CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200802243

Chloride-Free Method to Synthesise New Ionic Liquids with Mixed Borate Anions

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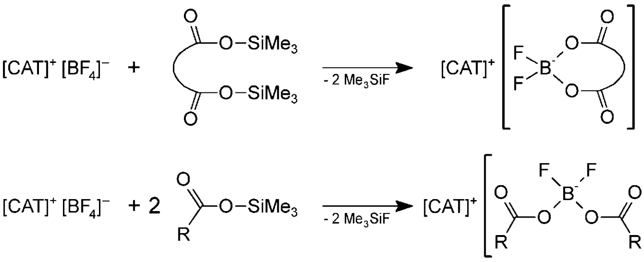
A new chloride-free method to synthesise ionic liquids (ILs) with mixed borate anions, starting from tetrafluoroborate compounds, has been developed and a number of examples including some new ILs are presented. It is widely applicable and allows access to mixed borates with various types of ligands in a straightforward manner.

ILs, especially room-temperature molten ionic liquids (RTILs), have received a great deal of attention because of their special properties, making them interesting in the fields of fundamental research and application, for example synthesis, catalysis, and electrochemistry.[1–5]

A large number of tetrafluoroborate-based salts and ILs are easily accessible or commercially available, making them interesting as starting materials for our investigations. The motivation behind the search for mixed borate anions is to decrease the ionic liquids' melting point by reducing the anion symmetry with respect to $[BF_4]^-$ to get new ILs with various cations.

The anions under investigation are derived from $[BF_4]^-$ by replacement of F^- by mono- or bidentate ligands (e.g. oxalate, malonate, acetate, trifluoroacetate), leading to anions with reduced symmetry, with respect to $[BF_4]^-$. Our previously used two synthesis routes[6–8] show some drawbacks, including chloride impurities[9] of synthesised ILs, that cannot be removed. Therefore, we have developed a new route overcoming these drawbacks. This route is widely applicable and allows access to mixed borate anions with various types of ligands in a straightforward manner. Together with the presentation of this new synthesis route, we give several examples for new ionic liquids synthesised and characterised for the first time. These results are not only valuable concerning the research on ionic liquids, they are also of general interest because the ease of the exchange reaction of fluoride has not been demonstrated so far. The general reaction Scheme is given in Scheme 1.



Scheme 1. General reaction scheme for synthesis of mixed borate anions from $[CAT]^+[BF_4]^-$ salts ($[CAT]^+$: any cation) and trimethylsilylated bidentate (top) or monodentate (bottom) ligands.

The applied experimental procedure depends on the type of ligand. Strict moisture exclusion and dried starting materials and solvents were used to minimise water content; the products were finally dried over P_2O_5 at room temperature in vacuum. For monodentate ligands, the starting materials were heated to reflux in acetonitrile (MeCN) as solvent for 3–7 days at about 85 °C, until no further change in the product distribution was noted by ^{11}B NMR measurements. For bidentate ligands, the $[BF_4]^-$ compounds were diluted in MeCN to avoid formation of bridged anions and the trimethylsilyl compounds, dissolved in MeCN, were slowly added while stirring at a temperature of about 45 °C. To complete the reaction (checked by ^{11}B NMR spectroscopy), stirring was continued for 1–3 days at the same temperature. Products were characterised by ^{1}H, ^{13}C, ^{11}B, ^{19}F NMR spectroscopy and MS-ESI+ and MS-ESI− measurements; the results confirm their identity and purity. Experimental details on synthesis and characterisation can be found in the Supporting Information.

Table 1 gives an overview on some ILs synthesised so far. Product distribution percentages (molar anion composition)

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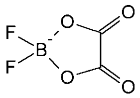
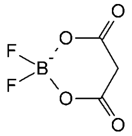
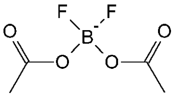
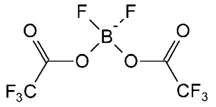
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200802243.

Table 1. Overview on synthesised ILs.

						
anion acronym	$[BF_2Ox]^-$			$[BF_2Ma]^-$		
average product distribution	$\approx$98–99 % $[BF_2Ox]^-$ (1 % $[B(Ox)_2]^-$, 1 % $[BF_4]^-$)			$\approx$85–90 % $[BF_2Ma]^-$ (5–7 % $[B(Ma)_2]^-$, 5–7 % $[BF_4]^-$)		
cation	$[EMIM]^+$	$[BMIM]^+$	$[TEA]^+$	$[EMIM]^+$	$[BMIM]^+$	$[TEA]^+$
IL status	RTIL	RTIL	IL	RTIL	RTIL	IL
H_2O content[a]	156×10^{-6}	159×10^{-6}	122×10^{-6}	94×10^{-6}	101×10^{-6}	86×10^{-6}
T_{fus}/T_g[b] [°C]	22 (−65*)	6 (−66*)	33	−68*	−62*	66
T_{dec} [°C]	297	292	319	202	202	224
ρ [$kg\cdot dm^{-3}$][c]	1.337	1.259	1.179[d]	1.331	1.258	–
water miscibility	yes	no	–	yes	yes	–
						
anion acronym	$[BF_2(Ac)_2]^-$			$[BF_2(TFA)_2]^-$		
average product distribution	17 % $[BF(Ac)_3]^-$, 46 % $[BF_2(Ac)_2]^-$, 32 % $[BF_3Ac]^-$, 5 % $[BF_4]^-$			15 % $[BF(TFA)_3]^-$, 57 % $[BF_2(TFA)_2]^-$, 27 % $[BF_3TFA]^-$, 1 % $[BF_4]^-$		
cation	$[EMIM]^+$	$[BMIM]^+$	$[TEA]^+$	$[EMIM]^+$	$[BMIM]^+$	$[TEA]^+$
IL status	RTIL	RTIL	RTIL	RTIL	RTIL	RTIL
H_2O content[a]	322×10^{-6}	310×10^{-6}	278×10^{-6}	–	–	–
T_{fus}/T_g[b] [°C]	−68*	−66*	−71*	−86*	−84*	−88*
T_{dec} [°C]	267	262	229	238	237	248
ρ [$kg\cdot dm^{-3}$][c]	1.228	1.174	1.134	1.428	1.357	1.319
water miscibility	yes	yes	yes	no	no	no

[a] Weight fraction. upper limit, see text. [b] Values marked with * are glass transition temperatures, obtained from the cooling runs (10 K min^{-1}). [c] At 25 °C. [d] At 40 °C.

were derived from integration of ^{11}B NMR spectra. Reported water content values are higher than the actual values due to side reactions with Karl Fischer reagents;[10] for $[BF_2(TFA)_2]^-$-ILs Karl Fischer titration (KFT) was not possible at all. Melting points T_{fus} and glass-transition temperatures T_g were obtained from onset analysis of DSC measurements (10 K min^{-1}); thermal decomposition temperatures T_{dec} from onset analysis of TGA measurements (N_2 flow, 10 K min^{-1}).

With monodentate ligands, an anion product distribution is usually obtained, as different numbers of fluoride ligands are replaced. Equilibration between different species seems to occur too. This may be somewhat disappointing at the first glance, but a mixture of different anions can also positively influence the properties of the resulting IL blend, for example, the melting point.

^{11}B NMR measurements show that the product distribution depends on the nature of the ligand; for example, for monodentate ligands the relative amount of difluorobis(*ligand*)borate, $[BF_2X_2]^-$, is 57 % for X = trifluoroacetate and 46 % for X = acetate, possibly due to steric and energetic reasons. With oxalate as bidentate ligand, difluoromono(oxalato)borate ($[BF_2Ox]^-$) was obtained with an amount of 98–99 %, and only small amounts of remaining $[BF_4]^-$ and bis(oxalato)borate ($[B(Ox)_2]^-$), respectively. For malonate, difluoromono(malonato)borate ($[BF_2Ma]^-$) was obtained with an amount of 85–90 %, and about 5–7 % $[BF_4]^-$ and bis(malonato)borate ($[B(Ma)_2]^-$) each. This demonstrates that the formation of $[BF_2Ox]^-$ is favoured over $[BF_2Ma]^-$, possibly due to ring size effects and energetic reasons.

To conclude, the described new synthetic method offers an easy way to a variety of new ILs, being interesting not only for fundamental research, but also for application, for example, for use as electrolytes in electrochemical double layer capacitors[11,12] and lithium ion batteries (chloride-free synthesis method, higher solubility than $[BF_4]^-$ salts[13]), and for synthesis.

Experimental Section

All work was done under N_2 atmosphere or in an Ar glove box. Most starting materials were synthesised according to established procedures: [EMIM][BF_4] and [BMIM][BF_4] cf. Ref. [6]; [TEA][BF_4] cf. Ref. [14] (EMIM = 1-ethyl-3-methylimidazolium, BMIM = 1-butyl-3-methylimidazolium, TEA = tetraethylammonium); all were colourless with H_2O content below 50 ppm and Cl^-/Br^- content below 25 ppm. Bis(trimethylsilyl)oxalate ($Ox(SiMe_3)_2$) and bis(trimethylsilyl)malonate ($Ma(SiMe_3)_2$) were made by reaction of trimethylsilylchloride (TMSCl) with oxalic or malonic acid in 1,2-dichlorethane.[15] $Ox(SiMe_3)_2$ (m.p. $\approx$65 °C) was purified by fractionating distillation (b.p. 95 °C/10 mbar), followed by dissolution in n-pentane and filtration to remove residual oxalic acid. $Ma(SiMe_3)_2$ was fractionated over a 30 cm Vigreux column (b.p. 92 °C/6 mbar). Trimethylsilyltrifluoroacetate was synthesised from TMSCl and a slight excess of sodium trifluoroacetate without any solvent and obtained in pure state by distillation of the batch. Li[BF_4] (Stella Chimifa, electrochemical grade) and acetonitrile (Merck, for DNA-synthesis, $H_2O < 10$ ppm) were used as received; Trimethylsilylacetate (Alfa Aesar, 98%) was fractionated prior to use.

In a typical experiment for monodentate ligands, [EMIM][BF_4] (29.7 g, 150 mmol), MeCN (130 mL) and trimethylsilylacetate (40.0 g, 302 mmol) were heated to reflux for 6 days at ≈85 °C. In a typical experiment for bidentate ligands, [EMIM][BF_4] (19.9 g, 100 mmol) was dissolved in MeCN (200 mL). $Ox(SiMe_3)_2$ (24.0 g, 102 mmol), dissolved in MeCN (70 mL), was then added through dropping funnel over a period of a few hours at ≈40 °C and stirring was continued for 2 days. After removing MeCN in vacuum, the products were dried at ≈45 °C (<1 mbar) over night. [EMIM][$BF_2(Ac)_2$] and [EMIM][BF_2Ox] were obtained as colourless RTILs in nearly quantitative yield.

Lithium salts of all anions shown in Table 1 were synthesised in the same manner. Anion product distributions were comparable to those of the according ILs. Attempts to remove residual MeCN from Li[$BF_2(Ac)_2$] and Li[$BF_2(TFA)_2$] under vacuum were not successful, as significant amounts of MeCN remained, leading to highly viscous, nearly glassy compounds. On the other hand, Li[BF_2Ox] could be obtained easily and often with 100% $[BF_2Ox]^-$. Li[BF_2Ox] is a very interesting candidate for application as electrolyte in lithium ion batteries, especially in its chloride-free form, while Li[BF_2Ma] seems to be not soluble enough for that purpose. For synthesis of Li[BF_2Ox] and Li[BF_2Ma], see the Supporting Information.

Acknowledgements

The authors are grateful for the financial support of this work by the DFG (German Research Foundation) priority program SPP 1191 on ionic liquids.

Keywords: borates • electrolytes • ionic liquids • room-temperature molten salts • synthetic methods

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Received: October 28, 2008