Alkyl vs. alkoxy chains on ionic liquid cations

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Salts

1. 1-butyl-2,3-dimethylimidazolium chloride
2. 1-(2-methoxyethyl)-2,3-dimethylimidazolium chloride
3. 1-butyl-2,3-dimethylimidazolium hexafluorophosphate
4. 1-(2-methoxyethyl)-2,3-dimethylimidazolium hexafluorophosphate

Salt Purity.

After drying, all of the salts were stored in sealed containers in a nitrogen glove box. Karl-Fischer analysis indicated that the water content of salts 1-4 was < 50 ppm. $^1$H and $^{13}$C NMR analysis verified the identity and purity of the salts (Figs. 1-4). Note that the solvent, methyl sulfoxide-$d_6$, contained a trace amount of water (Fig. 5).

Fig. 1. $^1$H and $^{13}$C NMR spectra of 1.
Fig. 2. $^1$H and $^{13}$C NMR spectra of 2.
Fig. 3. $^1$H and $^{13}$C NMR spectra of 3.
Fig. 4. $^1$H and $^{13}$C NMR spectra of 4.

Fig. 5. $^1$H NMR spectrum of the methyl sulfoxide-$d_6$ (99.9%) solvent.
Structure Determination of 2.

A crystal (approximate dimensions 0.40 x 0.20 x 0.15 mm$^3$) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a CCD area detector diffractometer for a data collection at 173(2) K.$^1$ A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 89 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 20 seconds and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.78 Å. Four major sections of frames were collected with 0.30° steps in $\omega$ at four different $\psi$ settings and a detector position of -28° in 2$\theta$. The intensity data were corrected for absorption and decay (SADABS).$^2$ Final cell constants were calculated from 2332 strong reflections from the actual data collection after integration (SAINT).$^3$

The structure was solved and refined using Bruker SHELXTL.$^4$ The space group $P_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R_1 = 0.0296$ and $wR_2 = 0.0857$ ($F^2$, all data).

Structure Determination of 4.

A crystal (approximate dimensions 0.35 x 0.30 x 0.25 mm$^3$) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a CCD area detector diffractometer for a data collection at 173(2) K.$^1$ A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 62 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 20 seconds and a detector distance of 5.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.78 Å. Four major sections of frames were collected with 0.30° steps in $\omega$ at four different $\psi$ settings and a detector position of -28° in 2$\theta$. The intensity data were corrected for absorption and decay (SADABS).$^2$ Final cell constants were calculated from 2361 strong reflections from the actual data collection after integration (SAINT).$^3$ Please refer to Table 1 for additional crystal and refinement information.

The $PF_6^-$ anion is disordered in an approximate 0.51:0.34:0.15 ratio (Fig. 6). These were refined as paradigm octahedral rigid bodies with a common P-F bond distance parameter. The F atoms of the unprimed fragment were refined with independent Uij parameters. The primed and double primed fragments were refined with common Uij parameters for 180°-opposed F atoms; this is a reasonable constraint to impose due to the local symmetry. Finally, because all three partially occupied P atom positions are close, these Uij parameters were made common by a constraint. The constraints imposed on $PF_6^-$ affect the precision in bond distances and bond angles for the anion alone: treat discussion of these with caution.
Fig. 6. Asymmetric unit of 4 showing PF₆⁻ anion disorder (80% probability).

Crystallization Kinetics of 3 and 4.
Fig. 7 shows DSC heating traces for 3 and 4. After melting (30 K above the m.p.), the salts were slowly cooled to 173 K. During this cooling step, 3 remained completely amorphous while approximately 54% of 4 crystallized near 271 K indicating that the crystallization kinetics of 3 are much slower than for 4 (the remainder of 4 recrystallized readily during the following slow heating step, while it was necessary to thermally cycle and anneal 3 below its m.p. to fully crystallize the salt).

Fig. 7. DSC heating and cooling traces (2 K min⁻¹) of (a) 3 and (b) 4.

Note: Both 1-(2-methoxyethyl)-2,3-dimethylimidazolium chloride and 1-(2-methoxyethyl)-2,3-dimethyl-imidazolium hexafluorophosphate are commercially available from Solchemar (www.solchemar.com).

References