

Phosphonium Chloromercurate Room Temperature Ionic Liquids of Variable Composition

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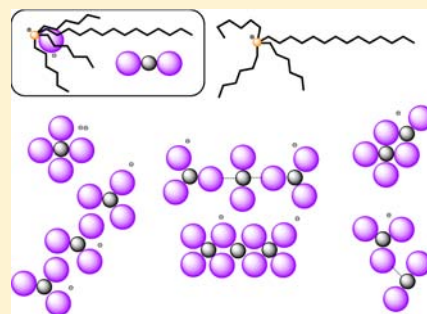
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S Supporting Information

ABSTRACT: The system trihexyl(tetradecyl)phosphonium ($[P_{66614}]Cl$)/mercury chloride ($HgCl_2$) has been investigated by varying the stoichiometric ratios from 4:1 to 1:2 (25, 50, 75, 100, 150, and 200 mol % $HgCl_2$). All investigated compositions turn out to give rise to ionic liquids (ILs) at room temperature. The prepared ionic liquids offer the possibility to study the structurally and compositionally versatile chloromercurates in a liquid state at low temperatures in the absence of solvents. $[P_{66614}]_2[HgCl_4]$ is a simple IL with one discrete type of anion, while $[P_{66614}]\{HgCl_3\}$ (with $\{\}$ indicating a polynuclear arrangement) is an ionic liquid with a variety of polyanionic species, with $[Hg_2Cl_6]^{2-}$ apparently being the predominant building block. $[P_{66614}]_2[Hg_3Cl_8]$ and $[P_{66614}][Hg_2Cl_5]$ appear to be ILs at ambient conditions but lose $HgCl_2$ when heated in a vacuum. For the liquids with the compositions 4:1 and 4:3, more than two discrete ions can be evidenced, namely, $[P_{66614}]^+$, $[HgCl_4]^{2-}$, and Cl^- and $[P_{66614}]^+$, $[HgCl_4]^{2-}$, and the polynuclear $\{HgCl_3\}^-$, respectively. The different stoichiometric compositions were characterized by ^{199}Hg NMR, Raman- and UV-vis spectroscopy, and cyclic voltammetry, among other techniques, and their densities and viscosities were determined. The $[P_{66614}]Cl/HgCl_2$ system shows similarities to the well-known chloroaluminate ILs (e.g., decrease in viscosity with increasing metal content after addition of more than 0.5 mol of $HgCl_2/mol [P_{66614}]Cl$, increasing density with increasing metal content, and the likely formation of polynuclear/polymeric/polyanionic species) but offer the advantage that they are air and water stable.



INTRODUCTION

Mercury is a very toxic element in all its oxidation states and is ubiquitous in the environment. It poses a danger to life especially in its organic form, such as methyl- and dimethylmercury,¹ and to metal parts of industrial equipment because of amalgamation.² Large amounts of mercury are emitted into the atmosphere by natural processes such as volcanic eruptions, but anthropogenic sources (fossil fuels, mining, etc.) account for half of the contemporary pollution from this element.³ In recent years, much research has been dedicated to develop technologies that either help to avoid mercury in industrial processes or to detect Hg even in very low concentrations.^{4,5} Even the field of ionic liquids (ILs, commonly defined as salts which melt below 100 °C)⁶ has addressed the study of mercury, for example, in the determination⁷ and speciation,⁸ in water, as well as, separation of Hg(II) from water^{9–13} and other media.¹⁴ The detection of mercury cations with task-specific ILs¹⁵ or with complexants encapsulated in cellulose regenerated from ILs¹⁶ are further examples of recently published studies.

Chloromercurates are known for their structural versatility,¹⁷ and to date it is not possible to predict the actual identity of the chloromercurate species in the solid state from the compound's stoichiometry alone. For example, when the stoichiometry is set to form a $[HgCl_3]^-$ anion, it is rare to obtain the corresponding monoanion.¹⁸ Dimeric¹⁹ and several polymeric species (e.g., $[2 + 4]_m$, $[3 + 2]_n$ chains) form more easily. The identity of the cation (size, hydrogen bonding ability, etc.) seems to be the most influential parameter.¹⁷ The nuclearity/degree of condensation of chloromercurate anions in the solid state depends to some extent on the preparation method of the compound, for example, the presence or absence of a solvent. However, if the stoichiometric ratio is set to form $[HgCl_4]^{2-}$, the most often encountered species is the dianionic monomer.

The variability of chloromercurate anions is of special interest because in the liquid state they might behave in an even more structurally flexible manner than in the solid state. The equilibrium between many different anions existing in

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parallel may even suppress melting points and prevent crystallization. For example, octahedrally coordinated Hg(II) is an often encountered structural motif in the solid state, forming, for example, infinite chains of edge sharing entities. It is conceivable that in the liquid state these infinite chains might interact with each other, forming dynamic, perpetually changing polyanions. One might take advantage of this dynamic situation to prepare a new series of ILs. It is also conceivable that liquid salts could be formed which contain a variety of other metals in addition to the Hg, for example, Zn or Al. The structural versatility of complex Hg anions, as well as, the partial substitution of Hg with other metals almost certainly results in a large variety of anionic species.

ILs have gained much attention in the last two decades, mainly because they can have extremely low vapor pressures and possess an inherent tunability and versatility. Initially developed as electrolytes and solvents, they are now under scrutiny as liquid materials for many applications, for example, as magnetic fluids,^{22–26} energetic materials,^{27–30} drugs,^{31–34} etc.

There are many examples in the literature of ILs with imidazolium-,^{35–44} pyridinium-,^{45,46} ammonium,^{47,48} phosphonium,^{49–51} and other cations that are paired with anions of the type $[MX_n]^{n-}$ (with X = halide and M = Al, Zn, Co, Cu, Mn, Fe, Gd, Sn, Ni, Pt, Nb, Au, Ta, Hf, Zr, Ga, In, Nb, Re, Pb, lanthanides,⁵² etc.). A paper about the solubility of HgCl₂ and other salts in imidazolium-based ILs was published by Branco et al.,⁵³ and Manan et al. recently published a paper discussing the electrochemistry of HgCl₂ in a variety of imidazolium ILs, with emphasis on the speciation of Hg-containing anions in $[C_4mim][NTf_2]/[C_4mim]Cl$ -mixtures.⁵⁴ $[P_{66614}]Cl$ (marketed as CYPHOS IL 101) immobilized in alginate was described by Guibal et al. as a useful extractant for metal ions, including Hg(II), from aqueous solutions.^{55,56} Zhang et al., following a similar approach using a PVA-alginate supported IL, also extracted Hg(II) from water.⁵⁷ $[P_{66614}]Cl$ was later described by Regel-Rosocka et al. for the extraction of Zn and Fe ions from acidic aqueous solutions.⁵⁸ A paper recently published by Vander Hoogerstraete et al. also underlines the potential of $[P_{66614}]Cl$ to interact with metal species.⁵⁹

Extracting a heavy metal cation from an aqueous phase often requires the presence of an expensive complexing agent such as CMPO, calixarenes, etc.; however, with a (task specific) hydrophobic IL having an anion that can form stable charged complexes with the metal cation, no additional complexant is required to remove at least a portion of the metal ions present.^{10,60} For example, when $[P_{66614}]Cl$ is mixed with 0.18 M aq HgCl₂, a dense lower phase forms, indicative of the IL removing Hg(II) ions from the water phase (vide infra and Supporting Information).

Some salts with $[Hg_xX_y]^{n-}$ anions and ammonium cations that are technically ILs (having a melting point lower than 100 °C) have been known in the literature for decades. For example, $[Et_4N][HgBr_3]$ is reported to melt as low as 72 °C,⁶¹ $[Bu_4N][HgCl_3]$ (with the anion forming dimers in the crystalline solid) is reported to melt at 92 °C,¹⁹ and Linden et al. describe polynuclear chloromercurate(II) compounds, with the lowest melting point reported being 94 °C.⁶² Recently, Mallick et al. published their findings on chloromercurate-ILs with imidazolium based cations; the lowest melting point found was 39.5 °C for $[C_3mim][HgBr_3]$.⁶³

¹⁹⁹Hg NMR as a technique for the investigation of biomolecules⁶⁴ and for advanced theoretical investigation of

NMR parameters has gained in popularity in recent years. Maliarik et al.⁶⁵ and Nilsson et al.⁶⁶ published their results on the effects of different solvent molecules (water, ammonia, trialkylphosphines, and -phosphites) on the Hg²⁺ coordination and the subsequent effects of temperature, concentration, etc. on the chemical shift observable by ¹⁹⁹Hg NMR. They observed a pronounced difference in chemical shift between tetrahedrally and octahedrally coordinated metal centers, while the effects of the other parameters were less pronounced but still clearly visible.

Metallate anions described in the literature usually are formed by contacting a metal halide with a halide salt to obtain the complexed metal anion. The same principle is followed by dissolving a metal chloride in an IL with chloride as anion. Hg²⁺ has a pronounced affinity for chloride, as a large number of papers discussing crystal structures with this class of anions prove.¹⁷ It therefore appears safe to assume that the dissolution of HgCl₂ in $[P_{66614}]Cl$ involves complexation of the metal cation by the chloride anion.

In order to develop useful systems and methodologies for the extraction of mercury and other metals into ILs, as well as, their subsequent removal from the ILs, it is important to understand how the metal content affects the physical properties (e.g., viscosity and density) of the IL with increasing metal content.⁵⁷ This information can be used to design metal recovery processes with increased extraction efficiency. Simple and fast approaches to quantification of the dissolved metal are also of interest.

In this paper, we present a group of new, room temperature ILs with a phosphonium cation and chloromercurate anions that have been designed to gain further knowledge about changes in the IL's properties as a function of the Hg content. Six different molar ratios of $[P_{66614}]Cl$ and HgCl₂ were investigated. The synthesis, characterization, and physical properties as a function of Hg content are reported here.

■ EXPERIMENTAL SECTION

Materials. $[P_{66614}]Cl$ was donated by Cytec, Niagara Falls, Canada, and was dried under high vacuum conditions at <1 mbar and 50 °C for several hours before use. HgCl₂ was purchased from Aldrich Chemical Co. (Dorset, UK) or Fluka AG (Buchs, CH) and was used as received.

Synthesis. To the carefully dried (by HV, < 1 mbar) $[P_{66614}]Cl$ (residual water content 0.015% determined by Coulometric Karl Fischer titration), the appropriate amount of HgCl₂ (used as received) was added, and the mixtures were stirred overnight at room temperature under ambient conditions in a closed vial. The two samples with the highest Hg content had to be heated to 35 °C to achieve complete dissolution of the added solid, and the solutions stayed clear after cooling to room temperature. While the ILs with low Hg content remained colorless, a faint yellow color appeared in the sample with a 1:1 molar ratio of the two starting materials. This color intensified with increasing amount of HgCl₂, and the sample with 2 mol equiv was brownish yellow. During attempts to further increase the amount of dissolved HgCl₂ by increasing the temperature to 90 °C, it was observed that HgCl₂ sublimed from the liquid. The same observation was made when the two samples with the highest Hg content were heated to 50 °C in an oil bath while a high vacuum (<1 mbar) was applied.

All ILs described in this paper were dried on HV (<1 mbar) and analyzed by IR (see Supporting Information) prior to density and viscosity measurements. Since Coulometric Karl Fischer titration cannot be performed on these substances without precipitating Hg-containing species inside the titrator, the water content was estimated to be lower than 100 ppm by IR spectroscopy, which did not show any traces of water (see Supporting Information). The data on the

viscosity and density of $[P_{66614}]Cl$ were taken from a recent paper published by Neves et al.⁶⁸

Characterization. ^{199}Hg NMR data on all reaction products were collected from the neat samples, on a Bruker (Coventry, UK) S00DRX spectrometer with 1.0 M $HgCl_2$ in $DMSO-d_6$ as external standard. The standard signal was assigned to -1501 ppm according to the literature.⁶⁹ 1H NMR (300 MHz), ^{13}C NMR (125 MHz), and ^{31}P NMR (202 MHz) were measured on a Bruker Spectrospin 300 with the solvent's signal as standard for 1H NMR and ^{13}C NMR. No standard was used for the ^{31}P NMR. Infrared spectra of all reaction products were recorded as neat samples from $4000-650$ cm^{-1} on a Perkin Elmer (Dublin, Ireland) Spectrum 100 FT-IR spectrometer. Raman spectra of all reaction products were recorded on a microscope slide with a Perkin Elmer Raman Station 400F Raman spectrometer as neat samples from 3200 to 100 cm^{-1} . Viscosities were measured on a Bohlin Gemini, Rotonetic Drive 2, with cone and plate viscometer, equipped with a Bohlin Instrument Peltier circulating heater under a N_2 atmosphere.

CAUTION: It has to be noted here that the investigated chloromercurate ionic liquids reacted with the metal parts of the viscometer, and a shiny film of amalgam formed in each case. The amalgam film was wiped off after each measurement by gentle rubbing with a towel.

Densities were measured with an Anton Paar DMA 4500 Density meter (Hertford, UK). differential scanning calorimetry (DSC) scans were recorded on a Mettler-Toledo DSC 1 STARe System cooled with a Huber TC 100 cryostat in sealed medium pressure iron crucibles (ME-29990) with a heating rate of 5 $^{\circ}C/min$ (thermal traces are shown in ESI). Electrospray mass spectrometry and elemental analyses were performed on a LCT Premier from Waters using an Advion nanomate injection system (Manchester, UK), and a Perkin Elmer 2400 Series II CHNS/O Elemental analyzer (Shelton, CT), respectively. Water content of the dried $[P_{66614}]Cl$ was measured using a Cou-Lo Aquamax from GRScientific (Bedfordshire, UK) Karl Fischer-titrator. UV-vis spectra were recorded using a Perkin Elmer Lambda 950 UV-vis spectrometer in acetonitrile solution in the range of $200-350$ nm.

ES-MS. All products were analyzed by positive and negative mode ES-MS, and in each case, the phosphonium cation was found as the only cation in the positive mode, with no higher aggregates detected. In the negative mode, the $[HgCl_3]^-$ (and/or $[Hg_2Cl_6]^{2-}$) anion was the dominant species for all samples, but some polyionic species of different composition also could be observed, such as $[P_{66614}]Cl_2^-$ and $[P_{66614}][HgCl_3]_2^-$ (and/or $[P_{66614}][Hg_2Cl_6]^-$). The former reaches an intensity of $\sim 40\%$ in $[P_{66614}][HgCl_3]$ (4) and of $\sim 20\%$ in $[P_{66614}]_2[Hg_3Cl_8]$ (5), while it stays well below 10% for the other samples. The second species is found with a relative intensity of $\sim 10\%$ in all samples. Apparently, $[HgCl_3]^-$ (and/or $[Hg_2Cl_6]^{2-}$) is the most stable anionic species under the applied conditions; it is known from the literature that $[MX_4]^{2-}$ species can lose X^- under MS conditions.⁷⁰ Aggregate formation seems to be possible to a certain degree in this kind of IL.

IR. In the investigated IR range ($550-4000$ cm^{-1}), all prepared compositions look basically identical to $[P_{66614}]Cl$, with only very minor differences in peak positions (± 1 cm^{-1}) for certain peaks. It can therefore be concluded that the presence of $HgCl_2$ or complex mercuric ions does not strongly impact the vibrational modes observable by IR, as in contrast to the Raman signals of the cation's alkyl chains, which are visibly altered after addition of less than 0.5 equiv of $HgCl_2$. Additionally, the IR spectra do not show any sign of moisture; see Supporting Information.

DSC. The DSC traces of most prepared compositions are completely featureless in the temperature range of room temperature to -70 $^{\circ}C$; the glass transition produced by $[P_{66614}]Cl$ at -56 $^{\circ}C$ disappears upon addition of $HgCl_2$, however. $[P_{66614}]_2[HgCl_4]$ (2) shows two small glass transitions at -37 $^{\circ}C$ and -42 $^{\circ}C$. These could stem from reorientations of the anion. No further transition between room temperature and -70 $^{\circ}C$ was observed. $[P_{66614}]_2[Hg_2Cl_5]$ (6) possibly shows a crystallization event at -70 $^{\circ}C$, but as this was the lowest temperature achievable it cannot be said with certainty that this

apparent peak is not an artifact. See Supporting Information for the thermal traces.

CV. The experimental CV curves were obtained with a micro Autolab type III (Eco Chemie BV, Utrecht, The Netherlands). The working electrode was a platinum electrode with a surface area of 3.142 mm^2 . As the reference electrode, a glassy carbon electrode was used. The CV experiments were carried out in a 0.025 M solution of the mercury containing ILs in 1-butyl-3-methylimidazolium bis-(trifluorosulfonyl)amide ($[C_4mim][Tf_2N]$) and referenced to ferrocene/ferrocenium (Fc/Fc^+) in $[C_4mim][Tf_2N]$. Scans were swept cathodically from the initial potential -0.2800 V vs. Fc/Fc^+ at a scan rate of 50 mV/s.

Extraction of $HgCl_2$ from aq Solution. As $[P_{66614}]Cl$ has a density lower than water, and all reaction products (except (1)) described in this paper consisting of $[P_{66614}]Cl$ and $HgCl_2$ have a density higher than water, it was anticipated that the $[P_{66614}]Cl$ should form a phase with a higher density than water if it extracts $HgCl_2$ from it.

Therefore, 2 equiv (0.2746 g; 1.01 mmol) of $HgCl_2$ were dissolved in 5.5 mL of DI water, and 1 equiv (0.2985 g; 0.57 mmol) of $[P_{66614}]Cl$ was added. At the same time, a control experiment with IL and pure water was performed. The emulsion formed by $[P_{66614}]Cl$ and water did not separate after more than 3 days, while the trihexyl(tetradecyl)-phosphonium chloromercurate separated within minutes from the aqueous phase for a dense lower layer (see Supporting Information).

ANALYTICAL DATA

(1) $4[P_{66614}]Cl + HgCl_2$ ($[P_{66614}]_2[HgCl_4] + 2[P_{66614}]Cl$). Molar mass: 2348.73 g/mol; Hg content: 8.45% w/w; mol fraction $HgCl_2 = 0.25$.

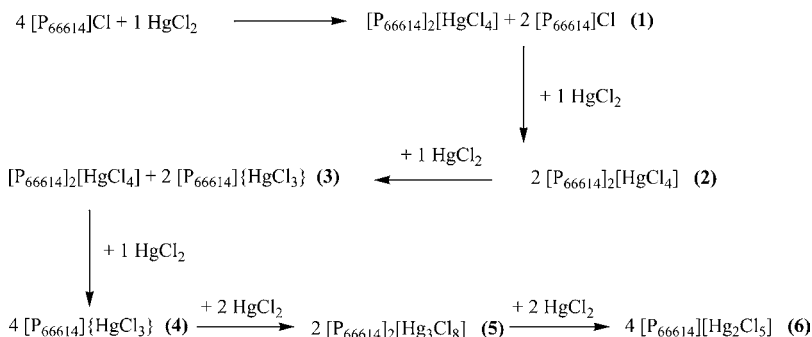
This product was obtained as a colorless liquid with relatively low viscosity. ^{199}Hg NMR (89.5 MHz, $DMSO-d_6/1.0$ M $HgCl_2$): -1120 ppm. UV-vis peak max (acetonitrile): 236 nm. Raman spectroscopy (neat, cm^{-1}): 2900 , 2876 , 2856 (C-H), 1440 , 1306 (CH_2 , CH_3), 1114 , 1076 ($\nu C-C$ aliph.), 261 ($[HgCl_4]^{2-}$).

(2) $2[P_{66614}]Cl + HgCl_2$ ($[P_{66614}]_2[HgCl_4]$). Molar mass: 1310.11 g/mol; Hg content: 15.31% w/w; mol fraction $HgCl_2 = 0.3$.

This compound was obtained as a highly viscous, colorless liquid. Anal. Calcd. for $[P_{66614}]_2[HgCl_4]$: C, 58.67 ; H, 10.46 . Found: C, 58.41 ; H, 10.31 . 1H NMR (300 MHz, $DMSO-d_6$): 0.86 (broad s, $12H$), 1.27 (m, $48H$), 2.30 (broad s, $8H$); ^{13}C NMR (125 MHz, $DMSO-d_6$): 13.33 , 17.34 , 17.96 , 20.52 , 21.53 , 21.80 , 28.02 , 28.49 , 28.84 , 29.35 , 29.56 , 29.83 , 30.23 , 31.05 ; ^{31}P NMR (202 MHz, no standard): 34.39 ; ^{199}Hg NMR (89.5 MHz, $DMSO-d_6/1.0$ M $HgCl_2$): -1129 ppm. ES-MS: ES+: 483.51 ($[P_{66614}]^+$, expected 483.86 (100)); ES-: 306.87 ($[HgCl_3]^-$, expected 306.87 , (100)); 553.44 ($[P_{66614}]Cl_2^-$, expected 554.41 , (<10)); 1099.24 ($[P_{66614}]_2[HgCl_4]^{2-}$, expected 1097.25 , (<10)); no $[HgCl_4]^{2-}$ was detected. UV-vis peak max (acetonitrile): 237 nm. Selected IR (neat sample; cm^{-1}): $2955s$, $2923s$, $2854s$, $1466m$, $1378w$, $1301w$, $1214w$, $1112w$, $811w$, $720m$. Raman spectroscopy (neat, cm^{-1}): 2902 , 2876 , 2858 (C-H), 1440 , 1306 (CH_2 , CH_3), 1064 ($\nu C-C$ aliph.), 261 ($[HgCl_4]^{2-}$). The compound could be heated to 50 $^{\circ}C$ and subjected to a high vacuum (<1 mbar) without loss of $HgCl_2$.

(3) $4[P_{66614}]Cl + 3HgCl_2$ ($[P_{66614}]_2[HgCl_4] + 2[P_{66614}][HgCl_3] \rightleftharpoons [P_{66614}]_4[Hg_3Cl_{10}]$). Molar mass: 2891.71 g/mol; Hg content: 20.81% w/w; mol fraction $HgCl_2 = 0.429$.

This liquid was obtained as a colorless liquid of medium viscosity. ^{199}Hg NMR (89.5 MHz, $DMSO-d_6/1.0$ M $HgCl_2$): broad peak of low intensity at -1118 ppm. UV-vis peak max (acetonitrile): 239 nm. Raman spectroscopy (neat, cm^{-1}): 2900 , 2876 , 2862 , 2858 , 2824 (C-H), 1404 , 1310 (CH_2 , CH_3),

Scheme 1. $[P_{66614}]Cl/HgCl_2$ Ratios That Have Been Prepared and Characterized

1176, 1112, 1066 ($\nu C-C$ aliph), 282 ($[Hg_2Cl_6]^{2-}$), 262 ($[HgCl_4]^{2-}$).

(4) $[P_{66614}]Cl + HgCl_2$ ($[P_{66614}]\{HgCl_3\}$). Molar mass: 790.80 g/mol; Hg content: 25.37% w/w, mol fraction $HgCl_2 = 0.5$.

This compound was obtained as a viscous, pale yellow liquid. Anal. Calcd. for $[P_{66614}]\{HgCl_3\}$: C, 41.48; H, 7.40. Found: C, 41.63; H, 7.56. 1H NMR (300 MHz, DMSO- d_6): 0.87 (m, 12H), 1.24 (m, 48H), 2.17 (m, 8H); ^{13}C NMR (125 MHz, DMSO- d_6): 13.81, 13.89, 17.10, 17.20, 17.73, 17.82, 20.43, 20.48, 20.54, 21.78, 22.06, 28.06, 28.61, 28.68, 28.93, 29.01, 29.61, 29.81, 30.03, 30.37, 31.27; ^{31}P NMR (202 MHz, no standard): 34.94; ^{199}Hg NMR (89.5 MHz, DMSO- $d_6/HgCl_2$): -1197 ppm. ES-MS: ES+: 483.51 ($[P_{66614}]^+$, expected 483.86, (100)); ES-: 306.88 ($[HgCl_3]^-$, expected 306.87, (100)); 553.44 ($[P_{66614}]Cl_2^-$, expected 554.41, (40)); 825.35 ($[P_{66614}][HgCl_4]^-$, expected 825.31, (<5)); 1097.25 ($[P_{66614}][HgCl_3]_2^-$, expected 1097.25, (10)). UV-vis peak max. (acetonitrile): 241 nm. Selected IR (neat sample; cm^{-1}): 2955s, 2923s, 2854s, 1465m, 1378w, 1301w, 1214w, 1111w, 809w, 720m. Raman spectroscopy (neat, cm^{-1}): 2990, 2934, 2930, 2904, 2876, 2860, 2856 (C-H), 1440, 1308 (CH_2 , CH_3), 1076, 848 ($\nu C-C$ aliph.), 282 ($[Hg_2Cl_6]^{2-}$). The compound could be heated to 50 °C and subjected to a high vacuum (<1 mbar) without loss of $HgCl_2$.

(5) $2[P_{66614}]Cl + 3HgCl_2$ ($[P_{66614}]_2[Hg_3Cl_8]$). Molar mass: 1853.09; Hg content: 32.47% w/w; mol fraction $HgCl_2 = 0.6$.

This reaction product was obtained as a viscous yellow liquid. Anal. Calcd. for $[P_{66614}]_2[Hg_3Cl_8]$: C, 48.60; H, 8.67. Found: C, 48.60; H, 8.80. 1H NMR (300 MHz, DMSO- d_6): 0.86 (m, 12H), 1.33 (m, 48H), 2.18 (m, 8H); ^{13}C NMR (125 MHz, DMSO- d_6): 13.71, 13.77, 17.23, 17.32, 17.86, 17.95, 20.53, 20.58, 21.75, 22.04, 28.09, 28.64, 28.68, 28.94, 28.99, 29.02, 29.58, 29.78, 30.02, 30.35, 31.26; ^{31}P NMR (202 MHz, no standard): 34.73; ^{199}Hg NMR (89.5 MHz, DMSO- $d_6/HgCl_2$): -1265 ppm. ES-MS: ES+: 483.51 ($[P_{66614}]^+$, expected 483.86, (100)); ES-: 306.88 ($[HgCl_3]^-$, expected 306.87, (100)); 553.44 ($[P_{66614}]Cl_2^-$, expected 554.41, (20)); 1099.25 ($[P_{66614}][HgCl_3]_2^-$, expected 1097.25, (10)). UV-vis peak max. (acetonitrile): 241 nm. Selected IR (neat sample; cm^{-1}): 2955s, 2924s, 2854s, 1465m, 1378w, 1301w, 1213w, 1111w, 808w, 719m. Raman spectroscopy (neat, cm^{-1}): 2932, 2928, 2904, 2876, 2858 (C-H), 1440, 1306 (CH_2 , CH_3), 306 (shoulder, $HgCl_2$), 286 ($[Hg_2Cl_6]^{2-}$). When subjected to heat (90 °C) or HV (50 °C, < 1 mbar), $HgCl_2$ sublimation was observed.

(6) $[P_{66614}]Cl + 2HgCl_2$ ($[P_{66614}][Hg_2Cl_5]$). Molar mass: 1062.29; Hg content: 37.77% w/w; mol fraction $HgCl_2 = 0.6$.

This reaction product was obtained as a viscous yellow-brownish liquid. Anal. Calcd. for $[P_{66614}][Hg_2Cl_5]$: C, 36.18; H, 6.45. Found: C, 36.99; H, 6.77. 1H NMR (300 MHz, DMSO- d_6): 0.86 (m, 12H), 1.33 (m, 48H), 2.17 (m, 8H); ^{13}C NMR (125 MHz, DMSO- d_6): 13.77, 13.83, 17.22, 17.31, 20.54, 20.59, 21.77, 22.06, 28.09, 28.64, 28.70, 28.95, 29.03, 29.60, 29.80, 30.04, 30.37, 31.27; ^{31}P NMR (202 MHz, no standard): 34.76; ^{199}Hg NMR (89.5 MHz, DMSO- $d_6/1.0$ M $HgCl_2$): -1328 ppm. ES-MS: ES+: 483.51 ($[P_{66614}]^+$, expected 483.86, (100)); ES-: 306.88 ($[HgCl_3]^-$, expected 306.87, (100)); 1097.24 ($[P_{66614}][HgCl_3]_2^-$, expected 1097.25, (10)). UV-vis peak max. (acetonitrile): 241 nm. Selected IR (neat sample; cm^{-1}): 2955s, 2924s, 2854s, 1465m, 1378w, 1301w, 1212w, 1111w, 809w, 719m. When subjected to heat (90 °C) or HV (50 °C, < 1 mbar), $HgCl_2$ sublimation was observed.

DISCUSSION

Scheme 1 presents an overview of the different compositions that were investigated in the $[P_{66614}]Cl/HgCl_2$ system, and Table 1 provides the analytical data obtained for each. For easy comparison throughout the discussion, the spectroscopic data for (1)–(6) are compared visually in Figures 1–4. Each ionic liquid is described in detail below.

The observed UV-vis absorptions are attributed to a Hg-Cl charge transfer. The absorption maxima of (1) and (2) appear at 236 and 237 nm respectively, which points to the presence of the same complex anion, $[HgCl_4]^{2-}$. The peaks of (3) and (4) are very close to each other (239 and 241 nm, respectively). The peak maximum for (3) lies exactly in the middle of the peak positions of (2) and (4). This points to a fast chloride exchange between the two anionic species observed by Raman in (3), and the peak maximum of (4) is in close agreement with the value found by Horváth et al.⁷¹ for their $[HgCl_3]^-$ compound. As polynuclear chloromercurate species are prone to dissociation by elevated temperature, a dissociating effect of the acetonitrile solvent can be assumed. This is supported by the fact that the reaction products (5) and (6) also show the same maximum wavelength as observed in (4).

($[P_{66614}]_2[HgCl_4] + 2[P_{66614}]Cl$) (1). The ^{199}Hg NMR spectrum of the $[HgCl_4]^{2-}$ anion has been described in the literature. A $[HgCl_4]^{2-}$ compound described by Bharara et al. has a chemical shift of -1144 ppm in DMSO- d_6 .⁷² A literature value for $[HgCl_4]^{2-}$ in aqueous solution was given to be -1152 ppm by Klose et al.,⁷³ and values of -1170 and -1180 ppm, also in aqueous solutions at specific pH and pCl, were found by Delnomdedieu et al.^{74,75} $[P_{66614}]_2[HgCl_4]$ in excess $[P_{66614}]Cl$ was investigated by ^{199}Hg NMR (Figure 1), and a sharp and narrow peak was observed at -1120 ppm compared to the standard. The ^{199}Hg NMR of (1) shows essentially the same

Table 1. Analytical Data on the Reaction Products Investigated

equiv of HgCl ₂ per [P ₆₆₆₁₄]Cl	0	0.25 (1)	0.5 (2)	0.75 (3)	1 (4)	1.5 (5)	2 (6)
color	colorless	colorless	colorless	colorless	pale yellow	light yellow-brown	light brown
relative viscosity	moderate		very high		high	moderate	low
density at 20 °C	0.895	0.99	1.08	1.15	1.24	1.39	1.53
T _g [°C]	–56 °C		–37 °C/–42 °C				
Raman [400–100 cm ^{–1}]		261	261 + shoulder	282 + 262	282	286 + shoulder	too colored to be measured
UV–vis [nm]		236	237	239	241	241	241
¹⁹⁹ Hg NMR ^a [ppm]		–1120 (s)	–1129 (s)	–1118 (broad s)	–1197 (broad s)	–1265 (s)	–1328 (s)

^aExternal standard 1.0 M HgCl₂ in DMSO-*d*₆ has a chemical shift of –1501 ppm.

chemical shift as for the neat [P₆₆₆₁₄]₂[HgCl₄] (2), with only a relatively small difference of 9 ppm (*vide infra*). This might be due to an interaction with the free chloride anions in that specific liquid, indicating that the excess chloride keeps the Hg(II) ion in the (monomeric) tetrachloro form. From the stoichiometry, a pentachloro/hexachloro coordinated form would be possible, but [HgCl₅]^{3–} and [HgCl₆]^{4–} were not observed in the vibrational spectra recorded. Thus the ¹⁹⁹Hg NMR peak shape and position suggest that the monomeric [HgCl₄]^{2–} species is predominant. The ¹⁹⁹Hg NMR signal for neat [P₆₆₆₁₄]₂[HgCl₄] is somewhat broader (*vide infra*), which might be caused by its very high viscosity. The formation of [HgCl₄]^{2–} was further proven by Raman spectroscopy. As Figure 2 shows that adding a small amount (0.25 equiv) of HgCl₂ to the parent IL generates a new peak that appears at 262 cm^{–1}; this peak corresponds to the [HgCl₄]^{2–} anion, where literature values of 261 and 269 cm^{–1} were reported.^{76,77} While the neat IL [P₆₆₆₁₄]Cl only shows Raman signals generated by the cation's alkyl chains, it is possible to discriminate between the {HgCl₃}[–] and [HgCl₄]^{2–} that were formed upon addition of HgCl₂. The signals generated by the cation undergo a marked change upon addition of HgCl₂ (Figure 3). The peak at 2930 cm^{–1} starts transforming from a shoulder to a real peak with the addition of 0.25 equiv of HgCl₂, and this change is more pronounced for larger amounts of the mercury compound. However, adding more than 1 equiv of HgCl₂ does not result in further changes to the shape of this peak. This shape-transforming band has been described as the ν_s(CH₃)_{FR} mode by Larsson and Rand,⁷⁸ who attributed an increase in its intensity to an increased disorder in the alkane assemblies. This disorder might stem from the fact that the bigger chloromercurate anion is attracted to a somewhat lesser extent to the cation by electrostatic forces and therefore has a decreased influence on the structuring of the cation's alkyl chains. An increase in this peak's intensity compared to the ν_s(CH₂) mode at 2850 cm^{–1} later was correlated to intermolecular coupling of alkane chains by Snyder et al.⁷⁹ Therefore we can assume that the addition of HgCl₂ leads to a significant change in the overall conformation of the parent IL's cation. Furthermore, the peak at 2892 cm^{–1} (ν_a(CH₂)) from the original IL, a peak with an adjacent shoulder, transforms and shifts with an increasing amount of HgCl₂. This peak's maximum for the phosphonium chloromercurates is shifted to 2900–2904 cm^{–1} with an increasing amount of HgCl₂. As pointed out by Fraser et al.,⁸⁰ [P₆₆₆₁₄]Cl is best described as a liquid ion pair, with the anion situated close to the cation and hence fitting in the cavities created by the interactions of the alkyl chains with each other. Our results obtained by Raman spectroscopy indicate that this proximity is decreased when the chloride anion binds to the Hg center. The bigger anionic species formed is attracted to the cation to a much lesser extent and therefore interrupts to a certain degree the order of the alkyl chains, leading to pronounced changes in the ILs' internal conformation. Chloromercurates can be observed in the UV–vis range of the electromagnetic spectrum (Figure 4). According to Horváth and Vogler,⁷¹ who studied chloromercurates in acetonitrile, [HgCl₄]^{2–} and [HgCl₃][–] generate peaks at 234 and 240 nm, respectively. The UV–vis signal of (1) was found to peak at 236 nm, which is only very slightly different from [P₆₆₆₁₄]₂[HgCl₄] (2). This reaction product should be seen as a case in which one cation and two anions are present, namely, [HgCl₄]^{2–} and Cl[–]. However, multiple anionic species could be present in very small quantities. Nevertheless, the

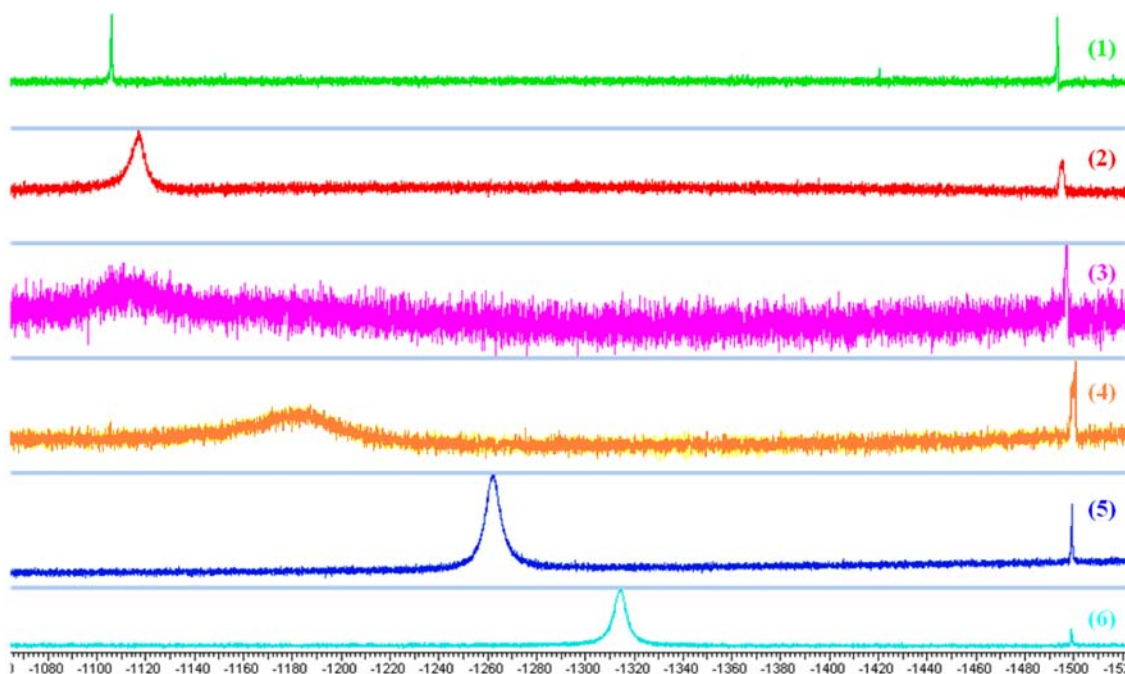


Figure 1. ^{199}Hg NMR spectra of all six $[\text{P}_{66614}]\text{Cl}/\text{HgCl}_2$ compositions; 1.0 M HgCl_2 in $\text{DMSO}-d_6$ as external standard (-1501 ppm).

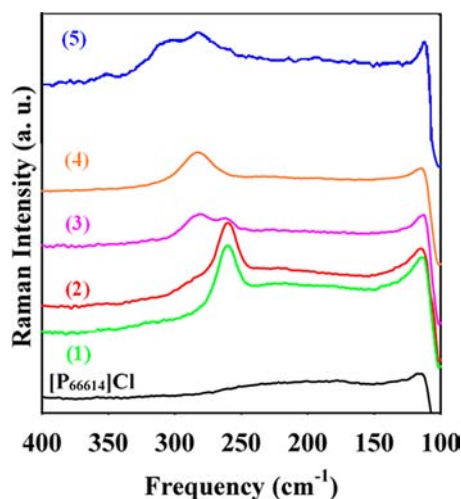


Figure 2. Raman spectra of the reaction products (1)–(5) and the parent IL in the range from 100 to 400 cm^{-1} .

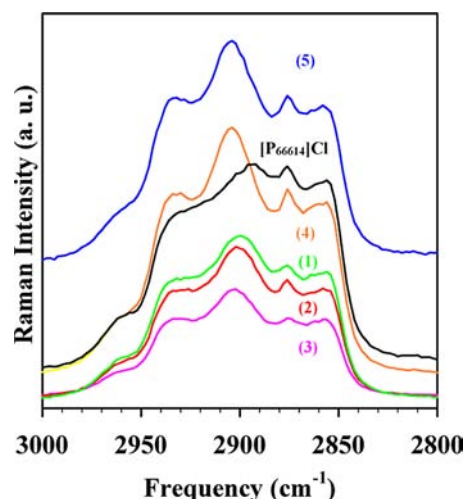


Figure 3. Raman spectra of the reaction products (1)–(5) and the parent IL in the range from 2800 to 3100 cm^{-1} .

composition consists of ionic species only and hence qualifies as an IL.

$[\text{P}_{66614}]_2[\text{HgCl}_4]$ (2). The most notable feature of this compound is its very high viscosity of 51200 cP at 293 K, which is indicative of a highly charged ion, which would be expected from the stoichiometry. The ^{199}Hg NMR of this compound showed a peak at -1129 ppm relative to the standard at -1501 ppm, see Figure 1, second from top. The chemical shift found for (2) fits well with those published by Bharara⁷² and Klose⁷³ for the anion in solution; the Hg in $[\text{HgCl}_4]^{2-}$ seems to be well shielded from the solvent's influence. The slightly more negative values for the ^{199}Hg NMR signal in solution also might indicate some degree of dissociation of chloride from the $[\text{HgCl}_4]^{2-}$; neat (4) with the $\{\text{HgCl}_3\}^-$ anion generates a broad signal with a peak at -1197 ppm (vide infra). Being deprived of excess chloride anions, the tetrachloromercurate anions can be imagined to form polyanions, which would result in a drastically

increased viscosity. The Raman spectrum recorded for this composition clearly shows the formation of the $[\text{HgCl}_4]^{2-}$ anion, with a peak at 262 cm^{-1} , and an appearing shoulder at 282 cm^{-1} indicates some degree of condensation of $[\text{HgCl}_4]^{2-}$ units has occurred. This assumption is supported by the broader shape of its ^{199}Hg NMR signal compared with (1). The UV–vis absorption maximum was detected at 237 nm, what is in close agreement with data published by Horváth and Vogler.⁷¹

$([\text{P}_{66614}]_2[\text{HgCl}_4] + 2 [\text{P}_{66614}]\{\text{HgCl}_3\} \rightleftharpoons [\text{P}_{66614}]_4[\text{Hg}_3\text{Cl}_{10}])$ (3). Being a liquid, this stoichiometric composition potentially represents a case with two interacting (poly)anionic species coexisting. When 3 equiv of HgCl_2 are dissolved in 4 equiv of $[\text{P}_{66614}]\text{Cl}$, the product's ^{199}Hg NMR spectrum only shows one broad peak of low intensity with a maximum at -1118 ppm (Figure 1, third from top), which indicates a fast chloride exchange between the two different anions on the NMR time

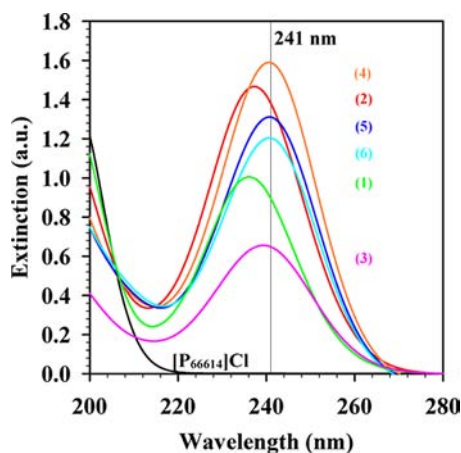


Figure 4. UV–vis spectra of the reaction products (1)–(6) and the parent IL in the range from 200 to 280 nm in acetonitrile solution.

scale, as well as an oligomeric/polynuclear character. The peak's shape resembles the peak shape of the $\{\text{HgCl}_3\}^-$ composition (4), indicating that higher adducts form (vide infra). The peak's position on the other hand is somewhat closer to the peak found for $[\text{HgCl}_4]^{2-}$, and this feature indicates that the two different anions share their chloride ligands and hence have at the same time a tetrahedral coordination and are oligomers or polymers. Polynuclear $\{\text{MCl}_x\}_n^-$ species give very broad signals at room temperature, as was observed by Hardacre et al. for Ga-based ILs,⁴¹ and by others for Al-based ILs.⁸¹ It is thus assumed that in this ionic liquid the polyanionic Hg species are predominant. Raman spectroscopy clearly identifies two different anionic species. As it operates on a faster time scale compared to NMR spectroscopy, it is possible to distinguish between species that form adducts on the NMR time scale. Two distinct peaks (282 and 262 cm^{-1}) can be observed, which indicates the existence of a mixture of anions, namely $[\text{Hg}_2\text{Cl}_6]^{2-}$ and $[\text{HgCl}_4]^{2-}$. Goggin et al. observed a peak at 286 cm^{-1} for their $[\text{NBu}_4]_2[\text{Hg}_2\text{Cl}_6]$.¹⁹ Linden et al. describe the chloromercurate anions with the stoichiometry of $[\text{Hg}_3\text{Cl}_{10}]^{4-}$ as made of two $[\text{HgCl}_4]^{2-}$ units bridged by HgCl_2 in a chainlike lattice.⁶² This is slightly different from the same stoichiometry in the liquid state, as we detect both $[\text{Hg}_2\text{Cl}_6]^{2-}$ and $[\text{HgCl}_4]^{2-}$. As Raman spectroscopy operates on a faster time scale compared to NMR, it seems that the $[\text{Hg}_2\text{Cl}_6]^{2-}$ dianion is the building unit for the polynuclear species observed by ^{199}Hg NMR. The $[\text{Hg}_3\text{Cl}_{10}]^{4-}$ anion described by Kabadou et al.^{82,83} consists of layers and polynuclear chains of $\{\text{HgCl}_3\}_n^-$ and $\{\text{HgCl}_4\}_m^{2-}$, respectively. Despite being composed of two different species, its Raman signal was reported to be a sharp and intense band at 272 cm^{-1} , not two peaks as observed in our liquid reaction product. It is worth noting that their Raman band at 272 cm^{-1} lies in the middle of the two Raman bands observed in our product. In the solid state the anionic species present for this composition apparently condense to form a single species. Kabadou et al. reported an increase in line width upon heating on their $[\text{Hg}_3\text{Cl}_{10}]^{4-}$ salt and attribute this observation to a distortion of HgCl_6 octahedra present in their crystal.⁸² Another possible interpretation of this finding would be that heating this particular anionic species leads to a split of their anion and the subsequent formation of the two anionic species we find in our product. It could be imagined, however, that the two species observed in our IL will eventually condense to a single

species, thereby merging the peaks observed in the Raman spectrum. UV–vis spectroscopy of the 2:1 mixture of $\{\text{HgCl}_3\}^-/[\text{HgCl}_4]^{2-}$ revealed a maximum at 239 nm (only 1 peak detected). This value is in between those for $[\text{P}_{66614}]_2[\text{HgCl}_4]$ and $[\text{P}_{66614}]\{\text{HgCl}_3\}$ which are observed at 237 nm and at 241 nm , respectively. This indicates a fast dynamic exchange of chloride ligands between the two anions present in acetonitrile solution, $[\text{HgCl}_3]^-$ and $[\text{HgCl}_4]^{2-}$.

$[\text{P}_{66614}]\{\text{HgCl}_3\}$ (4). When $[\text{P}_{66614}]\text{Cl}$ and HgCl_2 are reacted in a stoichiometric ratio of 1:1 the ^{199}Hg NMR spectrum showed a broad peak of low intensity with maximum at -1197 ppm (Figure 1, fourth from top). The broad signal suggests the presence of a distribution of several complex polyanions with a similar local coordination. It is likely that aside from $[\text{HgCl}_3]^-$ species of the type $\{\text{HgCl}_3\}_n^-$ (with $n > 1$) form. Thus, a complex equilibrium of different polyanions is envisioned. This hypothesis is backed by NMR studies at elevated temperature. At $50\text{ }^\circ\text{C}$ a single well-defined peak is observed; see Supporting Information. The peak narrowing could arise from the thermal breakup of the polynuclear species to a single anionic species or due to the reduced viscosity at higher temperatures. However, compound (2) produces a well-defined peak despite being very viscous. Both effects may play a role though. At room temperature, the broad peak observed is similar only to the mixture of $[\text{HgCl}_4]^{2-}$ and $\{\text{HgCl}_3\}^-$ species in liquid (3) (vide supra). Numerous crystal structures with an anion of this composition support our hypothesis, and House et al.¹⁷ reviewed the broad spectrum of possible structures vs their respective Hg/Cl ratio. Klose et al. found a chemical shift of -1436 ppm for their compound with the same anion,⁷³ and Delnomdedieu et al. published a value of -1298 ppm ;⁷⁴ both groups investigated aqueous solutions of Hg(II) salts, and an effect of the solvent on the chemical shifts cannot be excluded. The differences from published chemical shifts in solution are much bigger here than for the $[\text{HgCl}_4]^{2-}$ species, most likely because the solvent breaks up any oligomeric/polynuclear anions and makes chloride dissociation possible. From the data gathered and comparison with published data, it can be concluded that the polynuclear $\{\text{HgCl}_3\}^-$ are relatively easily broken up by increased temperature and solvent interactions to form monomeric or dimeric species. The Raman spectrum (Figure 2) of pure $[\text{P}_{66614}]\{\text{HgCl}_3\}$ shows a broadened peak with a maximum at 282 cm^{-1} ; this is indicative of a $[\text{Hg}_2\text{Cl}_6]^{2-}$ anion,¹⁹ although the peak shape in Goggin's compound is narrower. The broader shape in our product is very likely due to a further condensation of the $[\text{Hg}_2\text{Cl}_6]^{2-}$ units. The presence of small amounts of isolated, trigonal planar $[\text{HgCl}_3]^-$ cannot be excluded though. The observed signal is almost twice as broad as that of the $[\text{HgCl}_4]^{2-}$ anion. This also could reflect the oligomeric/polynuclear character of the $\{\text{HgCl}_3\}^-$ anion. Because of the broader shape of this peak, it seems likely that some higher aggregates, for example, dimers or trimers and higher, form to a noticeable extent. UV–vis spectroscopy produced a single peak at 241 nm for the compound $[\text{P}_{66614}]\{\text{HgCl}_3\}$, with an identical peak shape as the other compositions. This indicates that the polynuclear anion breaks up in acetonitrile solution under the conditions applied (room temperature). Interestingly, further addition of HgCl_2 does not result in a continued peak shift, so that we can assume that $[\text{HgCl}_3]^-$ is the only structural unit present in acetonitrile solution, apart from HgCl_2 , which is featureless in the range measured.⁷¹

($[P_{66614}]_2[Hg_3Cl_8]$) (5). ^{199}Hg NMR of this reaction product gave a chemical shift of -1265 ppm relative to the standard, see Figure 1, continuing the trend to increasingly negative chemical shifts with increasing $HgCl_2$ content. Because the ^{199}Hg NMR only shows a single peak, it can be anticipated that there is a rapid exchange of the chloride anions between the Hg atoms,⁸⁴ as observed by Godfrey et al. for aqueous solutions of $HgCl_2$ in the presence of $LiCl$.⁸⁵ In fact, this anion can be thought of as a complex of two monomeric $[HgCl_3]^-$ anions bridged by a molecular $HgCl_2$ molecule, as already described by Nockemann et al.⁸⁶ and Loukil et al.⁸⁷ for crystal structures based on the $[Hg_3Cl_8]^{2-}$ anion. The fact that $HgCl_2$ can be removed from 5 by heating to 90 °C supports this hypothesis. The Raman spectrum of 5 shows a peak with a maximum at 286 cm^{-1} and a shoulder at 298 – 306 cm^{-1} . The peak's maximum position lies well within the reported range for $[Hg_2Cl_6]^{2-}$, and the shoulder could stem from weakly coordinated $HgCl_2$ (literature value 314 cm^{-1}).⁸⁸ Because this shoulder is absent in the compositions with lower Hg content, it can be concluded that no isolated $HgCl_2$ units are present there. Data from UV–vis spectroscopy also supports the assumption that, in solution, $[Hg_3Cl_8]^{2-}$ consists of two $[HgCl_3]^-$ units which weakly coordinate a $HgCl_2$ molecule. The absorption maximum is at the same wavelength as the $[P_{66614}]\{HgCl_3\}$ compound. The spectroscopic data combined with the fact that the material loses $HgCl_2$ by sublimation when heated in a vacuum supports the assumption that weakly coordinated $HgCl_2$ is present in this liquid. It is thus conceivable that (5) exists as an IL at lower temperatures only and gradually changes into $HgCl_2$ dissolved in $[P_{66614}]\{HgCl_3\}$ at sufficiently high temperature.

($[P_{66614}][Hg_2Cl_5]$) (6). This reaction product shows the lowest viscosity, highest density, and the most intense color. The recorded ^{199}Hg NMR shows a sharp peak at -1328 ppm (Figure 1, bottom). No literature value was found for comparison on this species. The chemical shift does, however, follow the trend to lower values with increasing Hg content, suggesting that more and more $HgCl_2$ is present in a weakly coordinated form with increasing amounts of $HgCl_2$ added to the parent IL. The structure of this anion thus is likely to consist of a $HgCl_2$ weakly coordinated to a $[HgCl_3]^-$ anion, which explains the relative proximity to the standard, the sharp peak, as well as the readiness with which it sublimates $HgCl_2$ when heated to 90 °C or when subjected to a high vacuum at 50 °C. It is thus conceivable that (6) exists as an IL at lower temperatures only and gradually changes into $HgCl_2$ dissolved in $[P_{66614}]\{HgCl_3\}$ at sufficiently high temperature, just like (5) (vide supra). Because of the increasing coloration of the liquid obtained, the Raman-spectrometer used reached its limits; the more intense colored (6) could not be analyzed by this technique. UV–vis shows a peak at 241 nm, the same value as for $[HgCl_3]^-$ species. Therefore it appears that the aggregates dissociate in acetonitrile solution. The structural unit of $[Hg_2Cl_5]^-$ thus can be visualized as a $[HgCl_3]^-$ unit coordinating a $HgCl_2$ molecule.

^{199}Hg NMR: Chemical Shift As a Function of Hg Content. Additional support for the above assignments can be found by plotting the chemical shifts of ^{199}Hg versus the mole fraction of Hg present (Figure 5). For the first three reaction products with the lowest Hg contents, there is only a very slight change in the chemical shift, while from liquid (3) to liquid (6) there is a pronounced change in chemical shift with increasing Hg content. The similarity of the chemical shifts for liquids (1) and (2) points to a similarity in the chloromercurate anion's

structure, which is what would be expected if (1) is predominantly composed of $[HgCl_4]^{2-}$. The similarity between (2) and (3) points to a structural similarity to $[HgCl_4]^{2-}$ as well, with the $[Hg_2Cl_6]^{2-}/[HgCl_3]^-/[HgCl_3]^-$ probably being tetrahedrally coordinated by chloride in the same fashion as $[HgCl_4]^{2-}$ is. As the stoichiometry of (3) is set to $[Hg_3Cl_{10}]^{4-}$, it is conceivable that the identity of the anionic species could be $[HgCl_4]^{2-}$ and $[Hg_2Cl_6]^{2-}$. Upon further addition of $HgCl_2$, however, a relatively drastic change in the chemical shift is observed which suggests a profound change in the coordination of the Hg(II). The observed changes might result from the anions present in (3) undergoing a structural change upon further addition of $HgCl_2$. Any further addition of $HgCl_2$ to (4) continues to change the chemical shift of the ^{199}Hg nucleus, and the anion's structure undergoes a structural change from polynuclear arrangements, likely to the better defined bi- and trinuclear anionic species. The chloride coordination of the Hg(II), as well as the ratio chloride/Hg(II), is subject to drastic changes, which decreases with each further addition of $HgCl_2$. The chemical shifts of the ^{199}Hg thus represent the effects of two different factors: one being the coordination number of the Hg(II), the other being the transition from mononuclear species to polynuclear species and the further transition to bi- and trinuclear species. This could support a change in the coordination sphere around the Hg center, perhaps from an octahedral environment to a tetrahedral environment or vice versa.

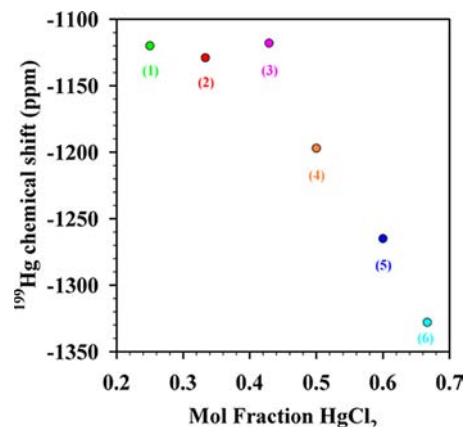
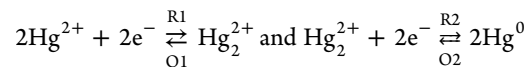


Figure 5. Chemical shift of ^{199}Hg vs Hg content for the reaction products (1)–(6).

Electrochemical Investigations. CV shows for all contents of $HgCl_2$ in $[P_{66614}]Cl$ the typical pattern of a two-step electron transfer mechanism. The proposed redox reactions are shown below.



In both cases, the separation of the oxidation and reduction peak is too large for a reversible electrochemical reaction (Figures 6 and 7). The peak with the assignment OCl describes the irreversible oxidation of the Cl^- to chlorine ($2Cl^- \rightarrow Cl_2 + 2e^-$). The observation that with increasing $HgCl_2$ content a decrease of the halfwave potential toward more negative values is observed corresponds well with the chemical shift to the high field region of the ^{199}Hg NMR-spectra. This shift of the reduction and oxidation potentials to more negative values with increasing $HgCl_2$ can be attributed to the decreased electron

density around the mercury cation with less chloride per mercury cation being present leading to a diminished readiness for the cation to be reduced. Figure 8 shows a graphical overview on the electrochemical data vs Hg content of all compounds prepared.

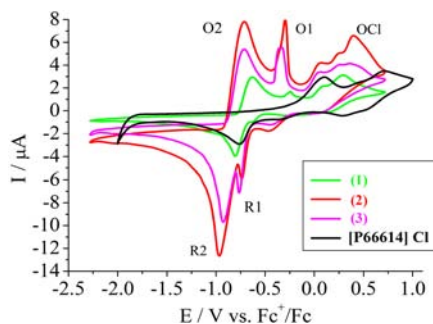


Figure 6. Cyclic voltammograms of a 0.025 M solution of reaction products (1), (2), (3), and $[P_{66614}]Cl$ in $[C_4mim][Tf_2N]$. Scan rate 50 mV s^{-1} .

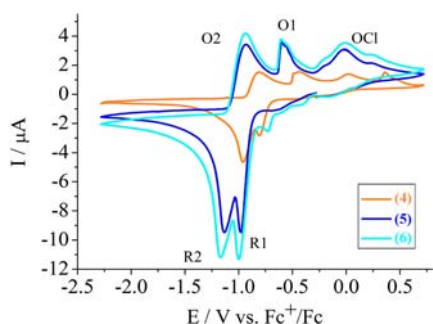


Figure 7. Cyclic voltammograms of a 0.025 M solution of reaction products (4), (5), and (6) in $[C_4mim][Tf_2N]$. Scan rate 50 mV s^{-1} .

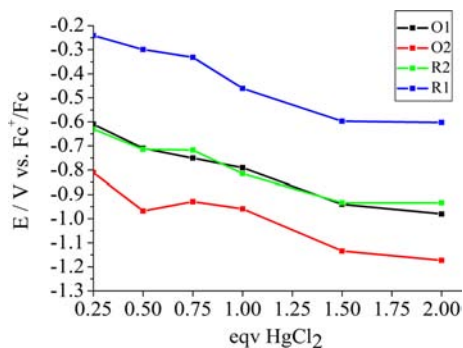


Figure 8. Electrochemical data vs Hg content.

Physical Properties. The viscosity and density data are compared visually in Figures 9–11. These are described individually below.

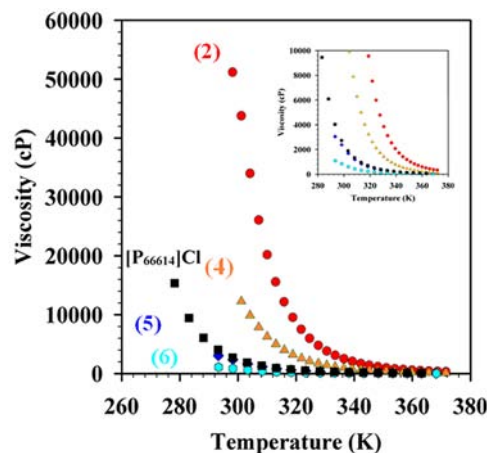


Figure 9. Viscosities of the reaction products (2), (4), (5), and (6) vs. temperature. (Data for $[P_{66614}]Cl$ taken from Neves et al.)⁶⁸

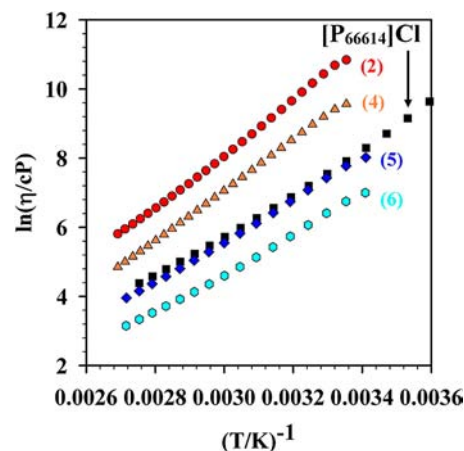


Figure 10. Arrhenius plots of the reaction products (2), (4), (5), and (6) viscosities. All R^2 values are greater than 0.997. (Data for $[P_{66614}]Cl$ taken from Neves et al.)⁶⁸

Viscosity of Reaction Products (2), (4), (5), (6), and the Parent IL. All prepared $[P_{66614}]^+$ chloromercurates are room temperature ILs with medium to very high viscosities. The highest viscosity was observed for (2), the second highest was for the most likely polynuclear compound (4), and the lowest was for (6). The observation that the IL with $[HgCl_4]^{2-}$ anions is the most viscous is attributed to the double charge of the

Table 2. Compiled Electrochemical Data for Reaction Products (1)–(6)

electrochemical potential (V)	0.25 eq (1)	0.50 eq (2)	0.75 eq (3)	1.00 eq (4)	1.50 eq (5)	2.00 eq (6)
$E_{O1} (Hg_2^{2+}/Hg^{2+})$	-0.610	-0.710	-0.750	-0.790	-0.940	-0.980
$E_{R1} (Hg^{2+}/Hg_2^{2+})$	-0.241	-0.299	-0.331	-0.461	-0.597	-0.602
$E_{1/2_1}$	-0.425	-0.504	-0.540	-0.625	-0.768	-0.791
ΔE_1	0.369	0.411	0.419	0.329	0.343	0.378
$E_{O2} (Hg^0/Hg_2^{2+})$	-0.810	-0.968	-0.929	-0.959	-1.134	-1.173
$E_{R2} (Hg_2^{2+}/Hg^0)$	-0.630	-0.714	-0.171	-0.815	-0.934	-0.934
$E_{1/2_2}$	-0.720	-0.841	-0.823	-0.887	-1.034	-1.053
ΔE_2	0.180	0.254	0.212	0.144	0.200	0.239

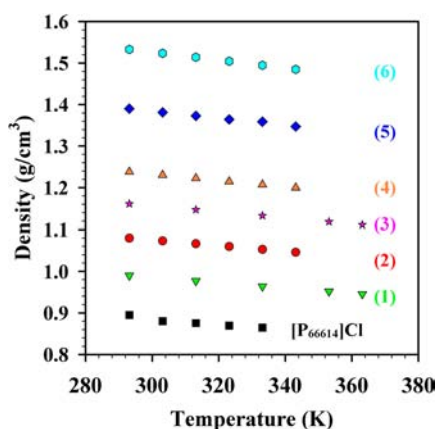


Figure 11. Densities of the investigated reaction products (1)–(6) and the parent IL vs. temperature. (Data for $[P_{66614}]Cl$ taken from Neves et al.)⁶⁸

anion and potentially stems from higher aggregates that might exist in the liquid state. The decreasing viscosity of all subsequently prepared ILs (by $HgCl_2$ addition) reflects the decrease in charge density carried by the anionic species. The ILs described here thus behave similar to the $[C_2mim]^+$ and $[C_4mim]^+$ chloroaluminate compounds described in the literature.⁸⁹ However, the overall viscosity of the phosphonium chloromercurates is high compared to these ILs.

It is remarkable that the addition of further 0.5 equiv of $HgCl_2$ to $[P_{66614}]_2[HgCl_4]$ reduces the viscosity at room temperature considerably to approximately one-third of its value in the $[HgCl_4]^{2-}$ compound (2). Even more remarkable is that this trend is continued throughout each further addition of 0.5 equiv of $HgCl_2$ (Figure 9). The temperature dependence of the viscosity follows the usual pattern observed for ILs and decreases exponentially with increasing temperature (Figure 9). IL (2) has a viscosity of 51200 cP at 293 K, and (4) has a viscosity of 14282 cP at the same temperature. Obviously, the doubly charged and comparably compact anion induces a much higher viscosity to the ionic liquid (2).

While the polynuclear $\{HgCl_3\}^-$ anion still ensures a high viscosity, a more pronounced change is observed when adding more $HgCl_2$ to reach the $[Hg_3Cl_8]^{2-}$ stoichiometry. Despite its doubly charged (but voluminous) anion, the viscosity at 293 K is 2383 cP, which is nearly a 6-fold decrease compared to the $\{HgCl_3\}^-$ species. This demonstrates that the electrostatic interactions between the ions are strongly dependent on the anion's structure. Additionally, the viscosity of reaction product (5) is similar to the viscosity of the parent IL. The effect of the two charges per anion is thus countered by the charge distribution over the bigger anionic species. From here, the viscosity drops upon further addition of another 0.5 equiv of $HgCl_2$ to 852 cP, again a decrease by roughly a factor of three. At higher temperatures, for example, 348 K, a similar trend is observable, with the viscosities changing from 1190 cP to 461.3 cP to 122.3 cP to 50.5 cP along the series of compositions investigated. If similar ILs are used in the future to extract Hg(II) ions from, for example, water, the viscosity of the extract at a given temperature can serve as a rough indicator to quantify the amount of Hg present in the IL.

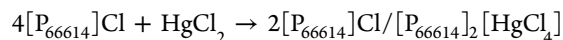
Okoturo et al. published a paper on the viscosities of ILs, and they show that their chosen examples are well described by the Arrhenius model.⁹⁰ As for the chloromercurates described in this paper, plotting the logarithm of the viscosity against the

inversed absolute temperature yields a straight line for each reaction product investigated (Figure 10). As can be seen in the same figure, the slopes for the two compounds with lower Hg loading ($[P_{66614}]_2[HgCl_4]$ (2) and $[P_{66614}]\{HgCl_3\}$ (4)) are slightly steeper than the slopes of the other two examples, with the two lines being close to parallel for the two examples with lower loading and also close to parallel for the two examples with higher Hg loading. This might reflect the presence of rather weakly coordinated $HgCl_2$ for the compounds (5) and (6), which might act as an internal "lubricant" for the ionic species present.

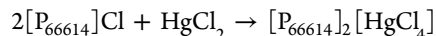
Density. The densities of the prepared reaction products vs temperature are shown in Figure 11. A similar trend as found for the viscosity was observed for the densities. The densities increase with metal content as observed for the $[C_2mim]^+$ and $[C_4mim]^+$ chloroaluminate ILs, but the increase in density with increasing metal content is more pronounced in the chloromercurates. This is perhaps not surprising given the generally much higher density of mercury compounds compared with similar aluminum compounds. The densities increase linearly with the metal content and decrease linearly with temperature. The highest value is thus found at room temperature for compound (6) which has a density of 1.53 g/cm³.

OVERVIEW & CONCLUSIONS

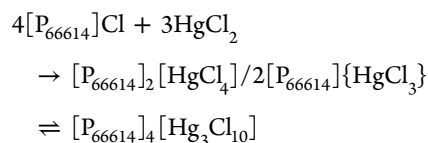
(1) mixture of ions



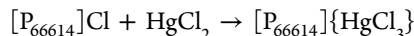
(2) IL stable against release of $HgCl_2$



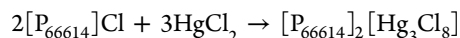
(3) (potential) mixture of ions



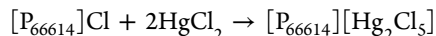
(4) IL stable against release of $HgCl_2$, polynuclear anions



(5) $HgCl_2$ weakly bound by $[P_{66614}]\{HgCl_3\}$; $HgCl_2$ sublimates at elevated temperature



(6) $HgCl_2$ weakly bound by $[P_{66614}]\{HgCl_3\}$; $HgCl_2$ sublimates at elevated temperature



For the first time, room temperature ILs with chloromercurate-anions have been synthesized and characterized. From the data presented here and due to the inherent complexity of coordination units in chloromercurate anions, only limited conclusions about the true structure of the anionic species can be drawn. Compositions (1) and (2) are believed to be structurally, as well as thermally, stable up to their decomposition temperature. It is the opinion of the authors that the anionic structures of the other ionic liquids prepared ((3)–(6)) consist of a temperature-dependent complex variety of different structural motifs, in addition to monomeric forms.

Table 3. Overview of Prepared Compounds

ILs stable against release of HgCl ₂	unstable ILs (HgCl ₂ weakly coordinated)	mixtures of anions
[P ₆₆₆₁₄] ₂ [HgCl ₄] (2)	[P ₆₆₆₁₄] ₂ [Hg ₃ Cl ₈] (5)	2[P ₆₆₆₁₄]Cl/[P ₆₆₆₁₄] ₂ [HgCl ₄] (1)
[P ₆₆₆₁₄]{HgCl ₃ } (4)	[P ₆₆₆₁₄][Hg ₂ Cl ₅] (6)	[P ₆₆₆₁₄] ₂ [HgCl ₄]/2[P ₆₆₆₁₄]{HgCl ₃ } (3)

The observed chemical shifts in the ¹⁹⁹Hg NMR can be rationalized by taking into account the Hg/Cl ratio and the chloromercurates' particular aggregation behavior. It was observed that an increasing amount of HgCl₂ in [P₆₆₆₁₄]Cl shifts the ¹⁹⁹Hg NMR signal in the direction of the external standard (HgCl₂ in DMSO-*d*₆), indicating an increasing similarity between HgCl₂ in DMSO-*d*₆ solution with the prepared compositions from (1) to (6). The two compositions with the highest amounts of HgCl₂ do sublime HgCl₂ when heated, also indicating a rather loosely bound HgCl₂ complex. These compounds therefore can be seen as borderline cases between true ILs and HgCl₂ dissolved in [P₆₆₆₁₄]{HgCl₃}. The ¹⁹⁹Hg NMR does only detect one peak in all cases investigated; this can be explained by the comparatively slow NMR measurements, meaning that the changes in Hg speciation can happen fast on the NMR time scale. Raman spectroscopy revealed the transition of the [HgCl₄]²⁻ anion to the [Hg₂Cl₆]²⁻ or [HgCl₃]⁻ anion with increasing Hg content, as well as the coexistence of both species in reaction product (3).

From the six different compositions discussed in this paper, one can be described as mixtures of discrete anions, namely, [HgCl₄]²⁻ and Cl⁻ in (1), and another one (3) as a liquid containing a well-defined anion ([HgCl₄]²⁻) and a not well-defined anionic species, {HgCl₃}⁻. One of the prepared compositions is best described as ILs with a single cation and anion species (2), and another one as a liquid with one cation and an anion which potentially is constituted of a variety of polynuclear aggregates (4). The other reaction products also would count as mixtures of molecular (or rather weakly coordinated) HgCl₂ in the chloromercurate IL [P₆₆₆₁₄]{HgCl₃}, although at low enough temperatures these compositions could count as true ILs. These liquids are a borderline case of ionic liquids, with a portion of the HgCl₂ being too weakly coordinated to bear a charge, most likely dependent on temperature. When these two highly loaded liquids were heated in a high vacuum to 50 °C or at ambient pressure to 90 °C, dissolved HgCl₂ sublimed, supporting this conclusion.

Compared to the well-described chloroaluminate and other metal containing anions, similar trends in physical properties are observed, for example, the decrease in viscosity and increase in density with increasing metal content. The reported viscosity of [P₆₆₆₁₄]₂[HgCl₄] of 51200 cP at 293 K is also among the highest reported to date. The ILs' densities increase with HgCl₂ content, and a value of 1.53 g/cm⁻³ at 293 K was measured for [P₆₆₆₁₄][Hg₂Cl₅], the highest density of a phosphonium IL reported to date. Overall, the physical properties of the reported liquids are reminiscent of the "classic" chloroaluminates in that the changes observed upon increasing the HgCl₂ content mirror the changes observed in chloroaluminates with increasing amounts of AlCl₃.

It is interesting to note that the density changes from lower than that of water to higher than that of water, even with only a small amount of HgCl₂ (from 0.5 equiv of HgCl₂) added. This could be advantageous if [P₆₆₆₁₄]Cl is ever used to extract Hg(II) species from water in the presence of excess chloride, as a simple mixer settler system could be used. Thus, adding [P₆₆₆₁₄]Cl to, for example, Hg(II)-contaminated seawater

would rapidly form the denser and hydrophobic chloromercurate ILs presented in this paper, which then would conveniently separate by gravity.

Knowledge of this class of compounds might be of interest for applications such as Hg(II) removal from water, oil, or gas with chloride based ILs, as well as for spectroscopic investigations. Investigations as to the nature of the anionic species vs temperature could shed some light on the polynuclear anions' effect on crystallization suppression, and including other metal species into the polynuclear chloromercurate anions might lead to some novel and useful insights into halogen-metal coordination compounds.

■ ASSOCIATED CONTENT

● Supporting Information

IR spectra, DSC traces, ¹⁹⁹Hg NMR spectra, figure of control experiment (H₂O + [P₆₆₆₁₄]Cl) and [P₆₆₆₁₄]Cl contacted with 0.18 M HgCl₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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