $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion was realized by the reaction of one equivalent of the dimethyl sulfide complex of BH_3 and four equivalents of difluorophosphoric acid in dichloromethane. It yielded the pure room temperature IL $[\text{H}(\text{S}(\text{CH}_3)_2)]^+ [\text{B}(\text{O}_2\text{PF}_2)_4]^-$ that could be purified from the solvent and residual unreacted reactants by applying high vacuum. FT-IR spectroscopy showed the expected vibrational bands for both $[\text{H}(\text{S}(\text{CH}_3)_2)]^+$ cation and $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion (see Table 2 below). In the area above 1450 cm^{-1} , the bands of the $[\text{H}(\text{S}(\text{CH}_3)_2)]^+$ cation could be found and assigned to the respective vibrational modes. The stretching mode of the S–H bond ($\tilde{\nu} = 2851 \text{ cm}^{-1}$) as well as the bending ($\tilde{\nu} = 1436 \text{ cm}^{-1}$) and stretching vibrations ($\tilde{\nu} = 2921 \text{ cm}^{-1}$ and 3042 cm^{-1}) of the CH_3 groups have been identified in the spectra. Only a deformation band of the CH_3 groups at $\tilde{\nu} = 1082 \text{ cm}^{-1}$ is overlapped by the symmetric stretch of the anion PO_2 groups. Multinuclear NMR spectroscopy is in complete agreement with the assigned structure: the integration of the ^1H -NMR signals of the $[\text{H}(\text{S}(\text{CH}_3)_2)]^+$ cation is in a ratio of 6 : 1 for the methyl protons ($\delta = 2.71 \text{ ppm}$) and the H–S proton ($\delta = 9.14 \text{ ppm}$) and thus confirms the complete protonation of the dimethyl sulfide. The structure of the anion was assigned by ^{11}B -NMR spectroscopy. A singlet at -4.1 ppm well in the chemical shift range of tetracoordinate boron proved the borate formation. As these NMR measurements were carried out with the neat liquid substance, the hyperfine structure of the spectrum was not well resolved in these experiments. However, the hyperfine structure of the anion was observed in the more fluid solution of the lithium salt $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ (see below). With the ^{19}F -NMR spectrum showing a doublet signal at a chemical shift of $\delta = -84.3 \text{ ppm}$ and the

^{31}P -NMR spectrum a triplet signal at $\delta = -30.9 \text{ ppm}$, the presence of difluorophosphato ligands in the anion was confirmed; potentially remaining B–H species were excluded by ^1H -NMR spectroscopy giving definite proof of the existence of the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion. In addition, ^{19}F - ^{11}B HSQC spectra confirmed the structure of the anion by showing a correlation of the fluorine atoms in the difluorophosphato ligands and the central boron atom.

Synthesis of $\text{H}[\text{B}(\text{O}_2\text{PF}_2)_4]$. Another access to the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion was provided by the reaction of boron tribromide and four equivalents of difluorophosphoric acid in *ortho*-difluorobenzene (*o*-DFB; eqn (6)). The synthesis led to a neat almost colorless liquid that could be purified from the solvent and byproduct at high vacuum. The composition was identified as the Brønsted acid $\text{H}[\text{B}(\text{O}_2\text{PF}_2)_4]$.



Again, a 1 : 3 stoichiometry did not lead to a Lewis acid, but rather a Brønsted acid. The experimental FT-IR spectrum of $\text{H}[\text{B}(\text{O}_2\text{PF}_2)_4]$ was in agreement with the DFT calculations for the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion. All vibrations were assigned to the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion, except for a weak band at $\tilde{\nu} = 1567 \text{ cm}^{-1}$. This broad band in the FT-IR spectrum provided first spectroscopic evidence of the coordination of a (bridging) proton in $\text{H}[\text{B}(\text{O}_2\text{PF}_2)_4]$ (see Stoyanov *et al.*³¹). In agreement with this assignment, this band disappeared after synthesis and purification of the lithium salt. As expected, the ^1H -NMR spectrum showed a singlet at a chemical shift of $\delta = 16.57 \text{ ppm}$ for the proton. The significant downfield shift in this compound compared to the signal of the protons in the reactant difluorophosphoric acid ($\delta = 14.61 \text{ ppm}$) may be interpreted as an explicit increase of the acidity of the system. The doublet signal in the ^{19}F -NMR spectrum at $\delta = -84.5 \text{ ppm}$ ($\delta = -85.1 \text{ ppm}$; ref. 27) possessed a coupling constant of $^1J_{\text{FP}} = 991 \text{ Hz}$ ($^1J_{\text{FP}} = 984 \text{ Hz}$; ref. 27) and corresponded to the triplet signal at $\delta = -32.3 \text{ ppm}$ ($\delta = -31.5 \text{ ppm}$; ref. 27) in the ^{31}P -NMR spectrum. ^{11}B -NMR spectroscopy displayed a singlet signal ($\delta = -4.0 \text{ ppm}$) belonging to the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion. As this sample was measured as a neat compound, the high concentration prevented the resolution of the hyperfine structure of the anion, which was analyzed in detail from the dissolved $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ salt. Nevertheless, the assignment by Dove *et al.*¹ in their NMR experiments was confirmed without a doubt. Furthermore, Dove *et al.* reported reactions of $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ with fluorine atoms present in their samples yielding heteroleptic borates of the $[\text{F}_x\text{B}(\text{O}_2\text{PF}_2)_{4-x}]^-$ -type, out of which they were able to characterize the $[\text{FB}(\text{O}_2\text{PF}_2)_3]^-$ anion. In our studies, we also found a certain instability of $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ in the presence of fluorine sources, such as $[\text{BF}_4]^-$, where we could identify all heteroleptic $[\text{F}_x\text{B}(\text{O}_2\text{PF}_2)_{4-x}]^-$ anions ($x = 0$ –3; see Table 1; elaborate discussion on these compounds will be published separately). Apart from these cases, the symmetrical borate is stable towards decomposition for weeks.



Table 1 Product distribution of ^{11}B species in the reaction of $[\text{H}(\text{S}(\text{CH}_3)_2)][\text{B}(\text{O}_2\text{PF}_2)_4]$ with the reactant in the first column. All data are given in percentages, determined by integration of the signals in the ^{11}B -NMR spectrum

	$\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$	$\text{Li}[\text{FB}(\text{O}_2\text{PF}_2)_3]$	$\text{Li}[\text{F}_2\text{B}(\text{O}_2\text{PF}_2)_2]$	$\text{Li}[\text{F}_3\text{B}(\text{O}_2\text{PF}_2)]$
LiH	69	25	3	3
<i>n</i> -Butyllithium	83	1	10	6
<i>t</i> -Butyllithium	92	4	2	2

Synthesis of $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$

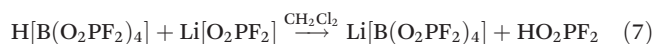
The large scale synthesis of electrochemically pure $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ was developed starting from different compounds containing the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion.

Starting from $[\text{H}(\text{S}(\text{CH}_3)_2)][\text{B}(\text{O}_2\text{PF}_2)_4]$. The protonated thioether was treated with lithium hydride, lithium metal and *n*- or *t*-butyllithium in order to allow for simple elimination of the gaseous byproducts hydrogen, *n*- or *i*-butane. In the heterogeneous reaction with lithium metal, only a small turnover was achieved due to the relatively small surface area of the metal. The reactions with lithium hydride in pentane or with butyllithium in *o*-difluorobenzene led to the desired lithium salt of the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion, but in each case in insufficient purity. The byproducts were assigned as the three mixed fluoro-(difluorophosphato)-borate species $[\text{F}_x\text{B}(\text{O}_2\text{PF}_2)_{4-x}]^-$ ($x = 1-3$) that were formed in a complex and not fully understood reaction (Table 1).

The main product $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ was identified clearly by multinuclear NMR spectroscopy. It showed a signal at $\delta = -4.2$ ppm with the hyperfine structure of a quintet of nonets in the ^{11}B -NMR spectrum (Fig. 2; $^2J_{\text{PB}} = 8.0$ Hz and $^3J_{\text{FB}} = 1.5$ Hz). In the ^{19}F -NMR spectrum the doublet of quartet signal at $\delta = -83.7$ ppm contained a $^1J_{\text{FP}}$ coupling constant of 983 Hz and the previously mentioned $^3J_{\text{FB}}$ coupling of 1.5 Hz. ^{31}P -NMR spectroscopy provided a signal at $\delta = -30.2$ ppm with the multiplicity of a triplet of quartets, containing coupling constants of 981 Hz ($^1J_{\text{FP}}$) and 8.0 Hz ($^2J_{\text{PB}}$). The $[\text{F}_x\text{B}(\text{O}_2\text{PF}_2)_{4-x}]^-$ byproducts were identified in the ^{11}B -NMR spectrum with the knowledge of further, separately performed investigations on this system that will be published separately. An increase of x in $[\text{F}_x\text{B}(\text{O}_2\text{PF}_2)_{4-x}]^-$ ($x = 0-4$) caused a definite low-field shift of the ^{11}B -NMR signals of the respective borate, indicating a

better electronic shielding of the boron center by difluorophosphato ligands compared to the fluoride ligands.

Starting from $\text{H}[\text{B}(\text{O}_2\text{PF}_2)_4]$. The synthesis of $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ of an adequate quality for electrochemical purposes required a resilient route comprising lithium difluorophosphate as a compatible and non-nucleophilic reactant with the symmetric borate anion $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$.



The exclusion of any other nucleophiles than $[\text{O}_2\text{PF}_2]^-$ led to a clean preparation of $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ without noteworthy impurities. Work up of the lithium salt only includes simple washing steps with dichloromethane to get rid of the formed difluorophosphoric acid. The exclusive formation of the $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ was verified by the recorded NMR spectra. A solitary multiplet in the ^{11}B -NMR spectrum (Fig. 2) at $\delta = -4.2$ ppm (quintet of nonets) demonstrated the stability of the anion under the chosen conditions; the matching ^{19}F - and ^{31}P -NMR spectra showed the expected doublet ($\delta = -84.0$ ppm; ^{19}F) and triplet ($\delta = -30.2$ ppm; ^{31}P) signals for the difluorophosphato ligands. Complete conversion to the lithium salt was confirmed by the ^7Li -NMR spectrum (singlet at $\delta = -2.0$ ppm) and the ^1H -NMR spectrum displaying the absence of a proton signal corresponding to the Brønsted acid.

The electrochemical stability of the lithium salt was tested by cyclic voltammetry (Fig. 3) to investigate the ability for usage as a conducting salt in lithium ion batteries (LIBs). The fifth cycle of the anodic measurement showed a smooth course of the current with a large plateau-like potential range of 3.3 to 4.3 V devoid of signs of redox processes in the electrolyte solution and with current values below 5×10^{-7} A. At potentials above 4.3 V, the inevitable oxidation of ethylene carbonate and dimethyl carbonate occurred, which led to an increase in the current values up to 1.5×10^{-6} A. For the cathodic measurement, a wide potential range of 2.8 to 0.9 V was observed in the forward sweep displaying current values of -2.0×10^{-7} to -6.0×10^{-7} A with peak current values of -1.0×10^{-5} A reaching at a potential of 0 V.

Therefore, it was concluded that the electrochemical window of $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ exceeds the stability of the electrolyte solvents. Further investigations with respect to the application of the compound in LIBs were undertaken and will be discussed in a follow-up paper with focus on the electrochemical properties.

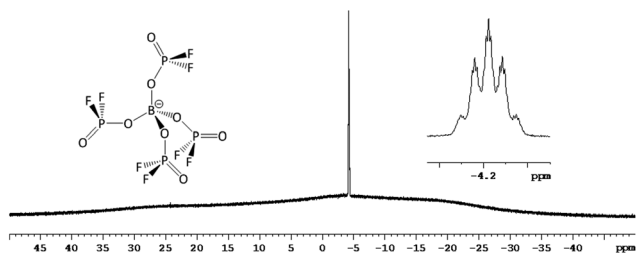


Fig. 2 ^{11}B -NMR spectrum of $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ (128.39 MHz, in ethylene carbonate–dimethyl carbonate (EC–DMC (1:1)), external toluene- d_8 lock, 298 K).



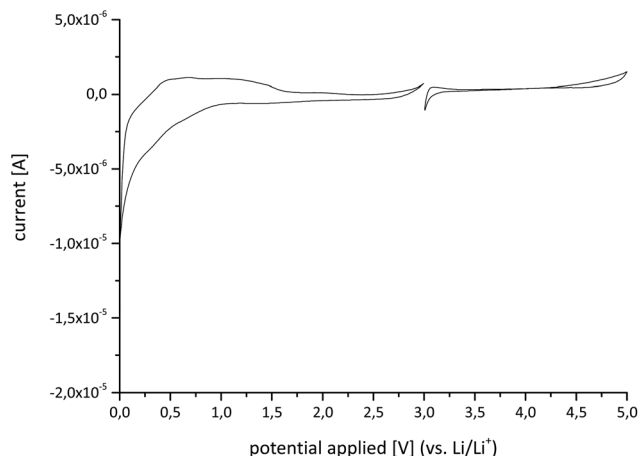


Fig. 3 Cyclic voltammogram of $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ (1.0 mol L^{-1} in ethylene carbonate–dimethyl carbonate (1 : 1)); fifth cycles of anodic (3 to 5 V vs. Li/Li^+) and cathodic measurement (3 to 0 V vs. Li/Li^+) combined.

Crystal structures

$\text{Li}_3[\text{Al}(\text{O}_2\text{PF}_2)_6]$. The product of the reaction of $\text{Li}[\text{AlEt}_3\text{Bu}]$ and difluorophosphoric acid was dissolved in diethyl ether and crystallized at a temperature of -40°C . The crystals were measured at a temperature of 100 K and determined to be the diethylether coordinated lithium salt of the homoleptic hexakis(difluorophosphato)aluminate $[\text{Li}(\text{Et}_2\text{O})_3][\text{Al}(\text{O}_2\text{PF}_2)_6]$. The compound crystallized in the trigonal space group $R\bar{3}$ with the unit cell dimensions of $a = 17.4058(4) \text{ \AA}$, $b = 17.4058(4) \text{ \AA}$, $c = 21.4947(6) \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ and $Z = 6$. The final R -index $[(I > 2\sigma(I))]$ of the refined structure converged to $R_1 = 0.0337$ ($wR_2 = 0.0824$). The asymmetric unit of $[\text{Li}(\text{Et}_2\text{O})_3][\text{Al}(\text{O}_2\text{PF}_2)_6]$ is constituted of a lithium cation coordinated by a diethyl ether molecule and by two difluorophosphato ligands bound to a central aluminum atom, one of them being dis-

ordered with a population of the two disordered sites in a ratio of 60 : 40. Fig. 4, left displays a section of the crystal structure with an emphasis on the aluminate part of the compound. The central aluminum atom shows an octahedral coordination with six difluorophosphato ligands with Al–O bond lengths of 187.4(1) pm for the ordered difluorophosphato ligands and 187.9(1) pm for the disordered ones.

The P–O distances in the difluorophosphato ligands are 145.1(5) to 148.7(5) pm (*cf.*: $d_{\text{P-O}}(\text{K}[\text{O}_2\text{PF}_2]) = 147.0 \text{ pm}$; ref. 32), whereas the corresponding P–F distances range from 152.2(8) pm up to 153.3(1) pm (*cf.*: $d_{\text{P-X}}(\text{K}[\text{O}_2\text{PF}_2]) = 157.5 \text{ pm}$; ref. 32). The shortening of the P–F bonds in the $[\text{Al}(\text{O}_2\text{PF}_2)_6]^{3-}$ anion compared to the ionic difluorophosphate in the potassium salt is probably induced by the increased electrophilicity due to the direct bonding of the ligand to the aluminum center resulting in strengthened P–F bonds. The coordination of the lithium cations is illustrated in Fig. 4, right. It includes a dimeric structure of two lithium cations each coordinated by one diethyl ether molecule and three difluorophosphato ligands. With a Li–O distance of 197.6(3) pm, the four-membered ring substructure is composed of two lithium cations and the terminal μ_2 -coordinated oxygen atoms of two difluorophosphato ligands. In each case, another disordered difluorophosphato ligand is coordinated μ_1 to the lithium cation at a distance of 186.4(3) pm and the fourth coordination site is occupied by the oxygen atom of a diethyl ether molecule with a distance of 194.5(3) pm. The compound $[\text{Li}(\text{Et}_2\text{O})_3][\text{Al}(\text{O}_2\text{PF}_2)_6]$ forms a layered structure along the c -axis of the unit cell with a two dimensional network in the a – b plane built from $[\text{Al}(\text{O}_2\text{PF}_2)_6]^{3-}$ anions interconnected by solvent coordinated lithium cations (see ESI† for figures).

Solvent free $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$. At room temperature, the colorless, highly viscous product from the reaction of $\text{H}[\text{B}(\text{O}_2\text{PF}_2)_4]$ and lithium difluorophosphate crystallized in colorless crystals that were measured at a temperature of 100 K. Structure solution and refinement showed the compound to be donor free

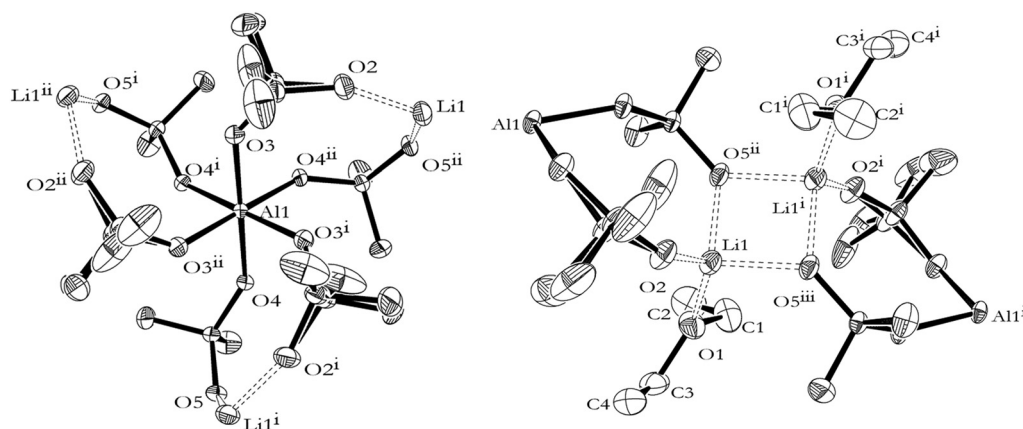


Fig. 4 Hydrogen atoms were omitted for reasons of clarity; thermal ellipsoids are shown at a probability of 50%. Left: section of the molecular structure of $[\text{Li}(\text{Et}_2\text{O})_3][\text{Al}(\text{O}_2\text{PF}_2)_6]$ with focus on the structure of the $[\text{Al}(\text{O}_2\text{PF}_2)_6]^{3-}$ anion; contacts to the lithium cations are displayed with dashed bonds. Right: coordination of the lithium cations by the diethyl ether molecules and the $[\text{Al}(\text{O}_2\text{PF}_2)_6]^{3-}$ anions shown in an excerpt of the crystal structure of $[\text{Li}(\text{Et}_2\text{O})_3][\text{Al}(\text{O}_2\text{PF}_2)_6]$; coordinative bonds are displayed as dashed bonds.



$\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$. Crystallizing in the monoclinic space group $P2_1/c$, the unit cell dimensions were determined as $a = 7.9074(2)$ Å, $b = 14.0602(4)$ Å, $c = 13.7851(3)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 121.9130(10)^\circ$ and $Z = 4$. The final R -index [$I > 2\sigma(I)$] of the refined structure of $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ converged to $R_1 = 0.0284$ ($wR_2 = 0.0772$). The asymmetric unit of $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ consists of one lithium cation coordinated by one $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion. The coordination of lithium is realized by the terminal oxygen atom of one of the three ordered difluorophosphato ligands bound to the central boron atom of the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion, comprising a fourth, disordered difluorophosphato ligand with a population of the two disordered sites in a ratio of 80 : 20.

The fourfold coordination of the central boron atom of the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion is illustrated in Fig. 5, left displaying B–O bond lengths between 145.6(1) and 146.1(1) pm. The difluorophosphato ligands include P–O distances in the ordered ligands of 152.1(1) to 152.2(1) pm for the oxygen atoms bound covalently to the central boron atom and P–O bond lengths of 144.0(1) to 145.0(1) pm for the terminal oxygen atoms coordinated to the lithium cation. In the disordered ligand, the P–O_{boron} distances were determined as 149.9(1) and 155.6(2) pm, respectively, whereas the P–O_{Lithium} bond lengths measured 144.2(4) and 147.7(13) pm respectively (*cf.*: $d_{\text{P-O}}[\text{K}(\text{O}_2\text{PF}_2)] = 147.0$ pm; ref. 32). The corresponding P–F distances range from 150.6(1) to 152.9(1) pm for the ordered difluorophosphato ligands and from 146.3(5) to 153.7(5) pm for the disordered ligands (*cf.*: $d_{\text{P-X}}[\text{K}(\text{O}_2\text{PF}_2)] = 157.5$ pm; ref. 32). As it was shown in the case of the $[\text{Al}(\text{O}_2\text{PF}_2)_6]^{3-}$ anion in the previous section, the direct bonding of the ligands to the electrophilic boron center resulted in a decrease of negative charge in the ligand in comparison with the ionic difluorophosphate and therefore, stronger bonds to the fluorine atoms. The embedding of the lithium cations into the structure of $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ is illustrated in Fig. 5 right. It shows the fourfold coordination of lithium by the terminal oxygen atom of difluorophosphato ligands belonging to four different $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anions. In this way, the

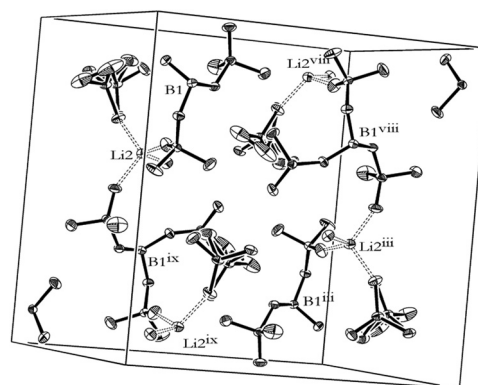


Fig. 6 Contents of one unit cell of $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$, displaying the inter-connection of the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anions via the fourfold coordinated lithium cation; coordinative bonds are displayed using dashed bonds; thermal ellipsoids are shown at a probability of 50%.

lithium cation interconnects the anions to three-dimensional networks showing Li–O distances of 191.7(2) pm to 194.2(2) pm for the ordered ligands and 187.0(20) pm to 194.5(4) pm for the disordered ligands with an approximately tetrahedral coordination geometry displaying O–Li–O bond angles from $105.6(1)^\circ$ to $114.4(1)^\circ$ (Fig. 6).

Vibrational spectroscopy of the difluorophosphates

This section provides a more in-depth insight into the coordination of the difluorophosphates in the previously mentioned compounds. The method of choice to determine structural motifs in the bonding of the difluorophosphates is vibrational spectroscopy due to the high sensitivity of their stretching vibrations. Several structural types of coordination are well known and described in the literature,³³ such as ionic $[\text{O}_2\text{PF}_2]^-$ in alkali metal salts,²⁰ monofunctional $\text{OP}(\text{O})\text{F}_2$ groups in $(\text{H}_3\text{C})_3\text{Si}(\text{O}_2\text{PF}_2)$ ³⁴ or bridging difluorophosphates in

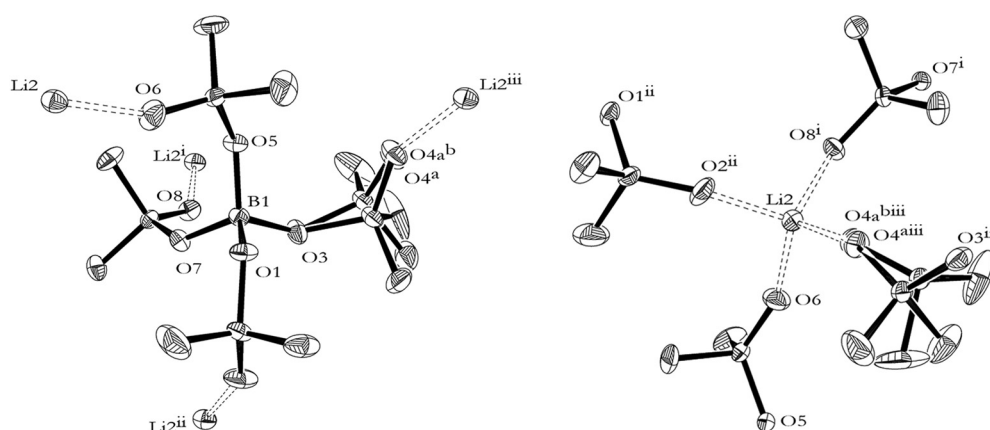


Fig. 5 Thermal ellipsoids are shown at a probability of 50%; coordinative bonds are displayed using dashed bonds. Left: section of the molecular structure of $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ with focus on the structure of the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion. Right: coordination of the lithium cation by four different $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anions, in each case with one terminal oxygen atom, shown in a section of the crystal structure of $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$.



Table 2 Vibrational frequencies for the different difluorophosphato species discussed in this paper in comparison with the literature data of [EMIm][O₂PF₂]. Bands corresponding to vibrations of the cations were left out. All data are given in cm⁻¹

[EMIm][O ₂ PF ₂] ³⁰	Li ₃ [Al(O ₂ PF ₂) ₆]	Al(O ₂ PF ₂) ₃	[H(S(CH ₃) ₂)][B(O ₂ PF ₂) ₄]	H[B(O ₂ PF ₂) ₄]	[H(N(Oc) ₃)]B(O ₂ PF ₂) ₄	Li[B(O ₂ PF ₂) ₄]	Assignment ^a
498 (s)	417 (w)	402 (w)	472 (w)	469 (w)	472 (w)	479 (w)	δ(PF ₂)
—	503 (w)	495 (w)	511 (w)	502 (w)	514 (w)	502 (sh)	δ(PO ₂)
—	536 (w)	512 (sh)	555 (w)	552 (w)	560 (w)	568 (w)	δ(MO ₂)
—	624 (w)	622 (w)	648 (vw)	647 (w)	724 (w)	—	δ(MO ₂)
—	723 (w)	—	—	—	—	—	—
—	—	847 (w)	—	—	—	—	—
820 (s)	891 (w)/922 (m)	916 (m)	832 (m)	836 (m)	832 (m)	833 (m)	ν _s (PF ₂)
—	964 (s)	956 (m)	933 (m)	940 (m)	931 (m)	945 (m)	ν _{as} (PF ₂)
—	—	—	993 (w)	994 (w)	983 (w)	1002 (w)	ν(MO ₂)
1140 (s)	1175 (s)/1204 (s)	1192 (m)	1083 (s)	1093 (s)	1086 (s)	1080 (s)	ν _s (PO ₂)/ν(P–O) ^b
1323 (s)	1283 (s)	1287 (s)	1337 (s)	1348 (m)	1346 (s)	1334 (s)	ν _{as} (PO ₂)/ν(P=O) ^b
—	—	—	1436 (vw)	—	1468 (w)	—	—
—	—	—	—	1567 (w)	—	—	—

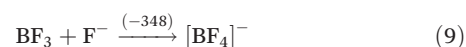
^a M stands for the group XIII elements boron or aluminum. ^b The denominations ν(P–O) and ν(P=O) apply to the monofunctional OP(O)F₂ groups in the [M(O₂PF₂)_x]^{y-} anion; the denominations ν_s(PO₂) and ν_{as}(PO₂) are for the aluminum species Al(O₂PF₂)₃ and the free [O₂PF₂]⁻ anion.

[(H₃C)₂Ga(O₂PF₂)₂]₂.²⁶ As a reference state for an undisturbed [O₂PF₂]⁻ anion with small interactions between the cation and anion, the literature data of the imidazolium based ionic liquid [EMIm][O₂PF₂]³⁰ were used in this work. The difluorophosphates in all the complex ions shown in this work are expected to possess four clearly recognizable stretching vibrations based on the asymmetric and symmetric vibrational modes of both the PO and PF bonds. Depending on the type of coordination, the corresponding vibrational frequencies can vary considerably, especially for the directly bound OP(O)F₂ groups. A summary of the IR spectroscopic data of the investigated compounds is given in Table 2. The stretching vibrations of the PO₂ group in [EMIm][O₂PF₂]³⁰ ($\tilde{\nu}$ = 1323 cm⁻¹ and 1140 cm⁻¹) displayed a difference of $\Delta\nu$ = 183 cm⁻¹, which is considered a rather small value due to the good resonance of the two oxygen atoms in the undisturbed ion (I in Fig. 7). Stronger bonding of one oxygen atom led to a monofunctional OP(O)F₂ group with a fixed P–O–σ bond and a formal terminal P=O double bond (II in Fig. 7). The [B(O₂PF₂)₄]⁻ anion includes this coordination mode II and therefore all of its presented compounds featured a much higher $\Delta\nu$ of 254–260 cm⁻¹, with the terminal P=O double bond blue-

shifted by 11 to 25 cm⁻¹, whereas the P–O–σ bond exhibited a redshift of 47–60 cm⁻¹. Coordination of the difluorophosphates in the aluminum species Al(O₂PF₂)₃ was realized differently: the aluminum centers in this structure were bridged by the two oxygen atoms of the phosphates. This structural variation (III in Fig. 7) led to a smaller difference between the asymmetric and symmetric stretching vibration of the PO₂ group, which decreased to $\Delta\tilde{\nu}$ = 95 cm⁻¹ for the Lewis acid Al(O₂PF₂)₃, underlining the similarity of the bonding situation for both coordinated oxygen atoms.

On the nature of the Lewis acid B(O₂PF₂)₃

The goal of synthesizing unsymmetric borates of the type [XB(O₂PF₂)₃]⁻ should be accomplished by the synthesis of the Lewis acid B(O₂PF₂)₃. This compound is expected to possess high Lewis acidity and therefore large potential as a synthetic building block on the way to the desired unsymmetric borates. However, experimentally in our hands it was impossible to obtain this molecule. Therefore, the Lewis acidity of B(O₂PF₂)₃ was investigated by quantum chemical calculations[‡] concerning its fluoride ion affinity (FIA).^{35,36} The FIA presents a way to classify Lewis acids respective to the energy that is released upon the binding of a fluoride anion and is determined for the respective substances in isodesmic reactions. The reactions taken into account for this particular compound were as follows:



The combination of both reactions resulted in the basic equation to establish the FIA(B(O₂PF₂)₃):

[‡] The components of reaction (9) were calculated at the G3-level; M(O₂PF₂)₃ and [FM(O₂PF₂)₃]⁻ (M = B, Al) were calculated at the PBE0/def2-TZVP(P)-level.

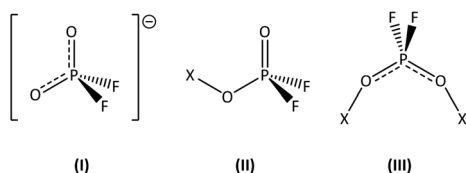


Fig. 7 Modes of coordination of the difluorophosphato ligand: ionic (I), monofunctional OP(O)F₂ groups (II), symmetrically bridging between two metal atoms (III). The terminal PO bond is written as a formal double bond, although it is clear that its Lewis structure is better represented by a P⁺–O⁻ notation. However, the formal double bond P=O intuitively accounts for the observed blue shift in the vibrational frequency.





According to the calculations, $\text{B}(\text{O}_2\text{PF}_2)_3$ displays a very high FIA of 469 kJ mol⁻¹ lying within the range of the system $\text{SbF}_5/[\text{SbF}_6]^-$ (493 kJ mol⁻¹) that represents the limit to superacidity.^{36,37} As shown above, the reactions of the dimethyl sulfide complex of BH_3 and difluorophosphoric acid led to the formation of the symmetric borate $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$. Alterations in the stoichiometry of the acid to two or three equivalents showed no influence on the resulting boron species, as the symmetric $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion obviously constitutes the thermodynamic minimum in these reactions. The synthesis of $\text{B}(\text{O}_2\text{PF}_2)_3$ probably failed because the tricoordinate central boron atom is not stable in the chosen environments due to its high Lewis acidity.

The aforementioned Lewis acid $\text{Al}(\text{O}_2\text{PF}_2)_3$ showed a similar behavior with respect to the threefold coordination of the central atom in these structures. As previously mentioned, the aluminum compound avoids the coordination number of three by the formation of a polymeric structure with a sixfold coordination of the central aluminum. The FIA of monomeric, gaseous $\text{Al}(\text{O}_2\text{PF}_2)_3$ gives an explanation for this behavior as well. It was calculated analogous to eqn (8)–(10) using the respective aluminum containing species on the same quantum chemical level.



In the case of $\text{Al}(\text{O}_2\text{PF}_2)_3$, the FIA was determined to be 494 kJ mol⁻¹. Thus, its very acidic character underlines the very pronounced tendency towards higher coordination numbers for aluminum.

The high Lewis acidity of $\text{B}(\text{O}_2\text{PF}_2)_3$ is reflected in the energetic level of its LUMO (lowest unoccupied molecular orbital) at -0.92 eV. According to G. Frenking *et al.*,³⁸ the energy of the LUMO dictates the interaction with a Lewis base, having a decisive influence on the acidity of a Lewis acid. Compared to BF_3 ($E_{\text{LUMO}} = +0.46$ eV), the lower LUMO level of $\text{B}(\text{O}_2\text{PF}_2)_3$ corresponds with the abovementioned increase of the Lewis acidity. For the analogous aluminum system ($E_{\text{LUMO}}(\text{AlF}_3) = -1.49$ eV; $E_{\text{LUMO}}(\text{Al}(\text{O}_2\text{PF}_2)_3) = -1.01$ eV), the orbital based impact on the acidity is less than the ionic contributions, which may relativize the inverse situation of the LUMO energy levels, therefore still being consistent with the high Lewis acidity of 494 kJ mol⁻¹ for $\text{Al}(\text{O}_2\text{PF}_2)_3$.

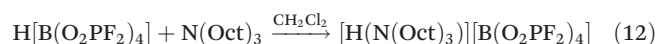
Evaluation of the WCA-performance of $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$: synthesis of $[\text{H}(\text{N}(\text{Oct})_3)][\text{B}(\text{O}_2\text{PF}_2)_4]$

For an experimental evaluation of the basicity of the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion, its tri-*n*-octylammonium salt was synthesized. C. A. Reed *et al.*³⁹ established a $\nu(\text{NH})$ scale for weakly basic anions, which allows for a comparison of the before mentioned anions (A^-), as well as their conjugate acids (HA). The compound $[\text{H}(\text{N}(\text{Oct})_3)][\text{B}(\text{O}_2\text{PF}_2)_4]$ was obtained as a

Table 3 $\nu(\text{NH})$ frequencies for $[\text{H}(\text{N}(\text{Oct})_3)]^+\text{A}^-$ salts in substance. All values apart from $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ were taken from the literature.³⁹ All frequencies are given in cm⁻¹

Anion	$\nu(\text{NH})$ frequency	Anion	$\nu(\text{NH})$ frequency
$[\text{B}(\text{C}_6\text{F}_5)_4]^-$	3241	$[\text{CHB}_{11}\text{Me}_5\text{I}_6]^-$	3100
$[\text{B}_{12}\text{F}_{12}]^{2-}$	3226	$[\text{B}(\text{O}_2\text{PF}_2)_4]^-$	3092(4)
$[\text{CMeB}_{11}\text{F}_{11}]^-$	3219	$[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$	3086 (in CCl_4)
$[\text{SbF}_6]^-$	3201	$[(\text{HSO}_4)_2]^{2-}$	3080
$[\text{B}_{12}\text{I}_{12}]^{2-}$	3116	$[\text{C}_5\text{H}(\text{CN})_4]^-$	3070
$[\text{CHB}_{11}\text{H}_5\text{I}_6]^-$	3106	$[\text{F}_3\text{CSO}_3]^-$	3056, 2815
$[\text{C}_5(\text{CN})_5]^-$	3105	$[\text{FSO}_3]^-$	3045

colorless room temperature ionic liquid in a reaction of the Brønsted acid $\text{H}[\text{B}(\text{O}_2\text{PF}_2)_4]$ and tri-*n*-octylamine in dichloromethane, according to eqn (9):



The tri-*n*-octylammonium cation caused the appearance of vibrational bands in the area of 2850 cm⁻¹ to 3100 cm⁻¹, additional to the bands of the anion (Table 2). Those were assigned to the C–H stretching vibrations ($\tilde{\nu} = 2859$ cm⁻¹; 2928 cm⁻¹ and 2957 cm⁻¹) and the N–H stretching vibration at $\tilde{\nu} = 3092$ cm⁻¹. The $\nu(\text{NH})$ frequency being slightly below the region of carboranates, but yet above the values for the least basic oxanions (Table 3) displayed the very low basicity of the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ anion and therefore the high acidity of its conjugate acid $\text{H}[\text{B}(\text{O}_2\text{PF}_2)_4]$.

Conclusion

A new class of WCAs with the difluorophosphato ligand was investigated. Tetracoordinate $[\text{Al}(\text{O}_2\text{PF}_2)_4]^-$ -type structures were aspired. However, the originally sought after tetracoordinate $\text{Li}[\text{Al}(\text{O}_2\text{PF}_2)_4]$ proved to be unstable in solution, leading to dismutation and formation of hexacoordinate aluminum species, *i.e.* the homoleptic aluminate $\text{Li}_3[\text{Al}(\text{O}_2\text{PF}_2)_6]$ and the Lewis acid $\text{Al}(\text{O}_2\text{PF}_2)_3$. In contrast to the results with Al as the central atom, the intended use as a WCA implies the realization of a singly charged anion. Thus, the preferred WCA-coordination number of four led to the exchange of aluminum by boron. The synthesis of such borates was attempted by the preparation of the Lewis acid $\text{B}(\text{O}_2\text{PF}_2)_3$ as an important building block. However, this was never successful. Syntheses of the tri-coordinated boron compound $\text{B}(\text{O}_2\text{PF}_2)_3$ always yielded the homoleptic anion $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$, regardless of the stoichiometry of the reactants. Thus, the room temperature IL $[\text{H}(\text{S}(\text{CH}_3)_2)][\text{B}(\text{O}_2\text{PF}_2)_4]$ was prepared in the reaction of $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$ and difluorophosphoric acid, whereas the route with boron tribromide as the reactant led to the room temperature liquid Brønsted acid $\text{H}[\text{B}(\text{O}_2\text{PF}_2)_4]$. The basicity of the $[\text{B}(\text{O}_2\text{PF}_2)_4]^-$ WCA was assigned to be in between the range of carboranates and oxanions by an IR spectroscopic analysis of the tri-*n*-octylammonium salt of this anion.

§ All LUMO energies were calculated at the PBE0/def2-TZVP(P)-level.



The preparation of lithium tetrakis(difluorophosphato) borate was investigated based on the two routes starting from $\text{BH}_3\cdot\text{S}(\text{CH}_3)_2$ and boron tribromide. Heterogeneous reactions of $[\text{H}(\text{S}(\text{CH}_3)_2)][\text{B}(\text{O}_2\text{PF}_2)_4]$ and lithium metal or lithium hydride delivered poor results, whereas homogeneous reactions using butyllithium led to purities up to 92%. The reaction of the Brønsted acid $\text{H}[\text{B}(\text{O}_2\text{PF}_2)_4]$ with lithium difluorophosphate led to excellent purities above 99% in large batches (up to 25 g).

Cyclovoltammetry in EC/DMC showed that the electrochemical window of $\text{Li}[\text{B}(\text{O}_2\text{PF}_2)_4]$ exceeds the stability of the electrolyte solvents leading to further investigations towards a potential application in LIBs as conducting salts or additives which will be discussed in a separate follow-up paper.

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