Mercuric Ionic Liquids: \([\text{Cnmim}][\text{HgX3}],\) Where \(n = 3, 4\) and \(X = \text{Cl, Br}\)

Bert Mallick
Andreas Metlen, University of Alabama - Tuscaloosa
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Bert Mallick,† Andreas Metlen,‡ Mark Nieuwenhuyzen,§ Robin D. Rogers,*‡§ and Anja-Verena Mudring*†‡§

1Anorganische Chemie I-Festkörperchemie und Materialien, Ruhr-Universität Bochum, D-44780 Bochum, Germany
2Department of Chemistry and Center for Green Manufacturing, The University of Alabama, Tuscaloosa, Alabama 35487, United States
3The Queen’s University Ionic Liquid Laboratories, QUILL, Queen’s, University of Belfast, Belfast BT9 5AG, U.K.

Supporting Information

ABSTRACT: A series of mercury(II) ionic liquids, \([\text{C}_n\text{mim}][\text{HgX}_3]\), where \([\text{C}_n\text{mim}] = n\text{-alkyl}-3\text{-methylimidazolium}\) with \(n = 3, 4\) and \(X = \text{Cl}, \text{Br}\), have been synthesized following two different synthetic approaches, and structurally characterized by means of single-crystal X-ray structure analysis of \(\text{Cs}_3\text{HgBr}_5\), \(\text{Cs}_2\text{HgBr}_4\), \(\text{CsHgBr}_3\), \(\text{CsHgCl}_2\), \(\text{CsHgClBr}_2\), \(\text{CsHg}_2\text{Cl}_5\), \(\text{CsHg}_5\text{Cl}_11\), \(\text{CsHg}_2\text{Br}_5\), \(\text{CsHg}_5\text{Br}_11\), \(\text{CsHg}_2\text{Cl}_5\), \(\text{CsHgCl}_3\), \(\text{CsHg}_2\text{Cl}_5\), and \(\text{CsHg}_5\text{Cl}_11\). Mixed \(\text{CsI}/\text{HgII}/\text{BrI}\) and \(\text{CsI}/\text{HgII}/\text{ClI}\) systems have been studied most extensively, and in the system \(\text{CsI}/\text{HgII}/\text{BrI}\) modulated structures has been observed. With melting points of 69.3 °C (1), 93.9 °C (2), 39.5 °C (3), and 58.3 °C (4), all compounds qualify as ionic liquids. 1, 2, and 4 solidify upon fast cooling as glasses, whereas 3 crystallizes. Cyclic voltammetry shows two separate, quasi-reversible redox processes, which can be associated with the \(2\text{Hg}^{2+}/\text{Hg}_2^{2+}\) and \(\text{Hg}_2^{2+}/2\text{Hg}^{2+}\) redox couples.
of Hg\(^{2+}\) cations becomes reality, knowledge of the physicochemical properties of the resulting salts is mandatory.

In addition, metal-based ILs are of interest because they offer the additional advantage that the properties of the metal, such as, for example, magnetism,\(^27\) luminescence,\(^28\) or catalytic behavior,\(^29\) can be introduced to the liquid. A variety of metal chloride-based (SnCl\(_2\), SnCl\(_4\), LaCl\(_3\), YCl\(_3\), TiCl\(_4\), MnCl\(_2\), FeCl\(_3\), CoCl\(_2\), NiCl\(_2\), PdCl\(_2\), PtCl\(_4\), IrCl\(_3\), CuCl, AgCl, AuCl\(_3\), ZnCl\(_2\), CdCl\(_2\), and InCl\(_3\)) ILs, aside from the well-known AlCl\(_3\)-based systems, have already been synthesized, and some of them have been structurally characterized.\(^30\)

Mercury-containing ILs are not only of interest in the context of extraction and environmental chemistry but are also important for fundamental research because mercury is, aside from gold, the element where relativistic effects in chemistry become most obvious and important.\(^31\) The pairing of mercury chemistry with ILs allows extension of the classical molten salt chemistry\(^22\) to the low-temperature regime. Polyatomic species\(^33\) by proportionation would allow for new insights into chemical bonding and how relativity affects chemistry. However, first the basics have to be explored and thus, here, we describe the syntheses and key properties of ILs comprised of complex mercury(II) halide anions and a prototypical class of IL cations, 1,3-diallylimidazolium.

**EXPERIMENTAL SECTION**

**General Procedures.** All chemicals, unless otherwise stated, were purchased from Aldrich (Steinheim, Germany, or Dorset, U.K.) and used without further purification. The imidazolium halides were prepared by the reaction of freshly distilled 1-methylimidazole (≥99%) with the respective alkyl halide, following a literature procedure.\(^34\) HgCl\(_2\) and HgBr\(_2\) were purchased from Sigma-Aldrich (Steinheim, Germany) or Merck (99.5%, Darmstadt, Germany) and used without further purification. Water was deionized in-house above 18 MΩ cm using a Barnstead (Dubuque, IA) deionization system.

**Syntheses.** The target compounds can be obtained via two different synthetic approaches: (a) An ionothermal synthesis, the respective mercuric halide is directly reacted with the desired alkylimidazolium halide at elevated temperature. The reactions were carried out under a dry nitrogen atmosphere using standard glovebox and Schlenk techniques. (b) An alternative route is classical solution chemistry where the respective imidazolium halide and the corresponding mercuric halide are reacted in water and/or ethanol.

**Method a.** \([\text{C}_4\text{mim}][\text{HgCl}_3]\) where \(n = 3, 4\) and \(X = \text{Cl}, \text{Br}\). HgCl\(_3\) or HgBr\(_3\) was added to an equimolar amount of the respective imidazolium halide in a glass tube of 12 mm inner diameter. The reaction tubes were sealed under a dynamic vacuum and heated to 130 °C in a laboratory furnace. The completion of the reaction was observed by the formation of a homogeneous, colorless liquid. To obtain single crystals of sufficient quality for single-crystal X-ray structure analysis, the reaction ampoules were slowly cooled (−3 °C/1) from 130 °C to room temperature (25 °C). Quantitative yields were achieved.

**Method b.** \([\text{C}_4\text{mim}][\text{HgCl}_3]\) (1a). Elem. Anal. Calcld. for C\(_{14}\)H\(_{24}\)N\(_2\)Cl\(_3\): C, 19.46; H, 3.03; N, 6.48. Found C, 19.10; H, 3.12; N, 6.40. Mp = 69.3 °C; \(T_{c} = −66.4{ }^\circ\text{C}\). \(^1H\) NMR (300 MHz, water-d\(_2\)): \(\delta_{C} 0.82\) (t, \(J = 7.38\) Hz, 3H), 1.76 (dt, \(J = 7.23\) and 7.38 Hz, 2H), 3.77 (s, 3H), 4.02 (t, \(J = 7.23\) Hz, 2H), 7.31 (s, 1H), 7.35 (s, 1H), 8.59 (s, 1H). \(^{13}\)C NMR (75 MHz, water-d\(_2\)): \(\delta_{c} 9.8, 22.82, 35.57, 51.06, 122.16, 123.44\). MIR (cm\(^−1\)): 3147w, 3106w, 3091w, 2966m, 2875m, 1629m, 1565s, 1461s, 1382m, 1316m, 1166s, 902m, 838s, 755s, 659m, 620s. \(^1H\) NMR (500 MHz, DMSO-d\(_6\)): 3152w, 3108m, 3093w, 2962w, 2893m, 2878w, 2618m, 1565s, 1459m, 1166s, 836s, 752a, 657w, 620s. FIR/Raman (cm\(^−1\)): 280w (IR/RA), 180s (IR), 170s (RA), 97w (IR). ESI-MS (positive): 139.1253 (100). 140.1289 (10). 143.7177 (10).

**Method b.** \([\text{C}_4\text{mim}][\text{HgCl}_3]\) (2a). A total of 1.00 mmol of each \([\text{C}_4\text{mim}][\text{Br}]\) and HgBr\(_2\) was dissolved in separate aliquots of 100 mL of DCM. Both solutions were mixed and allowed to evaporate at room temperature. Over time, a colorless crystalline mass formed in a yield of 28% as nearly colorless crystals. Elements of the target compounds were obtained after the bulk solvent evaporated with an estimated yield of ~100%. Elem. Anal. Calcld. for C\(_{14}\)H\(_{24}\)N\(_2\)HgCl\(_3\): C, 21.54; H, 3.39; N, 6.28. Found C, 21.50; H, 3.10; N, 6.22. Mp = 93.9 °C; \(T_{c} = −60.5{ }^\circ\text{C}\). \(^1H\) NMR (300 MHz, water-d\(_2\)): \(\delta_{C} 0.79\) (t, \(J = 7.60\) Hz, 3H), 1.19 (dt, \(J = 7.18\) and 7.60 Hz, 2H), 1.72 (quin, \(J = 7.18\) Hz, 2H), 3.76 (s, 3H), 4.07 (t, \(J = 7.18\) Hz, 2H), 7.30 (s, 1H), 7.34 (s, 1H), 8.58 (s, 1H). \(^{13}\)C NMR (75 MHz, water-d\(_2\)): \(\delta_{c} 12.5, 18.7, 31.2, 35.5, 49.2, 122.2, 123.4, 135.8\). MIR (cm\(^−1\)): 3134m, 3106s, 3091w, 2966m, 2933s, 2878w, 1623m, 1565s, 1461m, 1166s, 840s, 754s, 657w, 622w. FIR/Raman (cm\(^−1\)): 330w (IR/RA), 275s (IR/RA), 230w (IR/RA), 100s (IR/RA). ESI-MS (positive): 139.1251 (100). 140.1274 (10) (C\(_4\text{mim}\)); 313.2153 (5) 759.2126 (3). ESI-MS (negative): 306.8774 (100) (HgCl\(_3\)); 383.1560 (10); 578.7863 (5); 733.3532 (10); 907.4290 (10); 1083.5248 (10); 1257.6204 (10); 1431.7177 (10).

**Nuclear Magnetic Resonance (NMR).** NMR spectra of compounds prepared according to method a were recorded in water-d\(_2\) at 25 °C on a 300 MHz Bruker (Karlsruhe, D) Avance II 300 spectrometer, with the solvent as the internal standard, or according to method b in DMSO-d\(_2\) at 25 °C on a 500 MHz Bruker (Billerica, MA) AX500 spectrometer, with the solvent as the internal standard.

**Differential Scanning Calorimetry (DSC).** DSC scans were recorded on a Netzsch DSC 204 F1 Phoenix calorimeter in silica crucibles with a heating rate of 5 °C/min. An empty sample container of the same type was used as the reference, and the thermal cycles were repeated twice.

**Vibrational Spectroscopy.** IR spectra were recorded as neat samples either (method a) on a JASCO FT/IR spectrometer or (method b) on a Perkin-Elmer (Dublin, Ireland) Spectrum 100 FTIR spectrometer. The samples were ground to a fine
power and pressed in a KBr (MIR region) or a polyethylene matrix (FIR region). Raman spectra were measured (method 3) with a FRA 106-S Fourier transform Raman spectrometer. The samples were ground to a fine powder and sealed in glass capillaries with an inner diameter of 1 mm and a wall thickness of 0.15 mm. For samples prepared according to synthesis route (b), Raman spectra were recorded on a microscope slide with a Raman Station 400F Raman spectrometer (Perkin-Elmer).

Elemental Analysis. Elemental analyses for 1a–4a were carried out on a Heka Tech Euro EA 3000 elemental analyzer. Compounds 2b and 4b were analyzed using a Perkin-Elmer 2400 series II CHNS/O elemental analyzer (Shelton, CT).

Electrospray Ionization Mass Spectrometry (ESI-MS). ESI-MS was performed on an LCT Premier from Waters using an Advion nanomate injection system (Manchester, U.K.)

Cyclic Voltammetry (CV). The experimental CV curves were carried out on a HEKA Tech Euro EA 3000 elemental analyzer. Compounds 2b and 4b were analyzed using a Perkin-Elmer 2400 series II CHNS/O elemental analyzer (Shelton, CT).

Table 1. Single-Crystal Data Collection and Structure Refinement Parameters

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<th>unit cell dimensions</th>
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<th>b (Å)</th>
<th>c (Å)</th>
<th>α (deg)</th>
<th>β (deg)</th>
<th>γ (deg)</th>
<th>volume (Å³)</th>
<th>density (calcd, kg/m³)</th>
<th>Z</th>
<th>refinements used</th>
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<td>[C₄mim][HgCl₃] 1a</td>
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<td>17.093(3)</td>
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<tr>
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<td>Cc (No. 9)</td>
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<td>10.7332(13)</td>
<td>106.953(13)</td>
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<tr>
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<td>Cc (No. 9)</td>
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<td>14.5796(16)</td>
<td>14.2562(16)</td>
<td>106.953(13)</td>
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<tr>
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</table>

The best specimen of each compound was used to collect a complete intensity data set with the aid of a single-crystal X-ray diffractometer [Stoe IPDS II using graphite-monochromated Mo K α X-ray radiation (λ = 0.70073 Å)]. Essential experimental conditions and resulting crystallographic data are summarized in Table 1. Further information is given as Supporting Information and can be downloaded from the web.

Data reduction with the program X-Red25 in all cases included corrections for background, Lorentz, and polarization effects. A numerical absorption correction with the programs X-Red/X-Shape26 was undertaken after optimization of the habits of the crystal. The structures were solved by direct methods with the program SHELXS-97.27 The atoms were refined anisotropically against F² by a full-matrix least-squares procedure using the program SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained to ride on their respective parent atoms. Structure factors were taken from International Tables for Crystallography.28 For crystal structure drawings, the program Diamond was used.29

RESULTS AND DISCUSSION

Crystal Structures. 1, 2, and 4 are essentially isomorphous and crystallize in the acentric space group Cc (No. 9) with four formula units per unit cell. To check for the absence of an inversion center, structure solution in the corresponding centric space group C2/c was attempted. However, no satisfactory solutions could be found. In contrast, 3 crystallizes in the centrosymmetric space group P2₁/c (No. 14) with four formula units per unit cell.

1, 2, and 4 feature a planar HgX₃⁻ anionic unit that is close to ideal C₃ᵥ symmetry. The mean Hg–X interatomic distances within the trigonal-planar unit of 2.43(8) Å (1–Cl), 2.44(4) Å (2–Cl), and 2.56(3) Å (4–Br) (Table 2) are about 4–7% larger.

than those in mercuric halide with linear X–Hg–X moieties. These trigonal-planar \( \text{HgX}_3^- \) units are joined to a polymeric chain along the crystallographic \( c \) axis, by two long X⋯Hg interactions, forming the axial sites in an overall trigonal-bipyramidal structure around Hg\(^{II}\). A similar arrangement was observed, e.g., in \( [\text{SMe}_3][\text{HgI}_3] \). These bipyramids are connected via their shortest edge to linear chains along [001] (Figure 1, left). The chains are separated by imidazolium cations, as shown in Figure 1, right.

In contrast to 1, 2, and 4, compound 3 features \( [\text{Hg}_2\text{Br}_6]^{2-} \) units as the anionic building units (Figure 2). They are made up of two edge-sharing \( [\text{HgBr}_2\text{Br}_2/2] \) tetrahedra as in \( [\text{H(AsPh}_3\text{O)}_2][\text{Hg}_2\text{Br}_6] \). As expected, the bridging Hg–Br interatomic distances are somewhat larger \( [\sim 2.800(9) \text{ Å}] \) than the terminal ones \( [2.489(1) \text{ Å}] \).

Angles and interatomic distances found in the imidazolium cations of 1−4 are all in the expected range. However, some notable differences in the relative conformations are observed. The imidazolium head groups are planar, as expected, and the differences occur in the alkyl chain. The alkyl chains form angles of 102.2(2)° (1), 111.4(1)° (3), 113.4(5)° (2), and 109.1(2)° (4) with respect to the planar imidazolium head group (Figure 3). The orientation of the propyl side chain in 1 and 3 with respect to the planar imidazolium core deviates. Within the propyl side chain only, trans conformations along the C–C bonds are observed. While the relative orientation in the two butyl compounds, 2 and 4, is the same, the conformation of the side chains is different. The butyl side chain in 2 also adopts an all-anti conformation (as observed for the propyl compounds). In contrast, the substituents in 4 are arranged anti (along C5–C6) and gauche (along C6–C7).

### Table 2. Selected Interatomic Distances and Angles for \( [\text{C}_n\text{mim}][\text{HgX}_3] \), Where \( n = 3, 4 \) and \( X = \text{Cl}, \text{Br} \)

<table>
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<th></th>
<th>d/Å</th>
<th>Angle/deg</th>
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<tbody>
<tr>
<td>( [\text{C}_3\text{mim}][\text{HgCl}_3] ) (1)</td>
<td>Hg–Cl3 2.38(2) Cl3–Hg–Cl2 112.2(2)</td>
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<tr>
<td>( [\text{C}_3\text{mim}][\text{HgCl}_3] ) (2)</td>
<td>Hg–Cl2 2.412(3) Cl2–Hg–Cl3 125.8(2)</td>
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<tr>
<td>( [\text{C}_4\text{mim}][\text{HgCl}_3] ) (3)</td>
<td>Hg–Cl3 2.42(3) Cl3–Hg–Cl1 114.4(2)</td>
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<tr>
<td>( [\text{C}_3\text{mim}][\text{HgBr}_3] ) (4)</td>
<td>Hg–Br2 2.49(1) Br2–Hg–Br1 103.12(2)</td>
<td></td>
</tr>
<tr>
<td>( [\text{C}_4\text{mim}][\text{HgBr}_3] ) (5)</td>
<td>Hg–Br3 2.537(2) Br3–Hg–Br1 125.42(7)</td>
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</tr>
<tr>
<td>( [\text{C}_3\text{mim}][\text{HgBr}_3] ) (6)</td>
<td>Hg–Br1 2.54(2) Br1–Hg–Br3 115.24(7)</td>
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</tr>
<tr>
<td>( [\text{C}_4\text{mim}][\text{HgBr}_3] ) (7)</td>
<td>Hg–Br2 2.59(2) Br2–Hg–Br3 119.23(8)</td>
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**Figure 1.** Views of the crystal structure of 4 down [010] (left) and [001] (right).

**Figure 2.** Views of the crystal structure of 3 down [100] (left) and [010] (right).
Typically, an all-anti arrangement in the alkyl side chain is energetically favored. Because there is no phase transition observed for 4 (see below), it is assumed that packing effects lead to an anti–gauche conformation of the butyl side chain in 4 in order to allow for an efficient arrangement of the \[\text{[HgX}_3\text{]}\] polymeric strands with the cation (see the Supporting Information). Hydrogen bonding can be ruled out as the origin of the two conformations of the butyl cation in 2 and 4, as can be seen from Figure 3.

Hydrogen bonding in 1–4 is quite weak when judged on the basis of accepted interatomic values.\textsuperscript{44} Hydrogen-acceptor distances can be read from Figure 3. (For hydrogen-bonding interactions drawn from the perspective of the anion, see the Supporting Information.) Because the hydrogen atoms have been computed in idealized positions donor–acceptor distances might be more suitable (see the Supporting Information for a compilation). Obviously, the most acidic proton of the imidazolium ring (2-H) is engaged in all three compounds in hydrogen bonding; the less acidic protons in the 4 and 5 positions of the imidazolium ring participate in hydrogen bonding in the case of 1, 2, and 4, which contain \[\text{[HgX}_3\text{]}\] polymeric strands. However, in 3 with the \[\text{[Hg}_2\text{Br}_6\text{]}^{2-}\] anion, such an interaction is not observed. Some of the alkyl side-chain protons are involved in extremely weak hydrogen-bonding interactions.

**IR and Raman Spectroscopy.** The FIR/Raman spectra of compounds 1 and 2 are dominated by the asymmetric Hg–Cl stretching vibrations at wave numbers of \(\sim 275 \text{ cm}^{-1}\) (Figure 4). In the spectra of the isosstructural bromide 4, the symmetric Hg–Br stretching vibration is observed at 170 cm\(^{-1}\) and the asymmetric one at about 180 cm\(^{-1}\). This corresponds with the Hg–Br stretching of the terminal bromides (Figure 4). In 3 with the dimeric \[\text{[Hg}_2\text{Br}_6\text{]}^{2-}\], which consists of two edge-sharing tetrahedra, the symmetric Hg–Br vibration involving the terminal bromide is observed at 185 cm\(^{-1}\) and the asymmetric one at 213 cm\(^{-1}\) (Figure 4). The peak at 135 cm\(^{-1}\) corresponds to the symmetric Hg–Br vibration involving the bridging bromide. This is in good agreement with observations for other complex mercury(II) halides with similar anions.\textsuperscript{45} \(\delta(\text{X–Hg–X})\) below 100 cm\(^{-1}\) have been associated with deformation vibrations of the complex anions and may overlap between the stretching vibrations belonging to the weaker Hg–X contacts.

**ESI-MS.** ESI-MS of 1–4 reveals some interesting trends. In the case of the chloride ILs 1 and 2, no free chloride is detected in the negative mode, while bromide is found in the spectra of all bromide-containing mercuric ILs. In all cases, \[\text{[HgX}_3\text{]}^{-}\] anions could be detected but no higher aggregates. Neither a molecular peak nor substantial clustering was observed.

**Thermal Investigations.** Compounds 1–4 formally belong to the class of ILs because the melting point of the crystalline...
material is below 100 °C. The isostructural compounds 1, 2, and 4 show similar thermal behavior (Table 3). The DSC thermogram of 1 is given in Figure 5, top. As a typical example, for the thermograms of 2 and 4, see the Supporting Information.

Upon cooling from the melt, the formation of a supercooled liquid over a wide temperature range is observed until solidification as a glass occurs. Recrystallization to a crystalline material sets in upon heating. This thermal behavior is commonly found for ILs. However, upon extremely slow cooling (<3 °C/h), crystallization is observed. The melting point decreases upon going from a propyl to a butyl side chain on the imidazolium cation as a glass occurs. Recrystallization to a crystalline material is below 100 °C. This is significantly less than that for the other compounds. It seems that it is easy for compound 3, which contains isolated \([\text{Hg}_2\text{Br}_6]\) polyanionic units, to crystallize compared to 1, 2, and 4, which feature trigonal-planar \(\text{HgX}_3\) that are joined to a polymeric chain by two long \(X^-\)-Hg interactions.

**Electrochemistry.** CV shows for all mercury(II) ILs a two-step electron-transfer mechanism (Figure 6). Upon sweeping to negative voltage, one-electron reduction of \(\text{Hg}^{2+}\) to \(\text{Hg}^{2+}\) is observed first, followed by one-electron reduction of \(\text{Hg}^2\) to \(\text{Hg}^0\). When the potential is reversed, the respective oxidation steps are observed. However, the oxidation and reduction steps are too far apart to qualify for a reversible electrochemical reaction. It seems that both the IL cation and the halide of the complex anion have an influence on the measured half-wave potentials (Table 4).

The thermal behavior of 3 is different (Figure 5, bottom) insofar as crystallization occurs directly upon cooling from the melt and no glass formation takes place. Furthermore, the temperature range where the supercooled liquid can be maintained is about 40 °C. This is significantly less than that for the other compounds. It seems that it is easy for compound 3, which contains isolated \([\text{Hg}_2\text{Br}_6]\) polyanionic units, to crystallize compared to 1, 2, and 4, which feature trigonal-planar \(\text{HgX}_3\) that are joined to a polymeric chain by two long \(X^-\)-Hg interactions.

**Table 3. Compiled Thermal Data (°C) for Compounds 1–4**

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<tr>
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<tr>
<td>glass transition</td>
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**Table 4. Compiled Electrochemical Data for Compounds 1–4**

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<th>([\text{C}_3\text{mim}]) Cl (1)</th>
<th>([\text{C}_3\text{mim}]) Br (2)</th>
<th>([\text{C}_4\text{mim}]) Br (3)</th>
<th>([\text{C}_4\text{mim}]) Cl (4)</th>
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<tr>
<td>(E_{\text{ox}}^{1/2} (\text{Hg}^{2+}/\text{Hg}^0))</td>
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<td>(E_{\text{ox}}^{1/2} (\text{Hg}^{2+}/\text{Hg}^{2+}))</td>
<td>-0.6612</td>
<td>-0.7374</td>
<td>-0.6337</td>
<td>-0.6245</td>
</tr>
<tr>
<td>(E_{\text{red}}^{1/2} (\text{Hg}^{2+}/\text{Hg}^0))</td>
<td>-0.4952</td>
<td>-0.56865</td>
<td>-0.4377</td>
<td>-0.44265</td>
</tr>
<tr>
<td>(\Delta E^2)</td>
<td>0.332</td>
<td>0.3375</td>
<td>0.392</td>
<td>0.3637</td>
</tr>
<tr>
<td>(E_{\text{ox}}^{1/2} (\text{Hg}^{2+}/\text{Hg}^{2+}))</td>
<td>-0.6783</td>
<td>-0.7024</td>
<td>-0.752</td>
<td>-0.7784</td>
</tr>
<tr>
<td>(E_{\text{red}}^{1/2} (\text{Hg}^{2+}/\text{Hg}^0))</td>
<td>-0.7979</td>
<td>-0.8769</td>
<td>-0.8751</td>
<td>-0.8736</td>
</tr>
<tr>
<td>(E_{\text{red}}^{1/2} (\text{Hg}^{2+}/\text{Hg}^0))</td>
<td>-0.7381</td>
<td>-0.78965</td>
<td>-0.8155</td>
<td>-0.826</td>
</tr>
<tr>
<td>(\Delta E^2)</td>
<td>0.1196</td>
<td>0.1745</td>
<td>0.1231</td>
<td>0.0952</td>
</tr>
<tr>
<td>(E_{\text{ox}}^{1/2}(X^-/X_2))</td>
<td>0.413</td>
<td>0.357</td>
<td>0.1549</td>
<td>0.098</td>
</tr>
</tbody>
</table>

Changing the IL cation from \(\text{C}_3\text{mim}^+\) to \(\text{C}_4\text{mim}^+\) results in a shift of the half-wave potentials for both the \(\text{Hg}^{II}/\text{Hg}^0\) and \(\text{Hg}^{II}/\text{Hg}^0\) redox couples to more negative values. The half-wave potentials for the \(\text{Hg}^{II}/\text{Hg}^0\) pair are found at more negative values for the chloride ILs compared to the bromide ILs. This is in contrast to the \(\text{Hg}^{II}/\text{Hg}^0\) redox couple, where the trend is reversed. The difference between the \(\text{Hg}^{II}/\text{Hg}^0\) and \(\text{Hg}^{II}/\text{Hg}^{0}\) redox couples in all ILs is larger than that in aqueous solutions, and in both cases, \(\text{Hg}^0\) and \(\text{Hg}^0\) are less noble in the IL than in water.

**CONCLUSIONS**

We have shown that mercury-containing ILs are easily accessible via two different synthetic routes. They can be prepared using either classic solution chemistry or ionothermal/flux methods. 1, 2, and 4 were found to crystallize isostructurally.
They feature trigonal-planar HgX$_3$ units, which are connected to a chain in such a way that a trigonal-bipyramidal coordination environment is achieved for Hg$^{2+}$ in these structures. The bipyramids are connected via common edges to polymeric chains. In contrast, 3 contains isolated [HgBr$_4$]$^{2-}$ units. These are built up by two edge-sharing [HgBr$_4$]$^{2-}$ tetrahedra. This is a structure unit commonly found in halomercurates(II) with large organic cations. Vibrational spectroscopy confirms the crystal structures.

The structural differences between 1, 2, and 3 are mirrored in their thermal behavior. Albeit, all compounds qualify as ILs, as they melt below 100 °C, 1, 2, and 3 solidify at moderate to fast cooling rates only as glasses. Upon heating, CV reveals two separate redox processes belonging to the 2Hg$^{2+}$/Hg$_2$ oxidation state. Nevertheless, a strong degree of supercooling (~40 °C at 5 °C/min) is observed.

CV reveals two separate redox processes belonging to the 2Hg$^{2+}$/Hg$_2$ and Hg$^{2+}$/Hg redox couples. The measured half-wave potentials indicate that mercury behaves less noble in the IL than in water.

**ASSOCIATED CONTENT**

4 Supporting Information
X-ray crystallographic data in CIF format, powder X-ray diffraction analyses, and thermal investigations. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author
E-mail: anja.mudring@rub.de (A.-V.M.), rdrogers@as.ua.edu (R.D.R.).

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