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Ionic Liquids with Perfluorinated Alkoxyaluminates

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Ionic liquids with the weakly coordinating perfluoroalkoxyaluminate anions, $Al(OR_F)_4^-$, are obtained by a metathesis reaction of $LiAl(OR_F)_4$ and [bmim]Cl or [bmpyr]Cl in high yields. The compounds [bmim][$Al(hfip)_4$] and [bmpyr][$Al(hfip)_4$] have surprisingly low viscosities at elevated temperatures (60 °C) and an exceptionally high electrochemical window, which might render them useful for certain applications.

In recent years, ionic liquids, by a common definition saltlike compounds with a melting point below 100 °C, have become an extremely popular class of “neoteric” solvents. Their application reaches from organic synthesis and catalysis over separation processes to electrochemistry. However, mainly industrial interest seems to drive the research in this field. Astonishingly, in inorganic synthesis, the exploration and development of ionic liquids or low-melting salts as reaction media seem still to be neglected and underexplored[1] despite the fact that “conventional” salts as alkali halides, their eutectic mixtures (e.g., LiCl/KCl), or molten Lewis acids as $AlCl_3$ are traditionally used to carry out (high-temperature) solid-state reactions.[2] We believe that especially ionic liquids with weakly coordinating and, hence, weakly basic ions could open a field of chemistry. The Lewis basicity of the anion often limits the exploration of cationic cluster compounds.[3] Weakly coordinating anions (WCAs) have received considerable interest in inorganic chemistry over a long period of time.[4] The term “superweak anions” has been coined by Strauss to stress that these anions have minimal coordinating ability.[5] A popular class of compounds with WCAs is based on polyfluoroalkoxide or −aryloxide metalates with a general composition $[M(OR_F)_4]^-$ or $[M(OR_F)_6]^-$, where $M = B^{III}, Al^{III}, Nb^{V}, Ta^{V}, Y^{III}, La^{III}$.[6] A group of extreme WCAs are polyfluoroalkoxyaluminates, initially synthesized by the group of Strauss[7] and then extensively used by the group of Krossing.[8] Because of their extremely low basicity, they have been permitted as counteranions to study, and, in many cases, isolate and structurally characterize very reactive cationic species (strongly acidic gas-phase species, highly electrophilic metal and nonmetal cations, and weakly bound Lewis acid−base complexes of metal cations) like $[Ag(\eta^2\text{-}C_2H_4)_3]^+$ from solution (mostly CH_2Cl_2 was used as the solvent), which previously had only been seen in the mass spectrometer.[9] Other amazing species include Xe_2^+ and $[Au(Xe)_4]^{2+}$.[10] However, during synthesis, even weakly coordinating solvent molecules like CH_2Cl_2 may coordinate to the cationic species.[11] This circumstance could be overcome by replacing the conventional organic solvent by an ionic liquid based on polyfluoroalkoxyaluminates $[Al(OR_F)_4]^-$, like the ones we describe here. Furthermore, such ionic liquids are expected to surmount many more synthetic limitations. As mentioned above, conventional solvents generally have a higher coordinating ability, or basicity, than the polyfluoroalkoxyaluminates, which can result in a substantial and crucial destabilization of the cationic (cluster) species. Another advantage of $[Al(OR_F)_4]^-$ based on ionic liquids is the high electrochemical stability of the anions themselves,[12] which should allow for the

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(1) (a) Mudring, A.-V.; Babai, A.; Arenz, S.; Giernoth, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 5485. (b) Babai, A.; Mudring, A.-V. *Inorg. Chem.* **2005**, *44*, 8168. (c) Babai, A.; Mudring, A.-V. *Chem. Mater.* **2005**, *17*, 6230. (d) Babai, A.; Mudring, A.-V. *Inorg. Chem.* **2006**, *45*, 3249. (e) Babai, A.; Mudring, A.-V. *Dalton Trans.* **2006**, 1828. (f) Babai, A.; Mudring, A.-V. *J. Alloys Compds.* **2006**, *418*, 122. (g) Babai, A.; Mudring, A.-V. *Inorg. Chem.* **2006**, *25*, 4874. (h) Prondzinski, N.; Babai, A.; Mudring, A.-V.; Merz, K. *Z. Anorg. Allg. Chem.* **2007**, *633*, 1490. (i) Willems, J. B.; Rohm, H. W.; Geers, Ch.; Köckerling, M. *Inorg. Chem.* **2007**, *46*, 6197.

(2) (a) Hagenmuller, P. *Preparative Methods in Solid State Chemistry*; Academic Press: New York and London, 1972. (b) O’Odonee, T. A. *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*; Wiley-VCH: Weinheim, Germany, 1993.

(3) Ruck, M.; Steden, F. *Z. Anorg. Allg. Chem.* **2007**, *633*, 1556.

(4) (a) Reed, C. *Acc. Chem. Res.* **1998**, *31*, 133. (b) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (c) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (d) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066.

(5) (a) Lupinetti, A. J.; Strauss, S. H. *Chemtracts: Inorg. Chem.* **1998**, *11*, 565. (b) Ivanova, S. M.; Nolan, B. G.; Kobayashi, Y.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *Chem.*—*Eur. J.* **2001**, *7*, 503.

(6) See refs 47−53 in: Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066.

(7) Barbarich, T. J.; Handy, S. T.; Miller, S. M.; Anderson, O. P.; Grieco, P. A.; Strauss, S. H. *Organometallics* **1996**, *15*, 3776.

(8) Krossing, I.; Reisinger, A. *Coord. Chem. Rev.* **2006**, *250*, 2721.

(9) Krossing, I.; Reisinger, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 5725.

(10) (a) Drews, T.; Seppelt, K. *Angew. Chem., Int. Ed.* **1997**, *36*, 273. (b) Seidel, S.; Seppelt, K. *Science* **2000**, *290*, 117.

(11) (a) Krossing, I. *Chem.*—*Eur. J.* **2001**, *7*, 490. (b) Krossing, I.; Brands, H.; Feuerhake, R.; Koenig, S. *J. Fluorine Chem.* **2001**, *112*, 83.

10.1021/ic7009995 CCC: $37.00

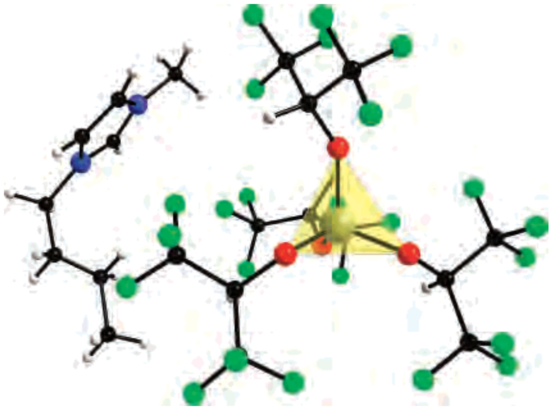

Figure 1. [bmim][Al(hfip)$_4$]: asymmetric unit of the structure.

synthesis and stabilization of highly redox-active cations. As a consequence, $[Al(OR_F)_4]^-$-based ionic liquids are expected to open a path to new chemistry and compound synthesis when used as a reaction medium.

Indeed, two ionic liquids, [bmim][Al(hfip)$_4$] [**1**; bmim = 1-butyl-3-methylimidazolium and hfip = $OCH(CF_3)_2$] and [bmpyr][Al(hfip)$_4$] (**2**; bmpyr = 1-butyl-1-methylpyrrolidinium), could be easily obtained by a direct metathesis reaction of Li[Al(hfip)$_4$] and [bmim]Cl or [bmpyr]Cl in dry dichloromethane. Thermal analysis shows [bmim][Al(hfip)$_4$] to melt at 34 °C. Upon cooling, the compound solidifies at −19 °C. The corresponding bmpyr compound melts at 47 °C. Again, a strong supercooling of 21 °C is observed. Thus, with compounds **1** and **2**, two room-temperature ionic liquids, although metastable, could be obtained. Although fairly viscous at room temperatures, the dynamic viscosities at 60 °C were determined to 7.85 mm^2/s for [bmim][Al(hfip)$_4$] and 12.92 mm^2/s for [bmpyr][Al(hfip)$_4$]. Astonishingly, these viscosities are below the values found for typical ionic liquids such as [bmim][PF$_6$] and [bmim][BF$_4$] at this temperature.[13] For both compounds, an exceptionally high electrochemical window of about 8 V was determined.[14]

For [bmim][Al(hfip)$_4$], crystals of sufficient quality for single-crystal X-ray structure analysis could be obtained. The asymmetric unit of the crystal structure (Figure 1) contains one cation and one anion of the ionic liquid compound. Figure 2 illustrates the ion packing, which can best be described as a heavily distorted CsCl type of arrangement; the cation as well as the anion are each surrounded by eight counterions. The butyl side chain of the bmim cation exhibits a gauche−anti−anti conformation. Because of the weaker cation−anion interactions in [bmim][Al(hfip)$_4$] compared to Li[Al(hfip)$_4$] and Li[emim][Al(hfip)$_4$]$_2$,[15] where Li$^+$ coordinates to the Al−O bond, the [Al(hfip)$_4$] anion deviates less from the ideal, with Al−O distances ranging from 1.72 to 1.74 Å and O−Al−O angles between 108.3° and 112.1°, which are close to the ideal tetrahedral angle. The hfip anion itself shows intermolecular hydrogen bonds with H···F distances ranging between 2.42 and 2.57 Å. Hydrogen bonds between fluorine atoms belonging to the hfip anion and hydrogen atoms of the bmim cations are even weaker and are found at the interatomic values between 2.66 and 2.80 Å.

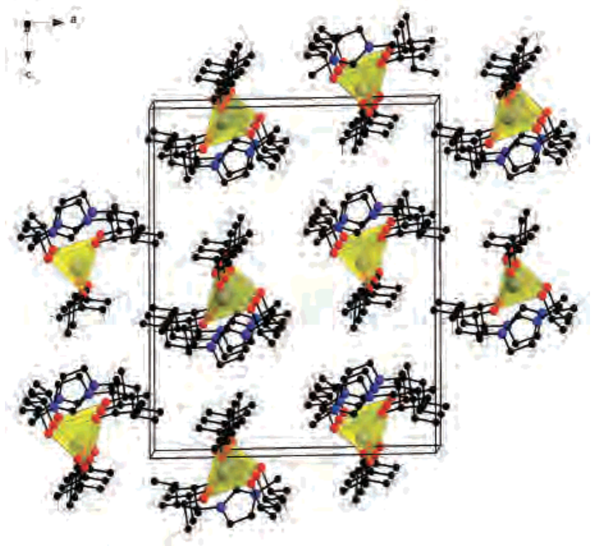

Figure 2. bmimAl(nftb)$_4$: view of the crystal structure along [010]. $-C(H)(CF_3)_2$ groups are omitted for clarity.

Because $[Al(hfip)_4]^-$ is decomposed by water, we intended to synthesize moisture-tolerating ionic liquids by exchanging the anion to $[Al(nftb)_4]^-$, where nftb = $[OC(CF_3)_3]^-$. $[Al(nftb)_4]^-$ has been shown to be extremely hydrolytically robust,[11a] and apparently even the Brønsted acids [H(OEt)$_2$]-[Al(nftb)$_4$] and [H(THF)$_2$][Al(nftb)$_4$] are known.[16] Furthermore, $[Al(nftb)_4]^-$ is even more weakly coordinating than $[Al(hfip)_4]^-$.

Indeed, by similar metathesis reactions, the compounds [bmim][Al(nftb)$_4$] (**3**) and [bmpyr][Al(nftb)$_4$] (**4**) could be obtained in high yields. Both compounds have a melting point above 100 °C but show an extremely strong tendency to form supercooled liquids. [bmim][Al(nftb)$_4$] has a melting point of 149 °C, and [bmpyr][Al(nftb)$_4$] melts at 202 °C. (All compounds melt without decomposition and seem to be thermally robust at least up to 300 °C.) In the case of [bmim][Al(nftb)$_4$], strong supercooling of the melt of more than 35 °C (for [bmpyr][Al(nftb)$_4$] of about 15 °C) was observed. Still, both compounds are quite low-melting salts and could be used as "molten salt" reaction media. Both compounds are stable toward water and the atmosphere.

In conclusion, [bmim][Al(hfip)$_4$] and [bmpyr][Al(hfip)$_4$] are two examples of extremely low-melting ionic liquids, although they contain a high-molecular-weight anion. They show low viscosities at elevated temperatures and high electrochemical stability, which might render them useful

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(12) Tsujioka, S.; Nolan, B. G.; Takase, H.; Fauber, B. P.; Strauss, St. H. *J. Electrochem. Soc.* **2004**, *151*, A1418.

(13) (a) Seddon, K. R.; Stark, A.; Torres, M.-J. *ACS Symp. Ser.* **2002**, *7*, 43. (b) Viscosities of ionic liquids are generally strongly temperature-dependent. For example, the viscosity of the low viscous [bmpyr]-[Tf$_2$N] at 200 °C is 71.50 mm^2/s. For data, see: http://ildb.merck.de/ionicliquids/en/SearchPage.htm.

(14) Cyclic voltammetry measured in the neat ionic liquids at 50 °C at a platinum working electrode gives potential windows for [bmim][Al-(hfip)$_4$] of −2.3/+6.3 V vs Fc/Fc$^+$ and for [bmpyr][Al(hfip)$_4$] of −2.6/+6.3 V vs Fc/Fc$^+$.

(15) Ivanova, S. M.; Nolan, B. G.; Kobayashi, Y.; Miller, S. M.; Anderson, O. P.; Strauss, St. E. *Chem.—Eur. J.* **2001**, *7*, 503.

(16) Krossing, I.; Reisinger, A. *Eur. J. Inorg. Chem.* **2005**, 1979.

for applications. Compounds **3** and **4** with the more weakly coordinating but higher symmetric anion $[Al(nftb)_4]^-$ have melting points of more than 100 °C above those of compounds **1** and **2** with the $[Al(hfip)_4]^-$ anion. It is often observed that higher symmetry structures lead to a better crystal packing and a higher melting point.

Experimental Section. All manipulations were carried out under inert conditions.

$[Al(OR_F)_4]$ (R = bmim, bmpyr; OR_F = hfip, nftp) are obtained by the reaction of stoichiometric amounts (1 mmol) of RCl and $Li[Al(OR_F)_4]$ in dry dichloromethane (50 mL). The reaction takes place quantitatively (the yields of LiCl and $[Al(OR_F)_4]$ are counterchecked) at room temperature by stirring for 24 h. The cloudy solution is allowed to settle for a few hours, and then the clear solution over the white byproduct (LiCl) is filtered. After distillation of the solvent at reduced pressure, the desired compound $[Al(OR_F)_4]$ is obtained. $LiAl(hfip)_4$, $LiAl(nftb)_4$ (Krossing, I. *Chem.—Eur. J.* **2001**, *7*, 490), [bmim]Cl (Dupont, J.; Consorti, C. S.; Suarez, P. A. Z.; de Souza, R. F. *Org. Synth.* **2002**, *79*, 236), and [bmpyr]Cl (Crowhurst, L.; Lancaster, N. L.; Arlandis, H. P.; Welton, T. *J. Am. Chem. Soc.* **2004**, *126*, 11549) were synthesized according to literature procedures.

[bmim][Al(hfip)$_4$] (1). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): 0.991 (t, $-CH_3$), 1.378 (sextet, $=CH_2$), 1.845 (p, $=CH_2$), 3.911 (s, $-CH_3$), 4.115 (t, $=CH_2$), 4.533 (m, $=CH-$), 7.187 (d, $=CH-$), 9.025 (s, $=CH-$). ^{19}F NMR ($CDCl_3$, 300 MHz, 25 °C): −77.117 (d, $-CF_3$). ^{27}Al NMR ($CDCl_3$, 300 MHz, 25 °C): 59.81 (s, Al). Raman and IR spectra are available as Supporting Information. Anal. Calcd: C, 28.77; H, 2.27; N, 3.35. Found: C, 28.81; H, 2.42; N, 3.32. Yield: 80.88%. Density (50 °C): 1.56 g/cm^3.

Crystal data: space group $P2_1/c$ (No. 14), a =16.204(2) Å, b = 11.087(1) Å, c = 17.977(3) Å, V = 3229.3(8) Å^3, T = 170 K, Z = 4, 3020 reflections collected, 478 independent reflections (R_{int} = 0.0764), R1 = 0.0451, wR2 = 0.0957.

[bmpyr][Al(hfip)$_4$] (2). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): 1.02 (t, $-CH_3$), 1.43 (sextet, $=CH_2$), 1.71 (m, $=CH_2$), 2.28 (m, $=CH_2$), 3.06 (s, $-CH_3$), 3.24 (m, $=CH_2$), 3.5 (m, $=CH_2$), 4.52 (septet, $=CH-$). ^{19}F NMR ($CDCl_3$, 300 MHz, 25 °C): −76.94 (d, $-CF_3$). ^{27}Al NMR ($CDCl_3$, 300 MHz, 25 °C): 59.37 (s, Al). Raman and IR spectra are available as Supporting Information. Anal. Calcd: C, 30.12; H, 2.89; N, 1.67. Found: C, 29.96; H, 3.75; N, 1.6. Yield: 78.65%. Density (50 °C): 1.47 g/cm^3.

[bmim][Al(nftb)$_4$] (3). ^{1}H NMR ($CDCl_3$ + TDF, 300 MHz, 25 °C): 0.991 (t, $-CH_3$), 1.378 (sextet, $=CH_2$), 1.845 (p, $=CH_2$), 3.911 (s, $-CH_3$), 4.115 (t, $=CH_2$), 7.187 (d, $=CH-$), 9.025 (s, $=CH-$). ^{19}F NMR ($CDCl_3$ + TDF, 300 MHz, 25 °C): −75.73 (s, $-CF_3$). ^{27}Al NMR ($CDCl_3$ + TDF, 300 MHz, 25 °C): 34.43 (s, Al). Raman and IR spectra are available as Supporting Information. Anal. Calcd: C, 26.03; H, 1.35; N, 2.53. Found: C, 25.93; H, 1.18; N, 2.46. Yield: 75.28%.

[bmpyr][Al(nftb)$_4$] (4). ^{1}H NMR ($CDCl_3$ + TDF, 300 MHz, 25 °C): 1.02 (t, $-CH_3$), 1.43 (sextet, $=CH_2$), 1.71 (m, $=CH_2$), 2.28 (m, $=CH_2$), 3.06 (s, $-CH_3$), 3.24 (m, $=CH_2$), 3.5 (m, $=CH_2$). ^{19}F NMR ($CDCl_3$ + TDF, 300 MHz, 25 °C): −75.87 (s, $-CF_3$). ^{27}Al NMR ($CDCl_3$ + TDF, 300 MHz, 25 °C): 34.29 (s, Al). Raman and IR spectra are available as Supporting Information. Anal. Calcd: C, 27.06; H, 1.81; N, 1.26. Found: C, 27.35; H, 2.13; N, 1.15. Yield: 75.26%.

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Note Added after ASAP Publication. This article was released ASAP on November 21, 2007, with an incorrect compound name in the Abstract and a spelling error in the first paragraph of the text. The correct version was posted on November 27, 2007.

Supporting Information Available: Raman and IR spectra of all compounds, together with the crystallographic information for [bmim][Al(hfip)$_4$] in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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