Halometallate ionic liquids – revisited

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Halometallate ionic liquids are reviewed, with emphasis on speciation studies and modern applications in catalysis and material science.

CRITICAL REVIEW

Halometallate ionic liquids – revisited

J. Estager,[a] J. D. Holbrey[b] and M. Swadźba-Kwaśny[b]

5 Ionic liquids with chlorometallate anions may not have been the first ionic liquids, however, it was their development that lead to the recognition that ionic liquids are a distinct, and useful, class of (functional) materials. While much of the phenomenal interest and attention over the past two decades has focussed on 'air and water stable' ionic liquids, research and application of chlorometallate systems has continued unabated albeit largely out of the main spotlight. The defining characteristic of chlorometallates is the

10 presence of complex anionic equilibria, which depend both on the type and on the concentration of metal present, and leads directly to their characteristic and individual properties. Here, we review the experimental techniques that can be applied to study and characterise the anion speciation in these ionic liquids, and using recent examples, illustrate how their applications base is evolving beyond traditional applications in Lewis acidic catalysis and electrochemistry through to uses as soft and component

15 materials, in the ionothermal synthesis of semiconductors, gas storage systems and key components in the development of biomass processing.

1. Chlorometallates, the first designer ionic liquids?

The ability to obtain organic salts that have relatively low melting
20 points and that are useful in their liquid state has been known for over one hundred years. As can be found in the introductory sections of most PhD theses relating to ionic liquids; ethylammonium nitrate reported by Walden[1] in 1914 and ethanolammonium nitrate described by Gabriel[2] in 1888 are
25 among the contenders for the description of the oldest ionic liquids studied. Even further back (1876) date publications on pyridine-acid mixtures from the Nobel prize winner Ramsey.[3]

However, from the pioneering work that emerged from the groups of Osteryoung[4] and Wilkes and Hussey,[5] until the surge of
30 interest in using air-stable ionic liquids kicked off in the 1990s following the work of Fuller et al.,[6] Wilkes and Zaworotoko,[7] and Bonhôte et al.,[8] the term 'ionic liquid' was largely synonymous with chlorometallate, or more widely halometallate, systems. These halometallate systems can be defined as ionic liquids
35 formed by the reaction of a metal halide with an organic halide salt. Notably, in the early days the research was limited almost exclusively to chloroaluminate(III) ionic liquids.

In 1974, Parshall reported that organic 'molten salts' containing coordinating chlorostannate(II) or germanate(II)
40 anions could be used as solvents for platinum catalysed hydrogenation of olefins,[9] recognising the importance of the coordinating chlorometallate anions to complex and stabilise the active platinum species and also how using the ionic liquid environment allowed products to be simply separated by
45 decantation or flash distillation without losing catalyst. These generic characteristics that are key to the use of ionic liquids as solvents or catalysts were largely unrecognised at the time.

Partially, this was because research on quaternary ammonium salts was concentrated on phase transfer systems[10] and partially
50 because development in ionic liquids – whether termed low temperature fused salts, molten salts or ionic liquids – was about to be focussed on electrochemical applications.

Wilkes[11] has described, from a personal perspective, how room temperature chloroaluminate(III) ionic liquids – formed as
55 eutectic compositions from organic chloride salts with aluminium(III) chloride – evolved from high temperature inorganic molten salts as a consequence of U.S. Air Force research into lower temperature thermal batteries. It was also recognised that these chloroaluminate(III) ionic liquids could also
60 be used as liquid Lewis acid catalysts, for example in Friedel-Crafts chemistry.[12] Key reviews from Hussey[13] in 1988 and Welton[14] in 1999 have examined in detail the preparation, handling and properties of chloroaluminate(III) ionic liquids.

These two components, namely: the ability to form and
65 stabilise transition metal catalysts in the liquid state, and the development of Lewis acidic room temperature chloroaluminate ionic liquids, were fused together in the transformation of the Institute Francais Petrole's Dimersol process for olefin dimerisation process using $NiCl_2$-$AlEtCl_2$ catalysts[15] into the
70 ionic liquid [C_2mim]Cl-$NiCl_2$-$AlEtCl_2$ Difasol process. This was a significant contribution to Chauvin's award of the Nobel Prize for Chemistry in 1995.[16] As befits a maturing field of science and technology, these 'older' processes that rely principally on the use of Lewis acidic chloroaluminate(III) ionic liquids[17] underpin a
75 number of processes that are either currently in use, or have been demonstrated, at industrial scales, as Pletchkova and Seddon described in a survey of ionic liquid technologies in 2008.[18]

Today, the interest in chlorometallate ionic liquid systems spans the entire metallic region of the periodic table, challenging

and expanding beyond these historical foci. Newer applications are of immense diversity: they provide transitional improvements in electroplating and polishing treatments,[19] supply the fundamental chemistry for new gas scrubbing processes,[20] allow syntheses of new inorganic semiconductor materials, transformation of biomass to energy products, and finally are central to controlled separations/extraction processes. Crucially, new studies are forging a path to make systematic correlations of anion speciation and properties across the series of different metals, leading to opportunities to introduce much finer control over properties such as Lewis acidity, stability, reactivity *etc*.

Within this new work, one thing is clear; anion speciation is of the utmost importance, and if this is not understood with the same degree of precision and care that was made for chloroaluminate(III) ionic liquids in the last century, then incomplete and mistaken conclusions will inevitably arise.

Aspects of metallate ionic liquid chemistry and applications have been reviewed recently, for example by Abbott *et al*.[19] and Binnemans (on An/Ln systems).[21] Here, we present a critical overview on metal ion speciation in chlorometallate ionic liquids, covering the experimental methods available and the current state of knowledge. Moreover, we illustrate how, taking advantage of the specific properties and complex coordination chemistry present in chlorometallates, a wide variety of innovative applications in chemistry and material science can be developed.

2. Anionic speciation

2.1. The importance of equilibria

Welton and co-workers[22] have demonstrated, in simple yet elegant experiments, that when simple salts such as [Hpy]I are dissolved in ionic liquids, they dissociate to form a binary ionic liquids, with two types of cations and two types of anions, rather than a solution with distinguishable solute and solvent. This result should be obvious, yet clearly needed to be stated. In the more complex case when a metal salt, MY_n, is able to expand its coordination sphere, contact with an ionic liquid, [cat][A], can lead to reactive dissolution forming metallate anions, as shown in Equation 1.

$$MY_n \xrightarrow{\text{[cat][A]}} \text{[cat]}[MY_nA] \xrightarrow{\text{[cat][A]}} \text{[cat]}[MA_n] + n\text{[cat][Y]} \quad (1)$$
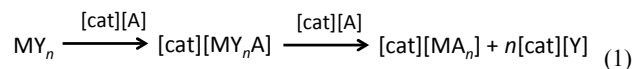
The product of such dissolution is a new ionic liquid containing several anionic species in equilibrium with each other and having physical and chemical properties which are different from those of the starting materials. Depending on the nature of the newly produced anions, these new ionic liquids may act as ideal solutions, or deviate from this behaviour.[23] Furthermore, if the cation contains functional groups that can coordinate to the metal centre, such as amine, nitrile or carboxylic acid, cationic complexes may be formed.[24] Both situations are compared in a scheme presented in Figure 1.

Halometallate ionic liquids are a particular case of the general scheme shown in Figure 1 and Equation Eq (1), where Y, A = Cl and/or Br. Since little work has been done with functionalised cations in halometallate systems we omit these from this discussion.

Addition of a *given amount* of a metal halide, MX_n, to a

halide-based ionic liquid, [cat]X, results in a mixture which may contain, next to a well-defined cation, halide and several halometallate anions in a dynamic equilibrium with each other. These equilibria constitute a fundamental characteristic of halometallate ionic liquids, where the anionic speciation can be complex. Typically, several halometallate anions can be formed in dynamic equilibrium. These species can be monomeric and/or oligomeric, with varying coordination numbers, depending on the composition of the ionic liquid, defined as a molar fraction of metal chloride, χ_{MCl_x}, the coordination chemistry of the metal, its oxidation state, and on the halide present. In the case of the mixed halide system, the statistically mixed distributions of bromochlorometallate anions can also be obtained, which adds further complexity to the systems.
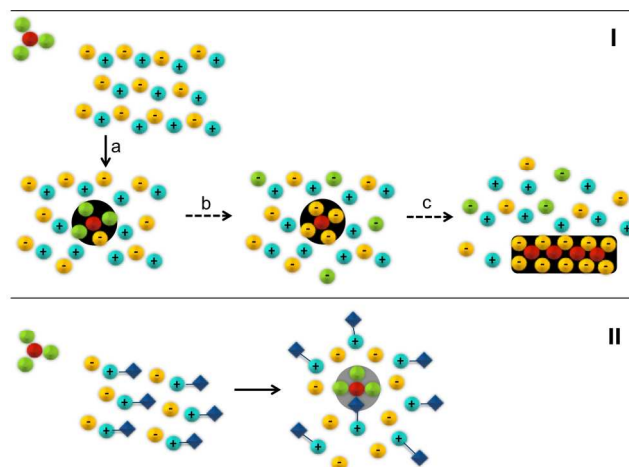

Figure 1. Schematic dissolution of a metal salt in an ionic liquid with a non functionalised cation (I) and a functionalised cation (II). Anions of ionic liquids become ligands to the metal by addition (a) or halide replacement (b). The formed metallate species may be oligomeric or even polymeric; in the latter case they may crystallise out from the solution (c).

The physico-chemical properties of halometallate ionic liquids, from their viscosity and electrical conductivity to Lewis acidity and stability towards moisture, depend on their anionic speciation. Consequently, in order to understand and control/modify their properties, it is necessary to clearly understand the nature of their anionic speciation.

2.2. Liquid-state speciation studies

It may be obvious but the experimental techniques of most value for studying ionic liquids are those that directly interrogate the liquid state. Information about solution- or solid-state structure may provide supporting information, but cannot necessarily be translated directly to the liquid phase. These issues have been highlighted briefly in a review by Abbot *et al*.[25]

2.2.1. Vibrational spectroscopy

Vibrational spectroscopy, in particular Raman and far IR spectroscopies, provides the most useful, versatile and straightforward techniques for a speciation study, often permitting direct identification of the chlorometallate species. The main foci are the M-Cl vibrations, typically found within the $600 - 650 \text{ cm}^{-1}$ range. Neat samples in both the liquid and solid states (including air-sensitive or hygroscopic compounds sealed

in glass capillaries[26] or quartz cuvettes[27]) can be examined without exposure to the atmosphere. Speciation in Ti(IV), Al(III), Ga(III), In(III), Fe(III), Zn(II), Au(I) and Cu(I)-containing systems has been studied, and the general applicability of Raman
5 spectroscopy for the investigation of ionic liquids has been reviewed by Berg.[28]

The key to a successful interpretation of Raman data is good spectral resolution and well-supported band assignments. The latter can be derived by comparison with the extant literature (on
10 high-temperature chlorometallate molten salts and solid state structures[29,30]) and/or derived from *ab initio* calculations.[31] For example, in 1978, Gale *et al.*[32] studied the speciation of $[C_4py]Cl$-$AlCl_3$ systems, having at their disposal medium quality Raman spectra (compared to contemporary standards) and a body
15 of work on high temperature molten salt systems. They demonstrated the existence of $[AlCl_4]^-$ at $\chi_{AlCl3} = 0.50$, $[Al_2Cl_7]^-$ at $\chi_{AlCl3} = 0.67$, and the presence of both anions at intermediate χ_{AlCl3} values (see Figure 2).
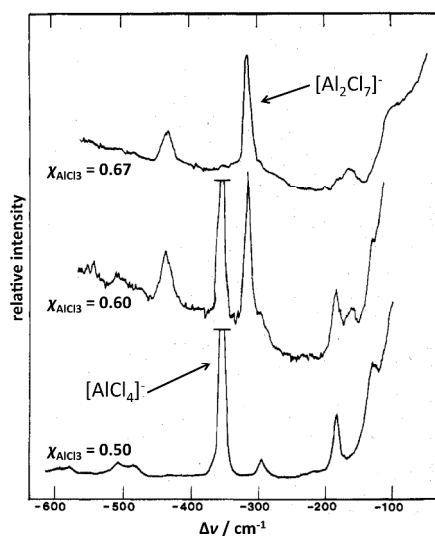

20 Figure 2. Raman spectra (room temperature) of three liquid samples of the $[C_4py]$-$AlCl_3$ system reproduced with permission from Ref. 32.

They suggested slightly distorted T_d symmetry for $[AlCl_4]^-$, and, erroneously, D_{3d} symmetry for $[Al_2Cl_7]^-$ (*i.e.* the structure of two corner-sharing tetrahedra with a linear Al-Cl-Al bridge). Almost
25 two decades later, by combining higher quality spectra from $[C_2mim]Cl$-$AlCl_3$ ionic liquids with *ab initio* calculations, Takahashi *et al.*[33] were able to correctly assign the correct C_2 symmetry (with Al-Cl-Al angle of 123.4°) to $[Al_2Cl_7]^-$ and also to identify the existence of $[Al_3Cl_{10}]^-$ in equilibrium with
30 $[Al_2Cl_7]^-$ at $\chi_{AlCl3} = 0.67$.

In 1974, Yoke and co-workers[26] unambiguously identified the presence of $[CuCl_2]^-$ anions in chlorocuprate(I) ionic liquids by comparison of their Raman and IR spectra to those of chlorocupate(I) molten salts. However, unambiguous assignment
35 of bands observed at $\chi_{CuCl} > 0.50$ to oligomeric anions such as $[CuCl_3]^{2-}$ and $[Cu_2Cl_3]^-$ could only be postulated in the absence of comparable supporting literature or *ab initio* calculations. It is notable that unambiguously assigned spectra of polynuclear metallate anions are rare in the literature, presumably because
40 these species are more prevalent in ionic liquids than in higher temperature molten salts, for which the bulk of published data

exists.

Raman spectroscopy provides much more information than simply stretching frequencies. Comparison of vertically, $I_{\parallel}$, and
45 horizontally, $I_{\perp}$, polarised spectra provide a great deal of information about symmetry. The intensity of bands from symmetrical vibrations (polarised) are dramatically reduced in the horizontal polarization mode, and this can be critical information allowing the existence, or non-existence, of possible anions to be
50 verified.

Wicelinski *et al.*,[34] in an early study of chlorogallate(III) ionic liquids, were able identify $[Ga_2Cl_7]^-$, as opposed to Ga_2Cl_6, at $\chi_{GaCl3} > 0.50$, because the band at 414 cm^{-1}, which could belong to either species, was not polarised, unlike the signal reported for
55 Ga_2Cl_6 in the literature. Similarly, at $\chi_{GaCl3} > 0.67$, it was possible to demonstrate that $[GaCl_4]^-$ was not present, however the actual speciation could not be definitively determined and species such as $[Ga_3Cl_{10}]^-$ or cationic complexes, such as $[C_2mim][GaCl_3]^+$, were hypothesised based on stoichiometry. Alves *et al.*,[35]
60 studying the $[C_4mim]Cl$-$NbCl_4$ and $[C_4mim]Cl$-$ZnCl_2$ ionic liquid systems, suggested that examining changes in the C-H stretching frequencies (from the cation) with increasing χ_{MClx} can help monitoring the development of oligonuclear anions. For the Nb(V)-based ionic liquids, the $[NbCl_6]^-$ anion was demonstrated
65 to hydrogen bond to the $[C_4mim]^+$ cation, which was reflected by the deformation of the anion O_h symmetry, and by the shift in the C-H stretching region to higher frequencies when compared to the pure $[C_4mim]Cl$ (where the cation was H-bonded to Cl$^-$). For the $[C_4mim]Cl$-$ZnCl_2$ system, the presence of $[ZnCl_4]^{2-}$ (T_d) for
70 $\chi_{ZnCl2} < 0.30$ and $[Zn_2Cl_6]^{2-}$ (D_{2h}) for $0.30 < \chi_{ZnCl2} < 0.70$ was proven based on the literature. For $\chi_{ZnCl2} > 0.70$, the existence of $[Zn_3Cl_8]^{2-}$ (S_4) and $[Zn_4Cl_{10}]^-$ (both cage, T_d, and linear, D_{2h}) was postulated, based both on the relevant literature data and on the shift in the C-H stretching towards higher frequencies, which was
75 justified by the decreasing amount of the hydrogen bonding with chlorides, as the anion size increased.

Comparing the experimental spectra with *ab initio* predicted Raman frequencies, Sitze *et al.*,[36] excluded the existence of measurable amounts of $[FeCl_3]^-$ in chloroferrates(II), Yang and
80 co-workers[37,38] showed that $[In_2Cl_7]^-$ was not formed in $\chi_{InCl3} > 0.50$ compositions of chloroindate(III) systems (additionally supported by DSC-derived phase diagram, and contrasting with the corresponding chloroaluminate(III) and chlorogallate(III) systems), while Schreiter *et al.*[39] demonstrated
85 that square-planar $[AuCl_4]^-$, but not dimeric $[Au_2Cl_7]^-$ anions were present in the $[C_2mim]Cl$-$AuCl_3$ system.

Raman spectroscopy can also be used for the construction of a provisional compositional diagram, for example, Gale *et al.*[32] estimated the molar ratios of $[AlCl_4]^-$ and $[Al_2Cl_7]^-$ at several
90 compositions in chloroaluminate(III) ionic liquids based on the intensity of the strongest peaks assigned to both species.

The main limiting constraint of Raman spectroscopy is the spectral resolution, which makes it unsuitable for the detection of species present in low concentrations (less than 5 or even 10 mol
95 % may pose difficulties). Additionally, the resolution may be dramatically reduced due to fluorescence, which generally increases with the χ_{MClx} value,[34,36] but can also derive from organic impurities. Hayashi *et al.*[40] reported that by using the 1064 nm line of a Nd:YAG laser as the excitation source, rather

than 785 nm frequency, problems with fluorescence arising from impurities in chloroferrate(III) ionic liquids could be overcome.

Raman studies of mixed-halide systems are rare, although they appear as a very convenient way of elucidation the speciation. For example, a solid $[N_{1\,1\,1\,16}]$Br-InCl$_3$ system was studied; the mixture of all $[InBr_xCl_{(4-x)}]^-$ anions in statistical distribution was detected in the $\chi_{InCl3} = 0.50$ sample (Figure 3), and the signals were assigned based on the literature data.[41]
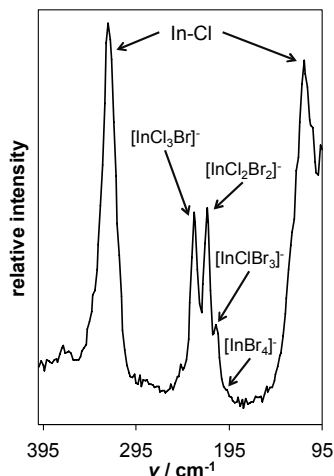

Figure 3. Raman spectrum of the $[N_{1\,1\,1\,16}]$Br-InCl$_3$ system ($\chi_{InCl3} = 0.50$) with bands assigned to indium-halide vibrations corresponding to haloindate(III) species of a general formula: $[InCl_xBr_{(4-x)}]^-$, $x = 0 - 4$ reproduced from Ref. 41 with permission from Wiley.

2.2.2. NMR spectroscopy

The most relevant NMR experiments for determining chlorometallate ionic liquid speciation are studies performed on the pure ionic liquids, using an external deuterium lock. For materials that are solids or too viscous at ambient temperature to obtain reasonably resolved spectra, elevated temperatures can be used to reduce viscosity, and the negligible vapour pressures of ionic liquids allow wide temperature ranges to be used. For air/moisture systems, samples can be loaded and sealed under an inert atmosphere in a glovebox.[42]

Chlorometallate ionic liquids may be studied using standard ^{1}H and ^{13}C NMR spectroscopy, with a focus on an organic cation and its interaction with anions, as well as by NMR spectroscopies of ^{35}Cl and of the anionic metal nuclei. However, it is worth noting that ^{35}Cl NMR spectra are generally of low quality[43] with very broad signals, and this is also compounded by difficulties in finding comparative data in the literature.

Metal NMR spectroscopy. NMR spectroscopy of metals with NMR-active nuclei has been successfully used to characterise a number of chlorometallate systems. Direct identification of anionic species based on chemical shift can be challenging, due to the dynamic equilibria between metallate species that may be present. Comparative literature data is limited and data on the chemical shifts of metal nuclei in chlorometallate anions may differ significantly from those observed in solution.[44] Consequently, a great caution must be adopted when assigning species to metal NMR chemical shifts. For example, in 1981, Grey and Maciel[45] studied the $[C_4py]$Cl-AlCl$_3$ system using ^{27}Al NMR spectroscopy and assigned a sharp signal at 97 ppm to $[AlCl_4]^-$. However, in 1993, Takahashi et al.[46] demonstrated that

this signal (in $[C_2mim]$Cl-AlCl$_3$) increased in intensity with the addition of water and derived from the hydration product. This latter assignment was also supported by IR spectroscopy.

Furthermore, ^{119}Sn NMR spectra from two chlorostannate(II) systems: $[C_4mim]$Cl-SnCl$_2$[47] and $[C_8mim]$Cl-SnCl$_2$,[48] show similar changes in chemical shift with χ_{SnCl2} (see Figure 4). Wasserscheid and co-workers[47] initially postulated the existence of three chlorostannate(II) species: $[SnCl_4]^-$, $[SnCl_3]^-$ and $[Sn_2Cl_5]^-$, based on the changes in ^{119}Sn NMR chemical shifts with χ_{SnCl2}. Currie et al.,[48] combining ^{119}Sn NMR spectroscopy with Raman spectroscopy, XPS and viscometric data, were able to demonstrate that only two metallate species: $[SnCl_3]^-$ and $[Sn_2Cl_5]^-$, were present in the ionic liquid.
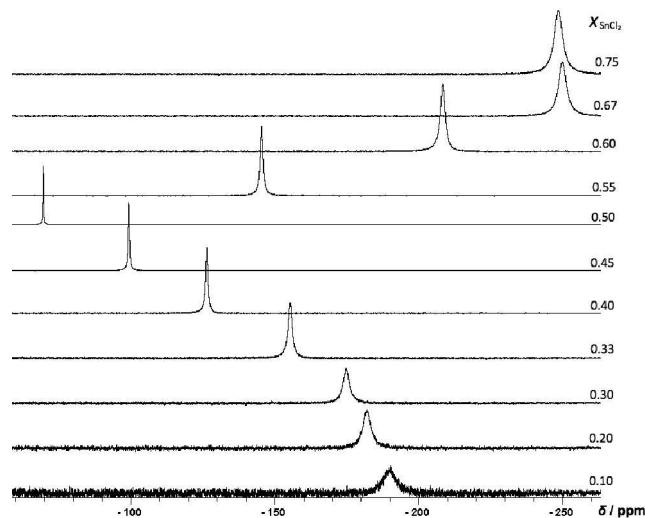

Figure 4. ^{119}Sn NMR spectra (186.48 MHz, 80 °C, neat liquid) of the $[C_8mim]$Cl-SnCl$_2$ system reproduced with permission from Ref. 48.

Although unambiguous assignment based on chemical shift can be problematic, the NMR signals can be very sensitive to even subtle changes in speciation around the metal nuclei, which are reflected in peak geometry (its width and shape). These signals (typically described by the full width at half-height, $\Delta\upsilon_{1/2}$) depends on several related factors:

- viscosity of the sample,
- spin of the nucleus,
- symmetry of the metal-containing species,
- presence of species in a dynamic equilibrium with each other,
- pre-acquisition delay time, DE,
- temperature.

High sample viscosities lead to long molecular reorientational correlation times, reducing the quadrupolar relaxation rate, which in turn produces broader NMR signals.[45] Apart from the obvious effect from increasing temperature, the viscosities of chlorometallate ionic liquids vary with χ_{MCln}. Viscosity is typically higher in the basic regime, where free chloride is present, and decreases with increasing the concentration of chlorometallate anions, which are larger and have a more dispersed charge. In the case of the $[C_4py]$Cl-AlCl$_3$ system, the ^{27}Al NMR $\Delta\upsilon_{1/2}$ values decrease from 40 to 10 Hz between $\chi_{AlCl3} = 0.44$ and 0.50.[45] Similarly, for the chlorostannate(II) system, $[C_8mim]$Cl-SnCl$_2$ shown in Figure 4, the signal width

correlates well with viscosity for all compositions where $\chi_{SnCl2} \leq 0.50$.[48]

Nuclei with $I > \frac{1}{2}$ induce quadrupolar line broadening in the NMR spectra. Table 1 compares the $\Delta\upsilon_{1/2}$ values for
5 tetrachlorometallate(III) anions ($\chi_{MCl3} = 0.50$) of group 13 metals, showing a dramatic signal broadening with the increase of the nuclear spin, even allowing for the viscosity changes between systems with different cations.

Table 1. Signal width for $\chi_{MCl3} = 0.50$ compositions of Group 13-based
10 chlorometallate systems, depending on the spin of the metal, at ambient temperatures.

system	nuclei	I	$\Delta\upsilon_{1/2}$ / Hz	Ref
[C$_4$py]Cl-AlCl$_3$	^{27}Al	$\frac{1}{2}$	10	45
[C$_2$mim]Cl-AlCl$_3$	^{27}Al	$\frac{1}{2}$	23	46
[C$_2$mim]Cl-GaCl$_3$	^{71}Ga	3/2	190	49
[C$_8$mim]Cl-GaCl$_3$	^{71}Ga	3/2	995	49
[C$_8$mim]Cl-InCl$_3$	^{119}In	9/2	6973	50

Data shown in Table 1 relate to highly symmetrical tetrahedral (T_d) anions, which give relatively narrow bands for their
15 respective nuclei. The appearance, in the acidic regimes, of [Al$_2$Cl$_7$]$^-$ (non-linear, corner-sharing tetrahedra, C_2)[45] or [Sn$_2$Cl$_5$]$^-$,[48] result in further signal broadening as the lower symmetry metal centres lead to increasing quadrupole relaxation times.
20 When the ionic liquid composition contains only a single discrete metallate anion (for example, at the 'congruent' point, or at low metal chloride concentrations), a single, symmetrical (Lorentzian) NMR signal is usually obtained. A single signal can also be observed where two or more chlorometallate anions are
25 present with rapid exchange (compared to the NMR time scale), but the peak shape deviates from Lorentzian, as observed for chloroaluminate(III)[45,46] and chlorostannate(II)[48] systems. In the case of the corresponding chlorogallates(III)[51] and chloroindates(III),[50,51] high quadrupole moments combined with
30 the formation of lower symmetry species and high exchange rates led to the complete collapse and disappearance of the signal at compositions containing multiple chlorometallate species. Consequently, the primary benefit of NMR spectroscopy as a speciation tool is the extreme sensitivity of peak shape to changes
35 in speciation, which allows detection of even small amounts of lower-symmetry polynuclear species.[52]

More advanced metal NMR studies have been carried out only for chloroaluminate(III) systems. Manipulating the temperature and the pre-acquisition delay time, DE (the time interval between
40 the observe pulse and the onset of data acquisition), Grey and Maciel[45] claimed to have had separated the contributions from [AlCl$_4$]$^-$ (narrow peak) and [Al$_2$Cl$_7$]$^-$ (broad peak). They found surprisingly high mol fraction of the binuclear anion in $\chi_{AlCl3} = 0.58$ composition (0.0013 to 0.9987, respectively).
45 However, Takahashi *et al.*[46] ascribed this narrow peak to hydration products, and considered that it would be impossible to separate peak contributions from [AlCl$_4$]$^-$ and [Al$_2$Cl$_7$]$^-$ on the NMR timescale. Instead, they analysed the line shapes and the $\Delta\upsilon_{1/2}$ values measured as a function of DE for the dominant ^{27}Al
50 NMR signal. Theoretical linewidths for non-exchanging [AlCl$_4$]$^-$ and [Al$_2$Cl$_7$]$^-$ were taken from $\chi_{AlCl3} = 0.50$ and 0.67, which were the only two compositions giving Lorentzian peaks, with $\Delta\upsilon_{1/2}$ independent of DE changes. Lifetimes and concentrations of

[AlCl$_4$]$^-$ and [Al$_2$Cl$_7$]$^-$ were thus calculated as functions of
55 temperature. Exchange between [AlCl$_4$]$^-$ and [Al$_2$Cl$_7$]$^-$ was first-order for both anions, exchange barrier estimated to be low, *ca.* 2 kcal mol^{-1} (8.4 kJ mol^{-1}), lifetime of an aluminium centre in [AlCl$_4$]$^-$ was estimated from *ca.* 30 μs at 25 °C to *ca.* 70 μs at 100 °C (*NB*, according to the well-known compositional diagram
60 presented by Øye *et al.*[53] for the same system, [AlCl$_4$]$^-$ is indeed the only anion for $\chi_{AlCl3} = 0.50$, but the $\chi_{AlCl3} = 0.67$ composition contains *ca.* 80% of [Al$_2$Cl$_7$]$^-$, with the remainder disproportionated to [AlCl$_4$]$^-$ and [Al$_3$Cl$_{10}$]$^-$).

Grey and Maciel[45] also studied mixed-halide systems, where
65 the $\chi_{AlCl3} = 0.58$ composition of [C$_4$py]Cl-AlCl$_3$ was saturated with [N$_{1\,1\,1\,1}$]I. The [Al$_2$Cl$_7$]$^-$ anion reacted with iodide and a range of mixed halide ions: [AlCl$_3$I]$^-$, [AlCl$_2$I$_2$]$^-$ and [AlClI$_3$]$^-$, were detected in the system next to the dominant [AlCl$_4$]$^-$. Discrete peaks for each species could be found because the
70 affinity of aluminium to chloride is much higher than that to iodide, consequently the exchange rate between the halides was slow compared to the NMR time scale. Interestingly, no exchange at all was observed for $\chi_{AlCl3} = 0.50$.
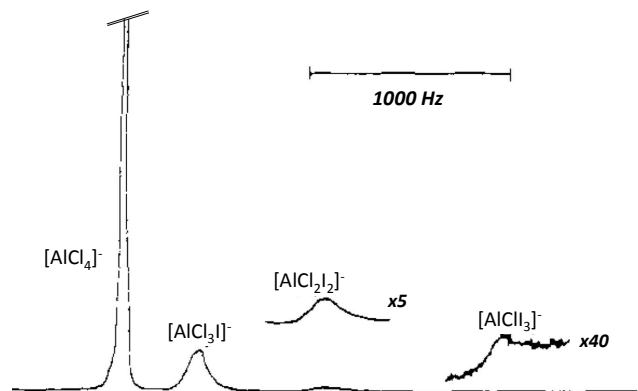

75 Figure 5. ^{27}Al NMR spectrum of [C$_4$py]Cl-AlCl$_3$, $\chi_{AlCl3} = 0.583$, saturated with [N$_{1\,1\,1\,1}$]I; chemical shifts of the signals assigned to haloaluminate(III) anions are as follows: $\delta = 0.0$ ppm (line width of 16 Hz), -16.1 ppm (line width of 110 Hz), -44 ppm (line width of 190 ± 10 Hz), and -81 ppm (line width of 220 ±10 Hz) reproduced with permission
80 from Ref. 45.

In conclusion, metal NMR spectroscopy is complementary to Raman spectroscopy in terms of anionic speciation studies. The latter technique is ideal for the assignments of dominant anionic species, which can be done unambiguously if coupled with
85 simulations and/or the reliable literature data, but is not sensitive to small speciation changes. Examining $\Delta\upsilon_{1/2}$ changes of NMR signals as a function of χ_{MClx} allows for detection of the appearance of new species of lower symmetry, even for very small concentrations.

90 **2.2.3. Electron paramagnetic resonance (EPR)**
EPR is a low-temperature (cryogenic to ambient) technique complementary to NMR spectroscopy, suitable for the studies of magnetic nuclei, such as copper(II) or iron(III). It appears to be particularly useful for the copper(II) speciation studies, as
95 paramagnetic chlorocuprate(II) anions cannot be studied using NMR spectroscopy, and are very difficult to investigate using Raman spectroscopy, as they absorb the laser energy and effectively burn during the measurement. Although the technique was found to be very suitable for the studies of speciation of

chlorometallate anions in liquid state, *viz.* excellent study of the chorobenzene solutions of chlorocuprate(II) salts,[54] it has not been widely used for neat ionic liquids.

Most notably, EPR spectroscopy was used for the *in situ* investigations of reactions where chlorocuprate(II) ionic liquids were involved. EPR studies of $[C_2mim]Cl$-$CuCl_2$ system used for the cellulose depolymerisation showed increased ion mobility when the system was doped with $PdCl_2$, and demonstrated reduction of Cu(II) to Cu(I) under the reaction conditions, in the presence of palladium, but not when neat $[C_2mim]Cl$-$CuCl_2$ was used, thus giving insight into the reaction mechanism.[55] In another study, a mixture of $[C_4py]_2[CuCl_4]$ and ascorbic acid was used as a precursor for the formation of copper(I) chloride nanostructures.[56] EPR studies combined with DFT calculations revealed that the reduction proceeds through a complex where ascorbic acid is monocoordinated to the copper centre, which is combined with the removal of a chloride and significant distortion of the tetrahedral geometry of starting $[CuCl_4]^{2-}$ anion.

2.2.4. X-ray photoelectron spectroscopy (XPS)

Photoelectron spectroscopy includes a group of surface analysis techniques, where the sample is irradiated with photons *in vacuo*, and the kinetic energy of the emitted electrons is measured.[57] The negligible vapour pressure of ionic liquids has allowed them to be the first liquids ever studied using XPS, opening up fascinating areas of study on liquid-gas surfaces and thin liquid films on solids.

In terms of speciation, XPS may provide information regarding elementary composition, oxidation states as well as coordination environments in the near-surface region of a sample, which makes it a very powerful technique. The drawbacks include lower availability of the equipment compared to Raman or NMR spectrometers and the relative complexity of data acquisition and processing (correction factors, charging). A detailed discussion on the scope and limitations of this technique for ionic liquids studies has been recently summarised in an excellent review.[57] To date, only a limited number of chlorometallate ionic liquids have been examined, most notably by Licence and co-workers.

In studies of $[C_8mim]Cl$-$InCl_3$ systems at two compositions, $\chi_{InCl3} = 0.50$ (homogenous ionic liquid) and $\chi_{InCl3} = 0.67$ (suspension of white solid in ionic liquid),[50] the surface sensitivity of XPS allowed the top (liquid) phase of inhomogeneous $\chi_{InCl3} = 0.67$ suspensions to be examined without separating the solid (which settled on the bottom). Comparison of the spectra from the homogeneous ionic liquid ($\chi_{InCl3} = 0.50$) and the liquid surface layers of the $\chi_{InCl3} = 0.67$ composition showed that the liquid phases were identical (within experimental error) and corresponded to $[C_8mim][InCl_4]$, indirectly demonstrating that multinuclear anionic chloroindate species were not formed from reaction with an excess of indium(III) chloride.

XPS combined with Auger spectroscopy were used to study $[C_8mim]Cl$-$SnCl_2$ systems ($\chi_{SnCl2} = 0.00$, 0.33, 0.50 and 0.67).[48] High-resolution Sn $3d_{5/2}$ XPS spectra yielded binding energies that were identical within the experimental error for all the systems, thus no speciation information could be derived. However, from the high-resolution Cl 2p XPS, $[SnCl_3]^-$ and Cl^- environments at $\chi_{SnCl2} = 0.33$ could be distinguished, which also simultaneously eliminated the possible existence of $[SnCl_4]^{2-}$ anions. Moreover, Auger parameters for tin corresponding to $[SnCl_3]^-$, were obtained at $\chi_{SnCl2} = 0.33$ and 0.50, whereas for the $\chi_{SnCl2} = 0.67$ composition, a slightly higher value, indicative of a more energy-deficient tin species, *i.e.* $[Sn_2Cl_5]^-$, was obtained.

An extension of these studies to other chlorometallate systems[58] confirmed that $[MCl_4]^{2-}$ were dominant for ionic liquids based on $FeCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$, at $\chi_{MCl2} = 0.33$. A tetrahedral $[FeCl_4]^-$ anion was detected in the $[C_8mim]Cl$-$FeCl_3$ ($\chi_{FeCl3} = 0.50$) system. Furthermore, several compositions of the $[C_8mim]Cl$-$ZnCl_2$ system were studied ($\chi_{ZnCl2} = 0.25$, 0.33, 0.50 and 0.60). The Cl 2p XP spectra suggested a single chlorozincate anion, $[ZnCl_4]^{2-}$, at $\chi_{ZnCl2} = 0.25$ and 0.33. Different environments found for $\chi_{ZnCl2} = 0.50$ and 0.60 correspond to terminal and bridging chlorides in $[Zn_xCl_{(2x+2)}]^{2-}$. Free chloride was found only for the $\chi_{ZnCl2} = 0.25$ composition.

Studies on $[C_6mim]Cl$-$AuCl_3$ system revealed the presence of tetrachloroaureate(III) anion, as confirmed by high resolution Au 4f XPS spectra,[59] but this work has been criticised[57] for insufficient experimental details and the lack of high resolution XPS spectra for other elements. Both points emphasise the need for experience and in-depth understanding when employing this technique.

The typically low to vanishing vapour pressure of ionic liquids at ambient temperatures allows them to be investigated using high vacuum techniques such as XPS. This, in turn, enables these techniques to be used in innovative new ways to study processes in ionic liquids. For example, using a custom-built cell, Licence and co-workers studied the *in situ* electrochemical reduction of Fe(III) to Fe(II) in $[C_4mim][Fe^{III}Cl_4]$.[60] High resolution Fe 2p XPS scans, recorded at the electrode surface region, revealed the presence of the pure $[Fe^{III}Cl_4]^-$ at the beginning of the experiment, and increasing concentration of $[Fe^{II}Cl_4]^{2-}$ (peak at a lower binding energy, see Figure 6) as the potentiostatic reduction took place.
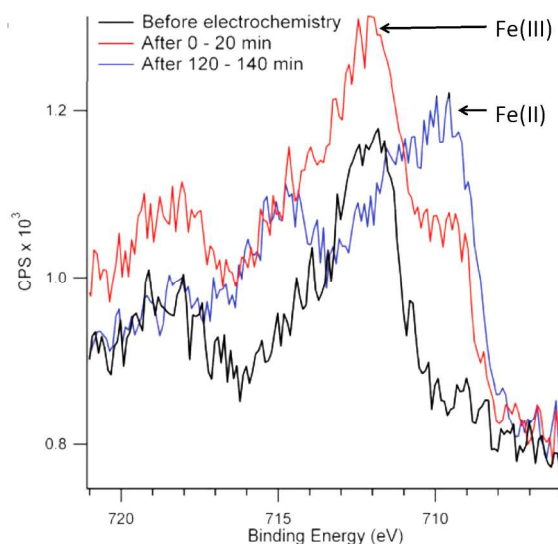

Figure 6. High resolution scans of the Fe $2p_{3/2}$ region taken at 0 (black), 20 (red) and 120 (blue) min of the coulometric experiment showing the decrease in peaks corresponding to Fe(III) and subsequent increase in peaks corresponding to Fe(II) reproduced from Ref. [60].

In general, the technique is limited by instrument availability, but rapid progress in the XPS investigation of metals in ionic liquids is expected in the near future.[57] This will likely include the development of customised setups, allowing *in situ* studies of

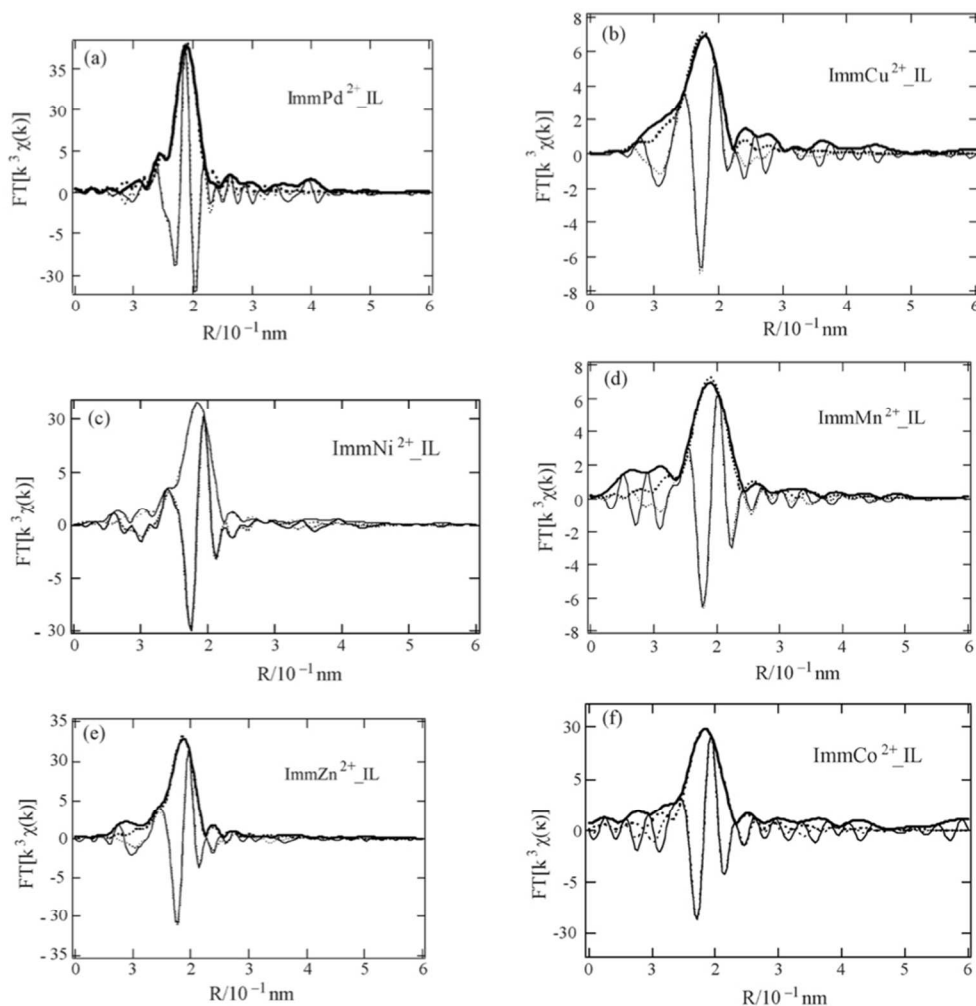reactive processes, handling air and moisture sensitive materials　　*etc*.

Figure 7. k^3-Weighted Fourier transform: amplitude (thick curve) and imaginary part (thin curve), of K-edge EXAFS for ImmM_IL (χ_{MCl2} = 0.33, M = Pd, Cu, Ni, Mn, Zn, or Co). Experimental data: solid lines; fitted data: dotted lines. Reproduced from Ref. [67] with permission from Elsevier.

2.2.5. X-ray absorption spectroscopy (XAS)

X-ray absorption encompasses a range of techniques, including X-ray absorption fine structure (XAFS), extended X-ray absorption fine structure (EXAFS), X-ray absorption near-edge structure (XANES) *etc*., which provide local geometric and/or electronic structural information about materials, in this case in the liquid phase. XAS techniques are atom-specific and extremely useful *in situ* probes applicable for both solid and liquid states, and a range of sample environments, temperatures etc. The major drawbacks are the need for a high energy X-ray source (synchrotron) and complex data processing and interpretation.

EXAFS is most suitable for the study of metal coordination environments, and the application of this technique to ionic liquids and molten salts in general, has been reviewed by Hardacre.[61] Measurement is based upon the irradiation of a sample with hard, monochromatic X-rays, tuned to an absorption edge of the chosen element. The X-ray absorption results from the excitation of a core electron in an atom; the ejected electron (it is useful to perceive it here as wave rather than a particle) is back-scattered by the surrounding atoms, giving an oscillatory structure at the energies past the absorption edge. From this structure, the local arrangement of atoms around the central atom can be elucidated (the type, number, and distance of the surrounding atoms up to 6 Å).[61]

Variable temperature EXAFS has been used to study both organic molten salts and compounds which are 'real' ionic liquids according to the 100 °C melting point threshold. In some cases, *e.g.* for $[N_{4\,4\,4\,4}]_2[MnBr_4]$,[62] $[C_2mim]_2[NiCl_4]$ and $[C_{14}mim]_2[NiCl_4]$,[63] EXAFS indicated that anions in the melt are isostructural with those found in crystal structures. More interestingly, the χ_{MnBr2} = 0.50 composition of the $[N_{4\,4\,4\,4}]Br$-$MnBr_2$ system was found to contain trigonal $[MnBr_3]^-$, as opposed to the solid-state structure, where hexacoordinate manganese(II) was found.[62] Studies of two $ZnCl_2$-based deep eutectics showed the presence of tetrahedral $[ZnCl_4]^{2-}$ in both cases, in agreement with the recent speciation study on chlorozincate(II) ionic liquids,[27] but contrasting with ESI-MS studies which erroneously indicate the existence of singly charged anions such as $[ZnCl_3]^-$.[64] Chlorogallate(III)[51] and chloroindate(III)[50,51] ionic liquid systems were studied as a function of both composition and temperature. A Ga···Ga distance could be determined in the acidic compositions of the $[C_8mim]Cl$-$GaCl_3$ system, supporting the existence of oligomeric

anions in this regime.[51] No In···In contact was detected, which again was in agreement with other techniques, such as XPS, suggesting the lack of formation of dimers in chloroindate(III) ionic liquids.[50]

[C$_2$mim]Cl-CuCl$_2$[65] and [ch]Cl-CuCl·2H$_2$O[66] systems, mixed with various amounts of water, were studied using EXAFS combined with UV-VIS spectroscopy. Combination of the two techniques allowed to elucidate the existence of discreet [CuCl$_x$(H$_2$O)$_{4-x}$]$^{y-}$ anions, where x = 1, 2 or 4, as well as tetrahedral [CuCl$_4$]$^{2-}$. For the [ch]Cl-CuCl·2H$_2$O system, crystals were grown from the studied compositions (from either ionic liquids or molecular solvents); these revealed a range of structural motifs, from discrete anions, through strands, to zwitterionic structures with choline acting as a ligand to copper(II), and showed contrast between the solid-state and the liquid-state speciation.

Sasaki et al.[67] studied the coordination of chlorometallate anions in supported ionic liquids, Imm_IL (χ_{MCl2} = 0.33, where M = Pd, Cu, Ni, Mn, Zn, or Co); the structure and synthetic procedure for such materials is shown in Figure 8.
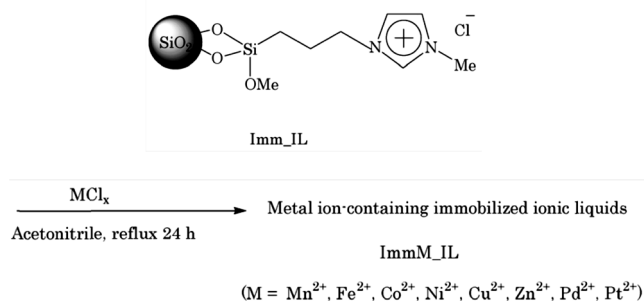

Figure 8. Preparation of metal ion-containing immobilized ionic liquids. (Reproduced from Ref. 67 with permission from Elsevier).

EXAFS of the metal edges revealed the existence of a single coordination sphere around the metal (i.e. no dimeric species were found) – see Figure 7. Coordination number of 4, within the experimental error, was obtained except for supported chlorozincate(II) and chloronickelate(II) systems were the apparent coordination numbers dropped to 3.6 ± 0.2. However, this difference was not discussed, or related to catalytic processes investigated in the same publication.

As discussed by Hardacre,[61] EXAFS can be an indispensible tool for examining mixed-metal chlorometallate systems, with the caveat that results based solely on EXAFS without reference to other complementary techniques can lead to spurious or chemically inconsistent assignments.

Dent et al.[68] studied solutions of MCl$_2$ salts (M = Ni, Co or Mn) in chloroaluminate(III) ionic liquids; in chloride-rich compositions (χ_{AlCl3} < 0.50), discrete mononuclear [MCl$_4$]$^{2-}$ and [AlCl$_4$]$^-$ anions were observed. Whereas, in acidic (χ_{AlCl3} > 0.50) compositions, tetrachloroaluminate(III) species acted as bidentate ligands to the added MCl$_2$ salts, forming [M(AlCl$_4$)$_3$]$^-$ species,

with six chlorine atoms in the first coordination sphere of M(II). Nickel(II) salts dissolved in acidic chlorometallate ionic liquids are of particular interest as catalysts for oligomerisation of olefins, e.g. in the Difasol process,[15] and were further investigated. Hardacre et al.[61] found that [NiCl$_4$]$^{2-}$ formed gradually in weakly acidic (χ_{AlCl3} = 0.55) chloroaluminate(III) ionic liquids, and that active [Ni(AlCl$_4$)$_3$]$^-$ was only detectable after the addition of a small amount of EtAlCl$_2$. Most recently, Roeper et al.[69] re-examined NiCl$_2$ dissolved in three compositions, χ_{AlCl3} = 0.43, 0.54 and 0.60, of the [C$_2$mim]Cl-AlCl$_3$ system. Using a modern beam-line, they obtained better quality data than Dent et al.[68] In their subsequent analysis, four chlorines were detected in the first coordination sphere at χ_{AlCl3} = 0.43, consistent with [NiCl$_4$]$^{2-}$ as the only specie in agreement with previous work. For χ_{AlCl3} = 0.54, the analysis indicated six chlorine atoms and this was interpreted as [NiCl$_6$]$^{4-}$, because the pseudo-radial distribution function featured only one symmetrical peak. No second shell was found around aluminium. Finally, for χ_{AlCl3} = 0.60, six chlorines were found in the first shell and eight aluminium atoms in the second one. Here, it was proposed that [Al$_2$Cl$_7$]$^-$ anions are stronger Lewis acids than [AlCl$_4$]$^-$ and share chlorine atoms with nickel(II), as shown in Figure 9.

In analogy with XPS, innovative applications of XAS techniques are being explored; in particular in situ investigations of various processes.

XAS (EXAFS and XANES) results combined with DFT calculations were used to study the behaviour of glucose dissolved in two chlorometallate(II) systems: [C$_2$mim]Cl-MCl$_2$, χ_{MCl2} = 0.33 (M = Cr or Cu). Neat ionic liquids were found, as expected, to contain the respective [MCl$_4$]$^{2-}$ anions. Glucose was found to substitute one of the chloride ligands, acting as a monodentate O-ligand. In contrast, the copper-based system contained only chlorocuprate anions – but Cu(II) was partially reduced to Cu(I). This indicated that upon dissolution of glucose in the chlorocuprate(II) system, a fast redox process occurs, but the oxidised glucose product does not coordinate to the copper(I) species formed from the reaction.[70]

In a recent study, [C$_4$mim][AuCl$_4$] (tetrahydrate) was exposed to synchrotron X-ray radiation, which induced the formation of Au(0).[71] X-rays were used in a dual role of reducing agent and a probe for EXAFS measurements. As shown in Figure 10, Au-Cl coordination number decreased gradually with time of the X-ray exposure. After several hours, the signal corresponding to Au-Au contact appeared, and then increased with time. Analysis of the results led the authors to propose a new and unique mechanism of the nanoparticles formation, depicted in Figure 11. The coordination of gold in chloroaureate cation is gradually reduced from 4 to 2, whence Au–Au bonds begin to form, which leads to the formation of clusters and then nanoparticles. Ionic liquid stabilises reduced cations of sub-valent gold; moreover, chloride ions act as capping agents to the formed nanoparticles.
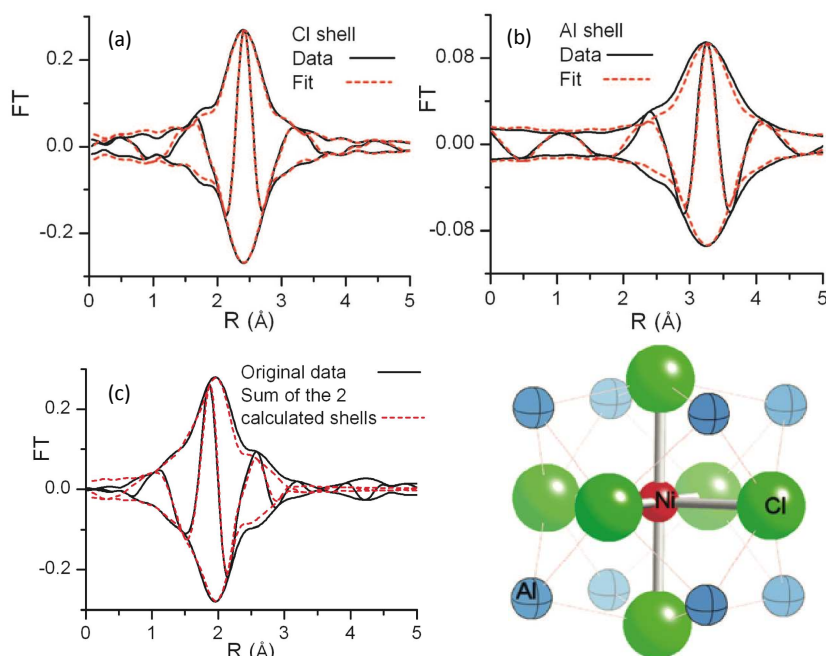
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Figure 9. Phase-corrected Fourier transforms of: (a) Cl shell fit, (b) Al shell fit and (c) the sum of the two calculated shells, Cl and Al, compared to the original data, for $NiCl_2$ dissolved in $[C_2mim]Cl$-$AlCl_3$, $\chi_{AlCl3} = 0.60$. Proposed is a model of the Ni(II) ion structure in $[C_2mim]Cl$-$AlCl_3$, $\chi_{AlCl3} = 0.60$, where the central atom surrounded by the octahedron of Cl with an Al above each face of the octahedron (from Ref. 68, reproduced by permission of The Electrochemical Society).
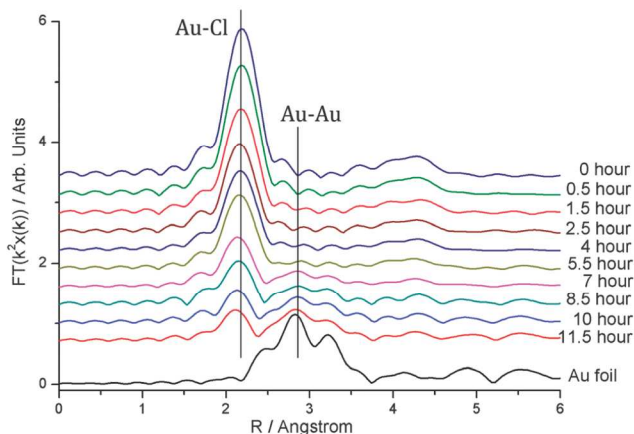

Figure 10. Evolution of the k^2-weighted *pseudo*-radial distribution functions in the $[C_4mim][AuCl_4]\cdot 4H_2O$ system as a function of time of exposure to the X-ray beam. The gradually decreasing peak *ca*. 2.2 Å, corresponds to the change in Au–Cl coordination number; the gradually increasing peak *ca*. 2.8 Å reflects increasing Au–Au contact (Reproduced from Ref. 71 with permission from the PCCP Owner Societies).
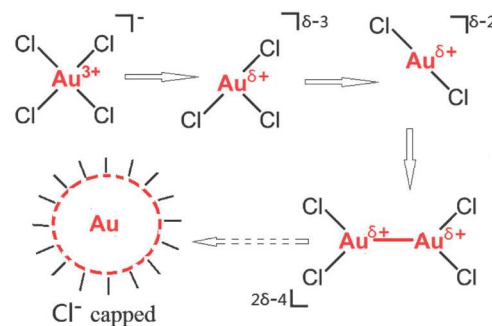

Figure 11. The proposed mechanism of gold nanoparticles formation under synchrotron X-ray irradiation of $[C_4mim][AuCl_4]\cdot 4H_2O$; $\delta = 0\text{-}3$ (Reproduced from Ref. 71 with permission from the PCCP Owner Societies).

2.2.6. UV-VIS spectroscopy

Chlorometallate complexes which absorb ultraviolet or visible light can be studied using UV-VIS spectroscopy. The measurements are simple and fast, the main limitation may be the very high extinction coefficient of neat systems, enforcing the use of very short path length cuvettes (even 0.1 mm), or dilution,[54] which can however alter speciation.

Schaltin *et al.*[72] have used UV-VIS spectroscopy to study Co(II) speciation in $[C_4mim]Cl$-$CoCl_2$ systems. At $\chi_{CoCl2} \leq 0.33$, a simple tetrahedral $[CoCl_4]^{2-}$ anion was identified, and at $\chi_{CoCl2} > 0.33$, several tetrahedrally coordinated cobalt environments

were observed; formation of the complex $[CoCl_2(CoCl_4)_2]^{4-}$ and $[Co(CoCl_4)_3]^{4-}$ anions was postulated at $\chi_{CoCl2} > 0.33$, by analogy with $[Co(AlCl_4)_3]^-$ complexes reported previously based on EXAFS studies.[68] As discussed in the EXAFS section, $[C_2mim]Cl\text{-}CuCl_2$[65] and $[ch]Cl\text{-}CuCl_2\cdot2H_2O$[66] systems, and their mixtures with water, were studied by UV-VIS combined with EXAFS. Both techniques provided consistent, complementary interpretations, which revealed a range of copper(II) species with chloride and aqua ligands ranging in colour from orange-brown $[CuCl_4]^{2-}$ anions to blue hexaquacopper(II) cations (Figure 12), hence particularly suited for UV-VIS spectroscopy.

Figure 12. Color changes of Cu^{2+} solutions (0.1 mol l^{-1}) in [ch]Cl-H_2O mixtures, with water content changing from 100 wt % (blue sample, left) to 27 wt % (yellow sample, right), reproduced with permission from Ref. 66.

Huang *et al.*[73] used UV-VIS spectroscopy to study the effects of iron salts on the γ radiation stability of $[C_4mim]Cl$. $[FeCl_4]^-$ was identified on addition of small amounts of $FeCl_3$ (thus effectively forming $[C_4mim]Cl\text{-}FeCl_3$, $\chi_{FeClx} = 0.05$) which was reduced to $[FeCl_4]^{2-}$ upon irradiation. Wellens *et al.*[74] have used UV-VIS spectroscopy to monitor the selective extraction of cobalt (in the form of chlorocobaltate(II) complex) from aqueous solutions containing Co(II) and Ni(II) into a hydrophobic ionic liquid, $[P_{6\,6\,6\,14}]Cl$ (Figure 13).
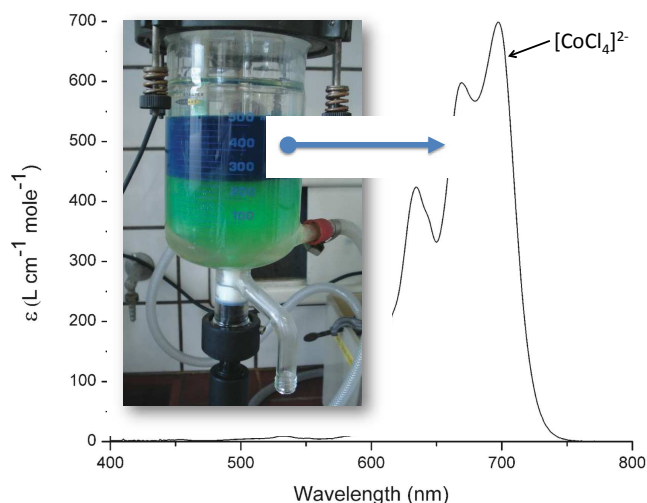

Figure 13. Absorption spectrum of the ionic liquid phase after extraction of the aqueous solution of Ni(II) and Co(II) salts with $[P_{6\,6\,6\,14}]Cl$, characteristic of $[CoCl_4]^{2-}$ anions. Insert: batch scale reactor after extraction test. Upper phase (ionic liquid) contains blue $[CoCl_4]^{2-}$ anions, while the green hydrated nickel(II) ions remain in the lower (aqueous) phase (reproduced from Ref. 74).

2.2.7. Bulk property measurements

Bulk properties of ionic liquids depend entirely on the ions present; consequently, for chlorometallate systems, changes in the bulk properties as a function of χ_{MCln} can be directly related to changes in anion speciation. Melting points, obtained from differential scanning calorimetry (DSC), or less commonly from polarised optical microscopy (POM) or from simple observation using melting point apparatus, allow the construction of a *phase diagram*, which is a convenient base for speciation studies of a system, even though it provides no information about the anions present.

The archetypical phase diagram, obtained by Fannin *et al.*[75] for the $[C_2mim]Cl\text{-}AlCl_3$ system, is shown in Figure 14. The peritectic point at $\chi_{AlCl3} = 0.50$ indicates congruent melting of a pure compound, $[C_2mim][AlCl_4]$, whilst the glass transition regions around $\chi_{AlCl3} = 0.33$ and 0.67 correspond to eutectics formed by this compound with $[C_2mim]Cl$ and $[C_2mim][Al_2Cl_7]$, respectively. A nearly identical pattern was found for the analogous bromide-based system, $[C_2mim]Br\text{-}AlBr_3$,[76] and the earlier-studied mixed-halide system based on 1-ethylpyridinium cation, $[C_2py]Br\text{-}AlCl_3$, closely followed the same trend.[77] This strongly suggest: (a) analogies in anionic speciation of all haloaluminates(III) as a function of composition, and (b) a relative independence of the anionic speciation from the cation. As discussed previously, in the last two decades aluminium(III)-based systems have often been treated as a 'Sèvres standard' of chlorometallates, therefore these observations, made on two cation groups and two halides with one and only one metal, were expected to stretch onto all chlorometallate ionic liquids.
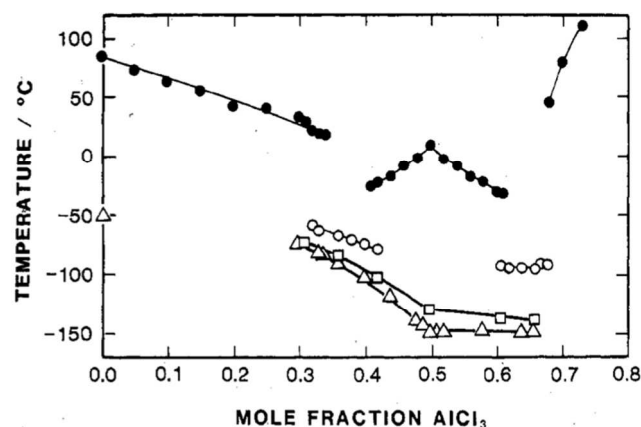

Figure 14. Phase diagram for the $[C_2mim]Cl\text{-}AlCl_3$ system: melting points, ●, experimental glass transitions, O, freezing points calculated from absolute viscosities, □, and freezing points calculated from conductivities, △ (reproduced with permission from Ref. 75).

Even within Group 13-based systems, anionic speciation and consequently phase diagrams differ significantly. For example, chloroindate(III) ionic liquids have three chloroindate(III) anions on the basic side: $[InCl_6]^{3-}$, $[InCl_5]^{2-}$ and $[InCl_6]^-$, but do not form dimeric anions at $\chi_{InCl3} > 0.50$. This reflects in phase diagrams of chloroindate(III) systems; for example, the phase diagram of $[C_4mim]Cl\text{-}InCl_3$ (Figure 15)[38,50] features a congruent melting point at $\chi_{InCl3} = 0.25$ (melting of $[C_4mim]_3[InCl_6]$), two crystalline phases for $\chi_{InCl3} = 0.30$ to 0.40, corresponding to the presence of $[C_4mim]_3[InCl_6]$ and incongruently melting $[C_4mim]_2[InCl_5]$, and a low-melting eutectic for $\chi_{InCl3} = 0.40$ to 0.50, related to the appearance of the $[InCl_4]^-$ anion. For

$\chi_{InCl3} > 0.50$, a constant melting point indicates the existence of a single compound, [C$_4$mim][InCl$_4$], as polynuclear anions are not formed.[38,50] Noteworthy are differences between the melting points of chloroindate anions bearing different charges: 73 °C for [InCl$_6$]$^{3-}$, *ca.* 45 °C for [InCl$_5$]$^{2-}$ and *ca.* -18 °C for [InCl$_4$]$^-$. In this case, the analysis of the DSC-derived phase diagram was aided by POM observations, which revealed the presence of crystalline structures suspended in an ionic liquid even at $\chi_{InCl3} = 0.47$, which was not detected by DSC.
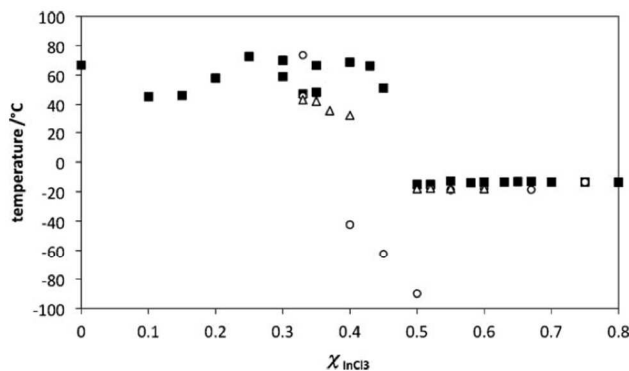

Figure 15. Phase diagram of the [C$_4$mim]Cl–InCl$_3$ system; data obtained from DSC experiments at three different heating/cooling regimes reproduced from Ref. 50.

On the other side of the spectrum, both complex anion speciation and materials incorporating cations with long hydrocarbon chains (which can generate ionic liquid crystallinity) may contribute to phase diagrams of increasing complexity. Figure 16 contains a phase diagram for the [N$_{1\,1\,1\,16}$]Cl-ZnCl$_2$ system.[78] Based on the author's own assignment and the literature, it may be assumed that peritectic points at $\chi_{ZnCl2} = 0.33$, 0.50, 0.67 and 0.75 correspond to compounds with [ZnCl$_4$]$^{2-}$, [Zn$_2$Cl$_6$]$^{2-}$, [Zn$_3$Cl$_8$]$^{2-}$ and [Zn$_4$Cl$_{10}$]$^{2-}$ anions, respectively. Interestingly, there is no obvious relation between the morphology of the phase of the liquid crystal and the anionic speciation.

Not only melting points, but also other physical properties of chlorometallate ionic liquids are directly related to speciation, and therefore are good indicators of changes in speciation. The most detailed thermodynamic model of distribution of chloroaluminate(III) species in the liquid phase (Figure 17) was provided by Øye *et al.*,[79] who combined vapour pressure measurements with EMF data published by Hussey *et al.*[80] It is noteworthy that, for any given χ_{AlCl3} value, only the concentration of [AlCl$_4$]$^-$ reaches 100% (for $\chi_{AlCl3} = 0.50$).

Both viscosity and specific conductivity measured for various compositions of the [C$_2$mim]Cl-CuCl system indicated a 'critical composition' at *ca.* $\chi_{CuCl} = 0.50$.[81] This was related to the relatively soft [Cu^{I}Cl$_3$]$^-$ anion replacing small and hard Cl$^-$, which resulted in decreasing viscosity and increasing ion mobility (*ergo* higher conductivity).
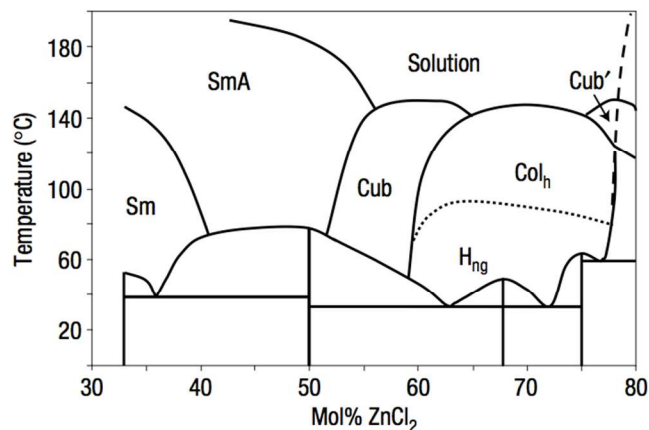

Figure 16. Phase diagram for the [N$_{1\,1\,1\,16}$]Cl-ZnCl$_2$ system: crystalline phases are identified by solid vertical lines on the phase diagrams, liquid-crystalline phases include crystal smectic, Sm, lamellar, SmA, continuous cubic, Cub, hexagonal non-geometric, H$_{ng}$, hexagonal columnar, Col$_h$, and cubic micelle, Cub′. Dashed (short) lines represent the composition boundary above which crystals of the binary metal halide are observed. The dotted line indicates the temperature of the H$_{ng}$ –Col$_h$ transition observed by a change in the optical texture on heating (reproduced from Ref. 78 with permission from Nature Publishing Group).

In contrast, viscosity of chlorochromate(III) ionic liquids based on a hexahydrate salt, [ch]Cl-CrCl$_3$·6H$_2$O, decreased with $\chi_{CrCl3·6H2O}$ value increasing from 0.50 to 0.71, and no eutectic composition was observed.[82] This indicates that measurements of physical properties are most informative for neat chlorometallate systems; when water or other solvents are present, they may act as ligands to the metal, or as molecular solvents dissociating the salt, and results may be more difficult to interpret in terms of anionic speciation.
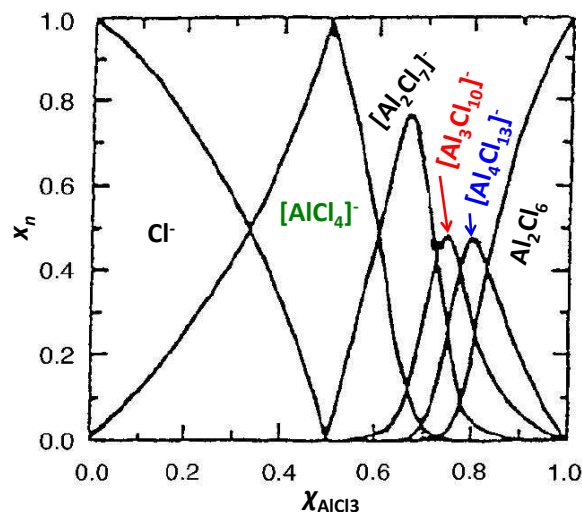
Figure 17. Concentration of anionic species in the [C$_2$mim]Cl-AlCl$_3$ system, at 200 °C, calculated from a thermodynamic model (adapted from Ref. 79).

2.2.8. Neutron scattering

Liquid neutron scattering (diffraction from liquid samples *cf.* crystalline materials) was used at an early stage to look at the liquid structure of molten salts.[83] Over the past ten years, great advances in the understanding of ionic liquids structure have been

made based on neutron scattering data and its direct analysis or indirect interpretation through modelling. However, for ionic liquids, apart from one study by Takahashi *et al.*[84] where data was collected on [C$_2$mim]Cl-AlCl$_3$ ionic liquids and was interpreted through simulation, the focus of neutron scattering experiments has been on ionic liquids with metal-free anions,[85,86] and particularly on materials with static anion configurations rather than the dynamic equilibria commonly found in the halometallate systems.

Neutron scattering provides information about the total structure within liquids (or glasses) and when combined with techniques such as XAS that inform on local environments, and computational modelling should be able to provide a detailed picture about how the changes in metallate anion speciation that occur with changing mole fraction affect the bulk structural properties of ionic liquids.

2.2.9. Theoretical studies

Like bulk physical properties, theoretical simulations cannot be treated as a 'standalone' method so study speciation, but can be a very valuable asset in conjunction with the above-discussed experimental methods.

For example, Mains *et al.*[87] used *ab initio* approach to model a range of haloaluminate(III) and alkylhaloaluminate(III) anions to calculate vibrational spectra and ^{27}Al quadrupole coupling constants; both were in a very good agreement with the experimental spectra, which strengthen the assignments and enabled better understanding of the spectroscopic results. Takahashi *et al.*[84] used *ab initio* modelling to understand short-range ordering observed in [C$_2$mim]Cl-AlCl$_3$ ionic liquids by neutron scattering; it was demonstrated that the structure of [Al$_2$Cl$_7$]$^-$ in the liquid is similar to that in the crystal, with tetrahedral 'AlCl$_4$' units merged by a bent Al-Cl-A bridge. In contrast, Lü *et al.*[88] have modelled the [C$_2$mim]Cl-CuCl system and optimised the structure of several chlorocuprate(I) anions, but provided neither comparison with crystallographic data, nor spectroscopic predictions, which significantly limits usefulness of such study.

De Andrade *et al.*[89,90] were looking at the structure of the bulk [C$_4$mim][AlCl$_4$] liquid, comparing force field simulations with neutron scattering data, density, diffusion coefficient vibrational frequencies and even solid-state crystallographic data. The computational model was validated by producing a very good fit between modelled and experimental values.

Kirchner and Seitsonen[91] used Car-Parrinello molecular dynamics approach to study an extremely acidic case of [C$_2$mim]Cl-AlCl$_3$ system, namely one molecule of [C$_2$mim]Cl dissolved in liquid aluminium(III) chloride. Under these conditions, tetrameric [Al$_4$Cl$_{13}$]$^-$ clusters converged as the dominant chloroaluminate(III) species. The study gave a valuable insight into the mechanism of formation of the Lewis acidic oligomeric anions; however, it is worth noting that in reality solid AlCl$_3$ precipitates from $\chi_{AlCl3} > 0.67$ compositions, and tetramers exist only in equilibrium with solid aluminium(III) chloride (see Figure 17). Consequently, ionic liquids based solely on [Al$_4$Cl$_{13}$]$^-$ clusters as anions are impossible to realise.
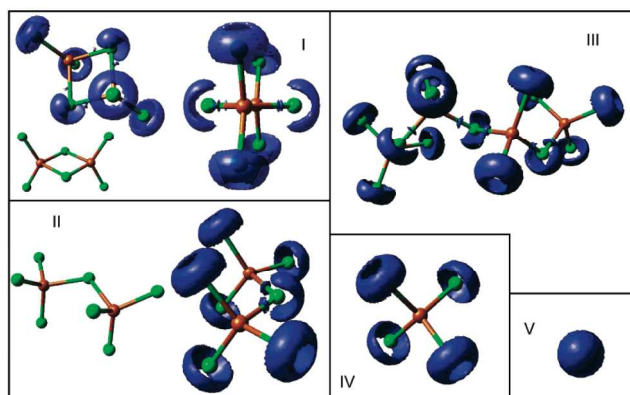

Figure 18. Electron localisation functions (Cl – green; Al – orange)derived for the species found in Car-Parrinello molecular dynamics simulations of [C$_2$mim]Cl-AlCl$_3$ systems reproduced with permission from Ref. [91].

Chaumont *et al.*[92] used molecular dynamics approach to model solvation of various lantanides and uracyl in neutral or basic chloroaluminate(III) ionic liquids. It was revealed that the [LnCl$_6$]$^{3-}$ anion, found in crystal structures of halolanthanide(III) salts, is also the dominant species in the ionic liquid solution. In analogy, [EuCl$_6$]$^{4-}$ and [UO$_2$Cl$_4$]$^{2-}$ anions, commonly found in crystal structures, were the most stable solutes of Eu^{2+} and uracil, respectively. This was contrasted with gas-phase quantum mechanics results, which rendered all these anions metastable and prone to loss of 1 or 2 Cl$^-$ ions. This leads directly to an important aspect of speciation studies, namely marked differences between speciation in liquid, solid and gas phases.

2.3. When an 'ionic liquid' is not a liquid…

Within the context of *ionic liquids*, organic chlorometallate salts are typically used as liquids, very seldom as solids, and never in a gaseous form. This may sound absurdly obvious, but it is important because the anion speciation depends on the environment in addition to χ_{MClx} and the metal. Measurements from samples in the solid state, in solution or in the vapour phase are not reporting directly on the ionic liquid environment and may, in some situations, lead to entirely spurious conclusions.

2.3.1. Mass spectrometry – why is it not suitable for anionic speciation studies?

Although mass spectrometry has been commonly used as a tool for characterisation of ionic liquids,[93-95] recent work has demonstrated how MS can lead to erroneous conclusions about anionic speciation in chlorometallate ionic liquids. Estager *et al.*[27] have shown that the presence of singly-charged anions, such as [ZnCl$_3$]$^-$ or [Zn$_2$Cl$_5$]$^-$, is suggested in chlorozincate(II) ionic liquids on the basis of MS. In contrast, all other techniques, from spectroscopic methods to physical properties measured as a function of composition, pointed firmly to the presence of doubly-charged anions, such as [ZnCl$_4$]$^{2-}$ or [Zn$_2$Cl$_6$]$^{2-}$. This latter speciation was also with agreement with coordination chemistry of zinc(II) known from inorganic chemistry textbooks.[96]

It seems to be a reoccurring theme that MS results can lead to confusion and erroneous conclusions about speciation. Campbell *et al.*[97] studied chlorohafnate(IV) and chlorozirconate(II) ionic liquids using a multi-technique approach, which unfortunately did not include vibrational spectroscopy. Based on DSC and known

coordination chemistry of both metals, they hypothesised the predominance of $[MCl_6]^{2-}$, $[M_2Cl_{10}]^{2-}$ and (unknown in the literature) $[M_2Cl_9]^-$ at $\chi_{MCl4} = 0.33$, 0.50 and 0.67, respectively. However, based on ESI-MS results, they postulated the existence of $[MCl_5]^-$ as the main anion at $\chi_{MCl4} = 0.50$ instead, which is less likely considering both high melting points of the $\chi_{MCl4} = 0.50$ compositions, and the unusual coordination number. MS studies on chloroindate(III) ionic liquids[98] also gave bizarre results; although it has been explicitly demonstrated that binuclear anions are not present in the liquid state,[38,50] the $[In_2Cl_7]^-$ anion was observed in mass spectra using both ESI-MS and FAB-MS (Figure 19).
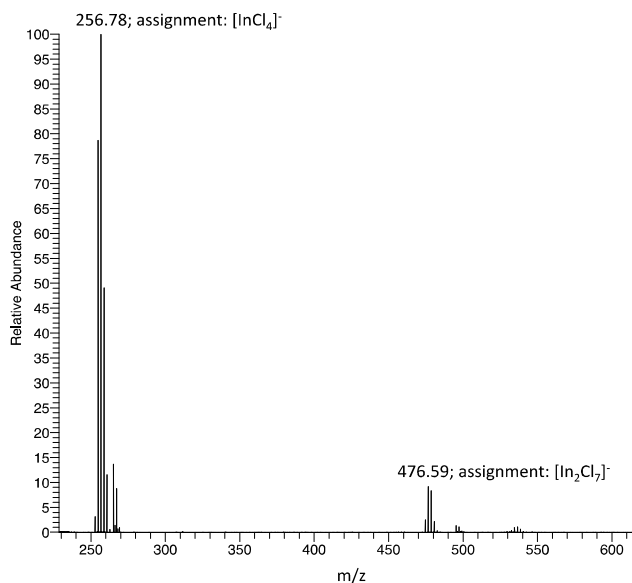

Figure 19. FAB-MS spectrum (negative mode) of $[C_8mim]Cl\text{-}InCl_3$, $\chi_{InCl3} = 0.55.98$

In some cases (*viz.* studies on chlorogallate(III) and chloroaluminate(III) systems)[99] MS results are in general agreement with other spectroscopic and electrochemical studies. However, this appears as much a coincidence as a rule when contrasted with the other examples above. Importantly, researchers from outside of the ionic liquids field have encountered similar discrepancies. Di Marco *et al.*[100-103] devoted a number of publications to studies of metal-ligand aqueous solution equilibria using electrospray mass spectrometry (ESI-MS) and stated that '*the ionization process can introduce perturbations which affect the speciation results in an unpredictable way*'[103] and that '*the identification of perturbations is a required task for any metal-ligand equilibrium study performed by ESI-MS*'.[103] In his review on ESI-MS, Kebarle[104] stated explicitly: '*the ions observed in the gas phase may be different from those present in the solution, owing to processes which occur at the threshold between solution and gas phase and ion – molecule reactions in the gas phase*'. The same issues are related to FAB-MS, where the studied sample is said to be either in the gas phase,[105] in a state where the gas phase is predominant,[106] or in a hybrid 'bubble chamber model'.[107] For chlorometallate ionic liquid systems (*viz.* studies on chlorozincate(II) systems), FAB-MS[64] and ESI-MS[27] experiments

gave the same results, indicating that both techniques are prone to the same measurement errors.

2.3.2. Crystallography – use with caution

Crystallography may aid to elucidate the liquid-phase speciation. In the same time, it can never be *a priori* assumed, that the examined produced single crystals correspond even to the bulk of the solid, let alone to the molten ionic liquid.

Crystal structures can be used to confirm and support the studies on liquid-phase speciation. For example, Dymek and co-workers[108] investigated the local structure present in the basic $[C_2mim]Cl\text{-}AlCl_3$ melts by combining crystallographic and infrared data with theoretical calculations. Based on crystal structures, accurate predictions regarding the vibrational spectra were made. Moreover, crystal structures of chloroaureate(III) systems based on 1,3-dialkylimidazolium cations contain square planar $[AuCl_4]^-$ anions (Figure 20);[109,110] this is not typical for crystallised ionic liquids with $[MCl_4]^{x-}$ anions, but is in agreement with the structure found in the liquid state by Raman and *ab initio* calculations,[39] and easily justified in terms of electronic structure of gold(III). Other examples, where solid and liquid speciation of chlorometallate complexes are consistent, include numerous halolanthanide(III) systems, $[C_nmim][LnX_6]$,[111-113] and most of the structures reported by Zhong *et al.* on the $[C_4mim][MCl_4]$ family (M = Cu, Ni, Mn, Fe, Co, Zn, and Pt).[114]
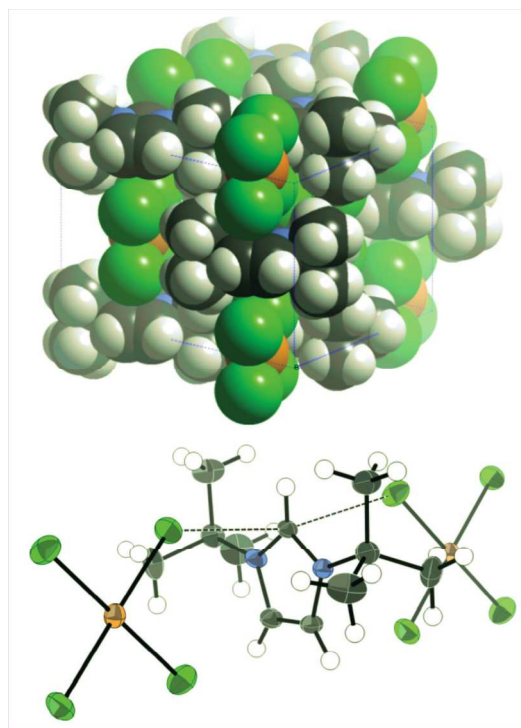
Figure 20. Two views of the crystal structure of $[^iC_4{}^iC_4im]Cl\text{-}AuCl_3$: *pseudo*-NaCl structure packing in space-filling representation (top), and detail of anion–π interactions (bottom). Thermal ellipsoids displayed at 50% probability (reproduced from Ref. 110).

In contrast, the structure of $[C_4mim]_2[SnCl_4]$, also reported by Zhong *et al.*,[115] is an interesting example of a discrepancy between crystal structures and speciation in the molten state. Despite numerous crystal structures featuring $[SnCl_4]^{2-}$ anion, in the liquid phase only $[SnCl_3]^-$ and $[Sn_2Cl_5]^-$ anions were detected.[48] It was established that crystals grown from a polar

solvent (typically acetonitrile) contained doubly charged $[SnCl_4]^{2-}$, whereas crystals grown from the melt featured singly-charged $[SnCl_3]^-$.

Furthermore, a number of halometallate salts has a tendency to crystallise in polymeric structures, which melt incongruently to give monomeric or oligomeric anions in the liquid phase. Organic chlorocuprate(II) salts where, in addition to discrete $[CuCl_4]^{2-}$ and $[Cu_2Cl_6]^{2-}$ anions with copper coordination geometries ranging from square planar to tetrahedral, polymeric chlorocuprate chains with copper coordination numbers ranging from 4-6 can be widely observed depending on the Cu:Cl ratios, cation, and crystallisation processes.[116] Willett and Geiser, while reporting the structure of a tetraethylammonium chlorocuprate (1:1) salts with a linear tetranuclear anion, comments on "*the peril of attempting to summarize the structural behavior of copper(II) halide species*".[117] The same can be observed for other metals, such as zinc(II) or lead(II), where halometallate ionic liquids crystallised to form polyanionic strands and networks. However, it has been observed that the structure of the polymeric strand is in a direct relationship with the structure of a monomeric anion present in the melt.[118]

2.4. Influence of the cation on anionic speciation

In the bulk of the discussion up to this point, there has been an implicit assumption that chlorometallate anion speciation is independent of the cations present, and that the cations (for example dialkylimidazolium, tetraalkylammonium, tetraalkylphosphonium or alkylpyridinium) only change physical properties (*e.g.* melting points). However, an effect of a non-functionalised cation on the anionic speciation has been observed in several cases.

2.4.1. NMR spectroscopy

^{1}H and ^{13}C NMR spectroscopy has been commonly used to investigate cation-anion interactions in chlorometallate systems. In probably the earliest study, Robinson *et al.*[42] investigated $[C_n py]X-AlX'_3$ (X,X' = Cl or Br) systems with $\chi_{AlX3} = 0.50$ and 0.67. Their results were interpreted as showing no ion pairing in the neat liquid, indicating that the cation does not compete with MX_3 for halide. However, all newer studies refute this observation. For example, using ^{13}C NMR spectroscopy Wilkes *et al.*[119] found significant amount of interactions between cations and anions in $[C_2mim]Cl-AlCl_3$ systems, particularly *via* hydrogen bonding with the acidic C-2 proton on the imidazolium ring. The ^{13}C NMR chemical shift of the C-2 carbon changes following a second order curve as a function of χ_{AlCl3} for $\chi_{AlCl3} < 0.50$. Above $\chi_{AlCl3} = 0.50$, the change was smaller and linear. Interpreting this data, Wilkes et al considered each cation to interact, on average, with two anions which would induce a large change from two Cl$^-$ to one Cl$^-$ and one $[AlCl_4]^-$ (around $\chi_{AlCl3} = 0.33$), and subsequently to two $[AlCl_4]^-$ ($\chi_{AlCl3} = 0.50$), and much smaller change when $[AlCl_4]^-$ was gradually replaced with $[Al_2Cl_7]^-$. An analogous trend has been reported for the ^{1}H NMR chemical shift of the C-2 proton in $[C_8mim]Cl-SnCl_2$ systems.[48] Furthermore, Axtell *et al.*[26] studied hydrogen bonding between anions and cations of systems based on trialkylammonium or trialkylphosphonium cations and copper(I) chloride, using ^{1}H NMR spectroscopy (*NB*, samples tested as solutions in deuterated solvents). NMR spectra for $[CuCl_2]^-$ based ionic liquids were compared with spectra of salts containing the same cations, but strongly coordinating Cl$^-$ anion, or non-coordinating $[B(C_6H_5)_4]^-$ anion. In all cases, ^{1}H NMR chemical shifts of the H-N or H-P protons were decreasing in order: Cl$^-$ > $[CuCl_2]^-$ > $[B(C_6H_5)_4]^-$. This demonstrated that chlorometallate anions do hydrogen-bond with the acidic protons in the cations, albeit more weakly that halides. However, in this work, not only were the measurements carried out in molecular solvents, but also the solutes concentration does not appear to be controlled, therefore such observations can only be treated qualitatively. Quantification of these investigations was provided by *ab initio* calculations on the $[C_2mim]Cl-CuCl$ system, where interaction energies for $[C_2mim]^+$ paired with $[CuCl_2]^-$, $[Cu_2Cl_3]^-$ or $[CuCl_3]^{2-}$ were predicted to be 309.0, 316.8 or 320.2 kJ mol^{-1}, respectively.[88]

Finally, the existence of extensive hydrogen bonding network in basic chloroaluminate(III) ionic liquids was explicitly proven using ROESY 2D NMR spectroscopy.[46] The $\chi_{AlCl3} = 0.33$ composition of a $[C_2mim]Cl-AlCl_3$ system was studied, and in order to differentiate between intramolecular and intermolecular interactions, the spectrum was compared to a ROESY spectrum obtained for an identical sample, albeit with 95% of cations fully deuterated. Signals missing in the latter sample were assigned to intermolecular NOE transfer.

2.4.2. Raman spectroscopy

Raman spectra of chloroplumbate(II) ionic liquids indicated that the structure of anions in the liquid phase may depend on hydrogen bond donor properties. In $[P_{6\,6\,6\,14}]^+$ the $[PbCl_3]^-$ anion appeared nearly trigonal planar, while in $[C_2mim]^+$ it seemed to be more *pseudo*-tetrahedral, experiencing distortion due to the steric effects of the free electron pair.[118] This structural sensitivity can be expected to apply mainly to metals of high ionic radii.

2.4.3. XP spectroscopy

Licence and co-workers[58] demonstrated that the hydrogen bond basicity (β) parameter can be estimated by examining shifts in the 1s binding energies from N and C atoms in the cations of ionic liquids under investigation. Comparing the results for different compositions of a chlorozincate(II) system with those for the corresponding ionic liquids with other anions, the chlorozincate(II) ionic liquids were shown to have hydrogen bond basicities intermediate between those of ionic liquids with strongly basic anions (Cl$^-$) and weakly basic, poorly-coordinating anions (*e.g.* $[NTf_2]^-$) – see Figure 21.

2.5. Speciation of known chlorometallate ionic liquids

2.5.1. Homometallic systems

A summary of the reliably characterised anionic species found in homometallic chlorometallate systems is shown in Table 2. Predominant anions detected in chlorometallate ionic liquids in their liquid state, for six compositions, which correspond to stoichiometric ratios of chloride to metal chloride, are listed. The $\chi_{MXx} = 0.60$ composition was included as in several cases chlorometallate systems have the ability to form binuclear anions, but these exist only in equilibrium with mononuclear ones. For example, for Fe(III)-based ionic liquids, it has been observed that $[Fe_2Cl_7]^-$ and $[FeCl_4]^-$ coexist at $\chi_{FeCl3} = 0.60$, albeit for $\chi_{FeCl3} > 0.60$ additional iron(III) chloride does not dissolve, and hence the ionic liquid containing purely $[Fe_2Cl_7]^-$ is never formed. This can be justified by the energy of formation of the dimeric anion being lower than the lattice energy iron(III) chloride.
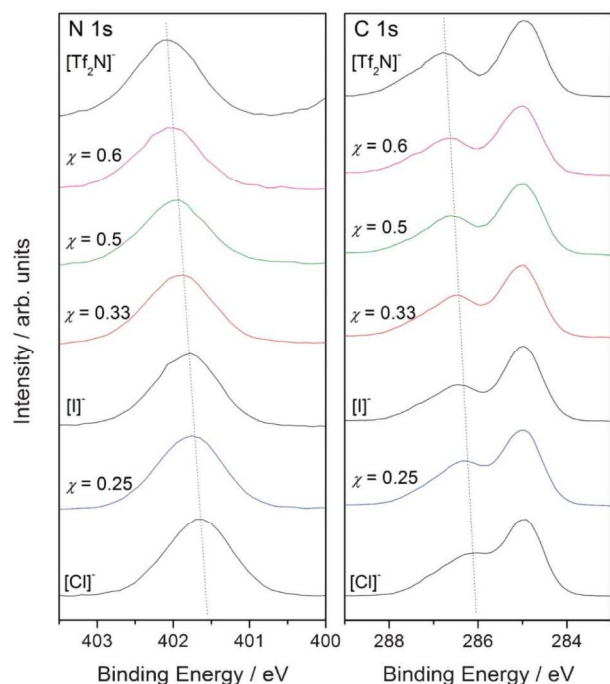
Figure 21. High resolution XP spectra of the N 1s and C 1s regions for four [C_8mim]Cl-$ZnCl_2$ (χ_{ZnCl2} = 0.25, 0.33, 0.50, 0.60), compared to [C_8mim]Cl, [C_8mim]I and [C_8mim][NTf_2]. All spectra have been charge corrected to $C_{aliphatic}$ 1s = 285.0 eV. (reproduced from Ref. 58).

2.5.2. Key aspects of speciation in mixed metal systems

Mixed metallate systems are formed when a metal salt is solubilised in a chlorometallate ionic liquid. A reactive dissolution process takes place and can lead to one of several outcomes: (a) dissolution and subsequent precipitation of another salt/coordination polymer; (b) reactive dissolution to form discrete mononuclear ions and (c) dissolution to form heteronuclear ions. The case where reactive dissolution leads subsequently to the precipitation of crystalline product is discussed later in the section on inorganic syntheses. Here, we consider only situations where all the metals remain in the liquid state, forming effectively a multi-component chlorometallate ionic liquid.

Metal chlorides in basic chloroaluminates(III). When a metal chloride, MCl_x, is dissolved in a basic chloroaluminate(III) ionic liquid, it generally reacts with the excess of chloride to form a mononuclear chlorometallate anion of a general formula $[MCl_{x+y}]^{y-}$, as exemplified in by dissolution of cobalt(II) chloride in a chloroaluminate(III) system, χ_{AlCl3} = 0.25 (Equation 2).[68]

$$[AlCl_4]^- + 2Cl^- + CoCl_2 \rightleftharpoons [AlCl_4]^- + [CoCl_4]^{2-} \qquad (2)$$
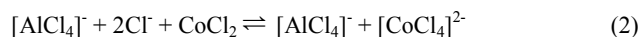
This behaviour has been observed with a number of metal chlorides, such as $CoCl_2$, $NiCl_2$, $FeCl_2$, $FeCl_3$, $CuCl_2$, $MoCl_3$ and $MoCl_4$.[120,121] A slightly more complex behaviour was found in chlorides of some monovalent metals: AgCl and CuCl. Three equilibrated anions were detected (see Equation 3), with the equilibrium constant strongly dependent on temperature.[122]

$$2[MCl]^{2-} \rightleftharpoons [MCl_2]^- + [MCl_4]^{3-} \qquad (3)$$
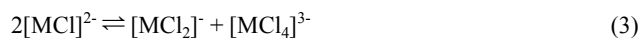
V(III) chlorides and chlorides oxides: VCl_3, $[VOCl_4]^{2-}$ and $[VO_2Cl_2]^-$, dissolved to form the expected anionic species: $[VCl_6]^{3-}$, $[VOCl_4]^{2-}$ and $[VO_2Cl_2]^-$, respectively. However, chlorides and chlorides oxides of vanadium in higher oxidation states were reduced by the excess of chloride and yielded V(III) anions: $[VCl_6]^{3-}$ and $[VOCl_4]^{2-}$.[123] Additionally, uranium and uranyl ions display complex coordination chemistry in chloroaluminate system, as described initially by Dent *et al.*,[68] and reviewed recently.[124]

In general, ionic liquids containing mononuclear chlorometallate anions of two (or more) different metals tend to behave as simple mixtures of two ionic liquids with a common cation, *i.e.* their properties get 'averaged'. For example, magnetic susceptibility of the [C_4mim]Cl-$GaCl_3$-$FeCl_3$ system, based on paramagnetic Fe(III) and diamagnetic Ga(III), is half of that of the neat [C_4mim]Cl-$FeCl_3$ ionic liquid[125] (as is discussed further in the materials section).

Metal chlorides in acidic chloroaluminates(III). In contrast to the solubility of many metal chlorides in basic chloroaluminate(III) ionic liquids, metal salts are much less soluble in acidic chloroaluminate(III) compositions as there is no free Cl^- to facilitate the dissolution. Instead, Cl-bridged, bimetallic, polynuclear anions can be formed; unfortunately, elucidating the actual speciation of these is rather challenging.

Liu *et al.*[126] studied bimetallic [$HN_{1\,1\,1}$]Cl-$AlCl_3$-CuCl (1:1:1) system using ESI-MS, as well as ^{27}Al NMR and FT-IR spectroscopies. The ^{27}Al NMR spectrum (shown in Figure 22) clearly confirmed the presence of significant amounts of binuclear, bimetallic $[CuCl(AlCl_4)]^-$ anion. The anion was also detected by ESI-MS, although the merits of using gas phase techniques to characterise species present in bulk ionic liquids has been already disputed in the characterisation section.

Dent *et al.*[68] showed that MCl_2 salts, where M = Mn(II), Co(II) or Ni(II), dissolved in the acidic [C_2mim]Cl-$AlCl_3$ system, form hexacoordinate $[M(AlCl_4)_3]^-$ anions (see EXAFS section). In analogy, $YbCl_3$ solution in acidic chloroaluminates(III) was suggested to contain $[Yb(AlCl_4)_n]^{n-3}$, and $[Yb(AlCl_4)_n]^{n-2}$ after reduction,[127] whereas $TiCl_4$ dissolved in [C_4mim]Cl-$AlCl_3$ (χ_{AlCl3} = 0.67) was suggested to form the $[Ti(Al_2Cl_7)_4]^{2-}$ complex;[128] in both cases, no evidence was provided to support these claims.

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Table 2. Anionic speciation of known chlorometallate ionic liquids in the liquid state. Dominant anions for given χ_{MXx} are presented, along with major techniques used to confirm the speciation and references to the relevant publications.

	χ_{MXx}						Analysis methods
	0.25	0.33	0.50	0.60	0.67	0.75	
Ti(IV)		$[TiCl_6]^{2-}$			$[Ti_2Cl_9]^-$		IR, Raman[129]
Zr(IV)	Cl⁻; $[ZrCl_6]^{2-}$ *	$[ZrCl_6]^{2-}$ *	$[Zr_2Cl_{10}]^{2-}$ *		$[Zr_2Cl_9]^-$ *		DSC,[97] crystallography
Hf(IV)	Cl⁻; $[HfCl_6]^{2-}$ *	$[HfCl_6]^{2-}$ *	$[Hf_2Cl_{10}]^{2-}$ *		$[Hf_2Cl_9]^-$ *		DSC[97]
Nb(V)	Cl⁻; $[NbCl_6]^-$		$[NbCl_6]^-$	$[NbCl_6]^-$; Nb_2Cl_{10}			Raman[35]
Mn(II)		$[MnCl_4]^{2-}$	$[MnCl_3]^-$ *				Raman, IR,[130] EXAFS[131]
Fe(II)		$[FeCl_4]^{2-}$		$[FeCl_4]^{2-}$; $FeCl_2\downarrow$			Raman,[36] XPS[60]
Fe(III)	Cl⁻; $[FeCl_4]^-$		$[FeCl_4]^-$	$[FeCl_4]^-$; $[Fe_2Cl_7]^-$	$[FeCl_4]^-$; $[Fe_2Cl_7]^-$; $FeCl_3\downarrow$		Raman,[36] XPS[60]
Co(II)	Cl⁻; $[CoCl_4]^{2-}$	$[CoCl_4]^{2-}$	$[CoCl_2(CoCl_4)_2]^{4-}$; $[Co(CoCl_4)_3]^{4-}$ *	$[CoCl_2(CoCl_4)_2]^{4-}$; $[Co(CoCl_4)_3]^{4-}$; $CoCl_2\downarrow$*			UV-VIS[72]
Ni(II)	Cl⁻; $[NiCl_4]^{2-}$	$[NiCl_4]^{2-}$	$[NiCl_4]^{2-}$; $NiCl_2\downarrow$				Crystallography,[132] EXAFS[133,134]
Pd(II)		$[PdCl_4]^{2-}$					Crystallography,[110,135] EXAFS[131]
Pt(II)		$[PtCl_4]^{2-}$					Crystallography[109] **Error! Bookmark not defined.**
Cu(I)	Cl⁻; $[CuCl_{(2+n)}]^{(1-n)-}$		$[CuCl_2]^-$		$[Cu_2Cl_3]^-$		IR, Raman,[26] viscometry[81]
Cu(II)		$[CuCl_4]^{2-}$	$[Cu_2Cl_6]^{2-}$ *				UV-VIS, EXAFS[65,66]
Au(III)	Cl⁻; $[AuCl_4]^-$		$[AuCl_4]^-$	$[AuCl_4]^-$; $AuCl_3\downarrow$			Raman, *ab initio*[39]
Zn(II)	Cl⁻; $[ZnCl_4]^{2-}$	$[ZnCl_4]^{2-}$	$[Zn_2Cl_6]^{2-}$	$[Zn_2Cl_6]^{2-}$; $[Zn_3Cl_8]^{2-}$	$[Zn_3Cl_8]^{2-}$	$[Zn_4Cl_{10}]^{2-}$	Raman,[35,27]
Cd(II)		$[CdCl_4]^{2-}$ *	$[Cd_2Cl_6]^{2-}$ *				Crystal structure[136]
Hg(II)		$[HgCl_4]^{2-}$ *					Crystal structure[137]
Al(III)	Cl⁻; $[AlCl_4]^-$		$[AlCl_4]^-$	$[AlCl_4]^-$; $[Al_2Cl_7]^-$	$[Al_2Cl_7]^-$	$[Al_xCl_y]^-$; $AlCl_3\downarrow$	Raman,[32,33] ^{27}Al NMR,[46]
Ga(III)	Cl⁻; $[GaCl_4]^-$		$[GaCl_4]^-$	$[GaCl_4]^-$; $[Ga_2Cl_7]^-$	$[Ga_2Cl_7]^-$	$[Ga_3Cl_{10}]^-$	Raman,[34,138] ^{71}Ga NMR, EXAFS[51]
In(III)	$[InCl_6]^{3-}$	$[InCl_5]^{2-}$	$[InCl_4]^-$	$[InCl_4]^-$; $InCl_3\downarrow$			Raman,[37,38] XPS
Sn(II)	Cl⁻; $[SnCl_3]^-$		$[SnCl_3]^-$	$[SnCl_3]^-$; $[Sn_2Cl_5]^-$	$[SnCl_3]^-$; $[Sn_2Cl_5]^-$; $SnCl_2\downarrow$		Raman,[48]
Pb(II)	Cl⁻; $[PbCl_4]^{2-}$	$[PbCl_4]^{2-}$	$[PbCl_4]^{2-}$; $[PbCl_3]^-$; $PbCl_2\downarrow$				Raman, ^{207}Pb NMR[118]

* speciation assumed based on stoichiometry, solid-state studies or indirect techniques, such as DSC
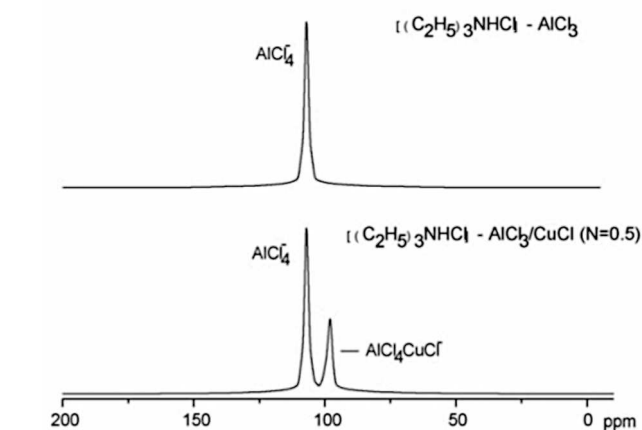

Figure 22. ^{27}Al NMR spectra identifying the presence of bimetallic $[CuCl(AlCl_4)]^-$ anions in $[HN_{111}]Cl$-$AlCl_3$-CuCl (1:1:1) system, compared to neat $[HN_{111}]Cl$-$AlCl_3$ reproduced with permission from Ref. 121.

Roeper *et al.*[69] recently re-visited the research of Dent *et al.*,[68] (details discussed in the section on EXAFS), and investigated the speciation of $NiCl_2$ dissolved in three compositions of the $[C_2mim]Cl$-$AlCl_3$ system. In agreement with the older work, they detected $[NiCl_4]^{2-}$ in the basic composition (χ_{AlCl3} = 0.43). However, data gathered for a solution in the weakly acidic system (χ_{AlCl3} = 0.54) pointed towards octahedral $[NiCl_6]^{4-}$, with no second coordination sphere detected. Finally, for χ_{AlCl3} = 0.60, 6 Cl atoms were detected in the first coordination sphere, and 8 Al atoms in the second. This led Roeper *et al.* to postulate $[Al_2Cl_7]^-$ sharing chloride ligands with Ni(II) atom, effectively forming $[Ni(Al_2Cl_7)_4]^{2-}$ as indicated in Figure 9. Either way, all investigations are based on EXAFS, and other spectroscopic techniques as well as high level *ab initio* calculations appear to be necessary to elucidate the actual speciation. This is problematic, as Raman would not detect small quantity of the complex, NMR studies are obstructed by the presence of paramagnetic metals, and *ab initio* investigations involving several metals in equilibrium are very challenging.

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CRITICAL REVIEW
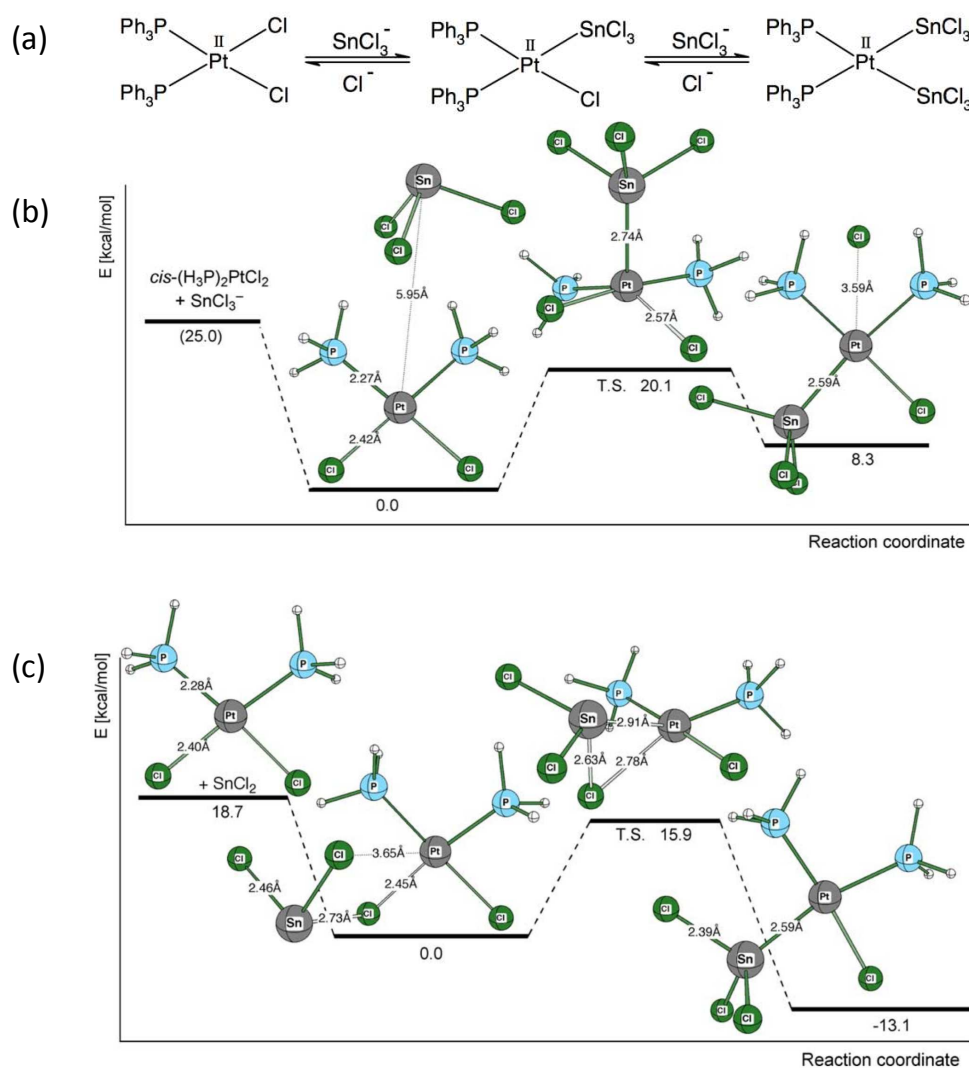

Figure 23. Equilibria leading formally to the formation of the catalytically activate cis-[Pt(PH$_3$)$_2$(SnCl$_3$)$_2$] complex upon dissolution of cis-[Pt(PPh$_3$)$_2$Cl$_2$] (a), and calculated reaction pathway of cis-[Pt(PPh$_3$)$_2$Cl$_2$] with [SnCl$_3$]$^-$ (b) and with SnCl$_2$ (c) reproduced from Ref. 47 with permission from Elsevier.

Metal-metal bonds in chlorometallate anions. In one of the very first papers on chlorometallate ionic liquids, Parshall9 reported that PtCl$_2$ (7 wt %) dissolved readily in chlorogermanate(II) and chlorostanate(II) ionic liquids; a [(C$_2$H$_5$)$_4$N]$_3$[Pt(SnCl$_3$)$_5$] complex was isolated from the ionic liquid and characterised. The bimetallic systems were used as hydrogenation catalysts, and a hydrogen-containing complex, [(C$_2$H$_5$)$_4$N]$_3$[HPt(SnCl$_3$)$_4$], was isolated from the ionic liquid after reaction. It is worthy of note that crystalline complexes isolated by extraction for the chlorostannate(II) ionic liquids are not necessarily corresponding directly to solution species, but give strong indication that [SnCl$_3$]$^-$ ligates to Pt(II) via Pt-Sn bond. In a newer study, Wasserscheid and co-workers[47,139] investigated dissolution of cis-[PtCl$_2$(PPh$_3$)$_2$] in various compositions of [C$_4$mim]Cl-SnCl$_2$ system. UV-VIS spectroscopy indicated fast

formation of cis-[PtCl(SnCl$_3$)(PPh$_3$)$_2$] and subsequent, slower formation of cis-[Pt(SnCl$_3$)$_2$(PPh$_3$)$_2$], according to the scheme in in Figure 23a. The reaction took place only for $\chi_{SnCl2} \geq 0.50$, and the reaction rate increased with acidity of the system. Indeed, DFT calculations indicated that the reaction progresses via dissociation of [Sn$_2$Cl$_5$]$^-$ and insertion of SnCl$_2$ unit into Pt-Cl bond, rather than through substitution of Cl$^-$ with [SnCl$_3$]$^-$ (see comparison in Figure 23b and c).

Significance of heterometallic, polynuclear anions. Upon the formation of heterometallic, polynuclear complexes, metals dissolved in an ionic liquid change their properties, most prominently redox potential and catalytic activity. Reduction of these species facilitates depositions of metals and alloys, which were challenging to access otherwise; this was extensively reviewed[140] and is still explored.[141] Catalytic applications of

bimetallic compounds, already signalled here, will be discussed in the section on catalysis.

2.6. Chlorometallate ionic liquids and water

The presence of water can have profound effects on the composition and properties of chlorometallate ionic liquids with their behaviour ranging from hydrolysis through hydration and simple dissociative dissolution in water, to hydrophobicity.

2.6.1 Hydrolysis

Chloroaluminate(III) ionic liquids, as well as anhydrous aluminium(III) chloride, are extremely oxophillic. High energy of Al-O bond translates to exothermic, violent reaction with water, including atmospheric moisture. The hydrolysis products have been studied by FAB-MS,[99] ^{17}O NMR[142] and ^{27}Al NMR[46] spectroscopy, among others, demonstrating the formation of oxo- and hydroxochloroaluminate(III) species combined with the release of hydrochloric acid, as exemplified in Equation 4.

$$2[AlCl_4]^- + H_2O \rightarrow [Al_2Cl_5O]^- + [HCl_2]^- + HCl \qquad (4)$$
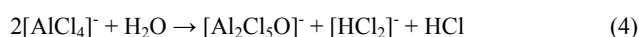
Chlorogallate(III) systems were shown to react similarly to the Al(III)-based ones, but at a lower rate.[99] Hydrophobic chloroferrate(III) systems undergo very slow hydrolysis, which is discussed in the further section.[143]

The mechanism of hydrolysis of chloroaluminates(III), as well as good handling and synthetic practice to avoid it, are described thoroughly in Welton's review from 1999.[14] The hydrolytic instability of chlorometallates(III) is, however, a double-edged sword. On one hand, their tendency to hydrolyse has been the major challenge in implementation of chloroaluminate(III) ionic liquids in the industry, and the main incentive for the scientist to turn their interest towards 'air- and water stable',[6,7] or hydrophobic,[8] ionic liquids based on non-metallic anions such as $[BF_4]^-$, $[PF_6]^-$ or $[NTf_2]^-$. On the other hand, this strong interaction with water arises from the very strong Lewis acidity of chloroaluminate(III) ionic liquids, the core property that makes them useful as catalysts. Moreover, it is the superacidic protons deriving from partial hydrolysis of the Lewis acidic chloroaluminates(III) which are behind acid catalysis in chloroaluminate(III) media. Both aspects are discussed in the further sections of this review.

In view of this, it must be emphasised that chloroaluminate(III) and chlorogallate(III) ionic liquids prepared in open air (without protection from the moisture),[144] or indeed prepared from the corresponding metal(III) chloride hydrates,[145] contain a mixture of oxo- and hydroxochlorometallate(III) anions of variable composition. They will display catalytic activity, even for neutral compositions ($\chi_{MCl3} = 0.50$), due to the presence of superacidic protons, but their activity will vary with the degree of hydrolysis, and there is high probability of gradual HCl release, which in general means that the use of such systems is simply a bad practice.

2.6.2. Hydration

Ionic liquids based on other metals, in particular chloroindate(III) and chlorozincate(II) systems, are often described as moisture-stable alternatives to chloroaluminate(III) systems.[146,147] Indeed, chloroindate(III) and chlorozincate(II) ionic liquids can be used in the open air and, moreover, are less oxophillic than the Al(III)-based analogues. This can be used to advantage, for

example as catalysts for reactions of alcohols or phenols[146,148] which are incompatible with chloroaluminate(III) ionic liquids.

However, even ionic liquids that do not hydrolyse may be prone to hydration; instead of decomposition with HCl release, stoichiometric amounts of water molecules may coordinate to the metal centre. For example, it was demonstrated for the $[C_2mim]Cl$-$InCl_3$ system that, whilst $[C_2mim]_3[InCl_6]$ ($\chi_{InCl3} = 0.25$) remains unaffected by the atmosphere, $[C_2mim]_2[InCl_5]$ ($\chi_{InCl3} = 0.33$) gradually transforms to $[C_2mim]_2[InCl_5(OH)]$, upon overnight exposure to the atmosphere. $[C_2mim][InCl_4]$ ($\chi_{InCl3} = 0.50$) becomes deliquescent within minutes of exposure, presumably incorporating two molecules of water.[149]

Hydration changes the speciation, and therefore the properties, of chlorometallate ionic liquids, but HCl is not released. Therefore, hydrated ionic liquids can either be made anhydrous by simple drying under high vacuum, or can be used as hydrates (which are safe due to the lack of HCl release and have well-controlled compositions due to stoichiometric reaction with water).

Chlorocuprate(II) systems, $[C_2mim]Cl$-$CuCl_2$ and $[ch]Cl$-$CuCl_2$·$2H_2O$, mixed with various amounts of water, were studied using EXAFS and UV-VIS.[65,66] The $[CuCl_4]^-$ anion present with high ionic liquid content ($\chi_{H2O} = 0.10$) was gradually replaced by mixed chloroaquacuprate(II) complexes ($\chi_{H2O} = 0.95$) and completely hydrated $[Cu(H_2O)_n]^{2+}$ (n = 4-6) cation for dilute aqueous solution of ionic liquid ($\chi_{H2O} \approx 1.00$), as depicted in Figure 24.
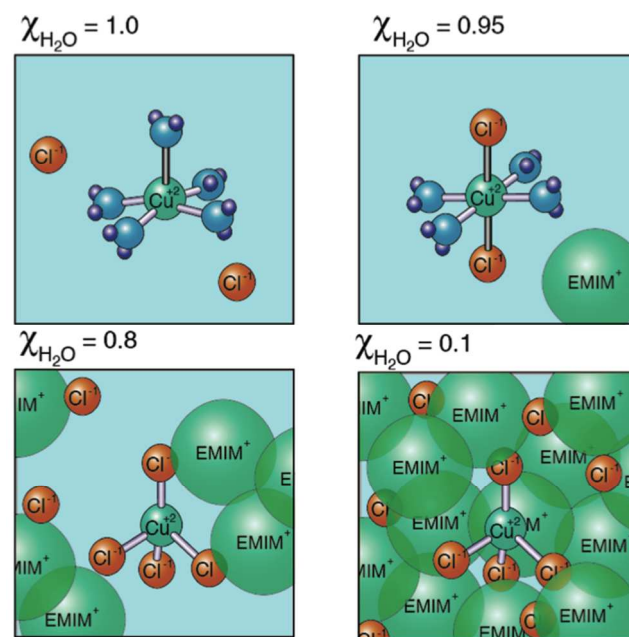
Figure 24. Schematic of various cation-anion structures in ionic liquid-water mixture for various mole fractions of water as indicated (reproduced with permission from Ref. 65).

The choline-chromium(III) $[ch]Cl$-$CrCl_3$·$6H_2O$ system has the eutectic composition at $\chi_{CrCl3·6H2O} = 0.67$, and forms a dark green, viscous, room temperature ionic liquid.[150] Surprisingly, it was reported that the hydrate ionic liquid cannot be formed by the reaction of $[ch]Cl$, $CrCl_3$ and six equivalents of water. Even more interesting is that the anhydrous salt is insoluble in the

hydrate-based ionic liquid. The authors use this argument to demonstrate that ionic liquids based on metal chloride hydrates are compounds in their own right, not merely concentrated aqueous solutions.

The use of metal chloride hydrates appears to be a convenient method to generate inexpensive choline-based ionic liquids, such as [ch]Cl-MgCl$_2$·6H$_2$O,[151] or [ch]Cl-CuCl$_2$·2H$_2$O,[66] which would be high-melting salts in the anhydrous form, and have been successfully used in both electrodeposition and Lewis acid catalysis.[152]

2.6.3. Hydrophobicity

The most common strategies to make hydrophobic ionic liquids are to introduce either highly fluorinated anions such as [NTf$_2$]$^-$ or cations with long alkyl chains, [P$_{6\,6\,6\,14}$]$^+$ being the most common example. Hydrophobic ionic liquids can, however, also be prepared containing chlorometallate anions. Systems containing large cations as described above are discussed further in the context of metal ion extraction later. Here, hydrophobicity arising from the nature of the halometallate anion, including systems based on *e.g.* Fe(III), Sn(II) or Pb(II) are considered. It is known that the reaction of [C$_n$mim]Cl (n = 4 or 12) with FeCl$_3$ is exothermic, but is endothermic with FeCl$_3$·6H$_2$O.[143] Furthermore, the ionic liquids formed from iron(III)chloride hydrate readily separates from the aqueous layer. Similarly, chlorostannate(II) and chloroplumbate(II) systems can also form biphasic systems with water. There may be more similar examples, but in general the phenomenon of hydrophobicity of chlorometallate ionic liquids is not well understood. Among most interesting studies is the contribution of Xie and Taubert,[143] who worked on the [C$_n$mim]Cl-FeCl$_3$ systems (n = 4 or 12; χ_{FeCl3} = 0.50). In both cases, ionic liquid-water mixtures displayed LCST-type thermomorphic behaviour; one phase was formed for lower ionic liquid ratios and lower temperatures, and phase separation was observed upon heating, and when ionic liquid loading was increased (Figure 25).
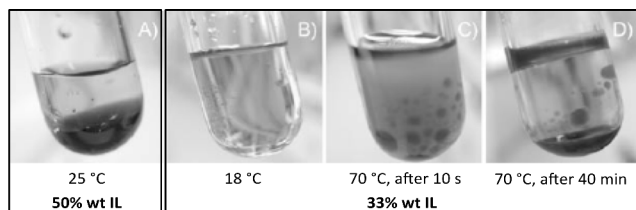

Figure 25. Photographs of [C$_4$mim][FeCl$_4$] in water, at various temperatures and concentrations of the ionic liquid (reproduced from Ref. 130 with permission from Wiley).

The authors offer several possible explanations to the LCST-type behaviour: (a) cohesive energy of water causing 'solvophobic' immiscibility, after Weingärtner;[153] (b) long-range Coulomb forces, described by Debye-Hückel theory, after Schröer and co-workers;[154] (c) competitive hydrogen bonding between cation…anion and anion···H$_2$O···anion.[154] Be it due to the long-range Coulombic interactions or due to differences in the hydrogen bond strength, it was demonstrated that cation-anion interactions are more thermodynamically favourable than those between ions and water; namely that the reaction of [C$_n$mim]Cl (n = 4 or 12) with FeCl$_3$ is exothermic and with FeCl$_3$·6H$_2$O is endothermic.[143]

Xie and Taubert[143] examined the mechanisms for hydrophobicity proposed for ionic liquids in general. However, these do not explain why structurally similar anions, *e.g.* tetrahedral [InCl$_4$]$^-$ and [FeCl$_4$]$^-$, combined with identical cations, have very different behaviour when it comes to miscibility with water. We would like to speculate that nephelauxetic effects[155] may contribute to hydrophobicity of chloroferrate(III) systems. Namely, that Fe-Cl bonds would have more covalent character than In-Cl, with lower partial negative charge on chloride, and consequently decreased ability to form hydrogen bonds. This is in-line with the negative enthalpy of reaction of [C$_n$mim]Cl with FeCl$_3$·6H$_2$O and also explains the LCST behaviour resulting from breaking of weaker than expected [FeCl$_4$]$^-$···H$_2$O bonds with increasing temperature.

3. Acidity

The Lewis acidity of chlorometallate ionic liquids is controlled by both the electrophilicity of the metal and the mole fraction of metal chloride (χ_{MXn}) used to prepare the ionic liquid. Consequently, Lewis acidity is yet another property of chlorometallate ionic liquids closely related to speciation, which depends on both the metal and on the ionic liquid composition.

The widely studied changes in speciation within chloroaluminate(III) ionic liquids can be considered as a representative example. When aluminium(III) chloride is dissolved into an excess of a chloride-based ionic liquids, [cation]Cl (χ_{AlCl3} < 0.5), tetracoordinate [AlCl$_4$]$^-$ anions are formed through reactive dissolution according to Equation 5; the excess of free chlorides will make the composition *basic*.

$$n\text{Cl}^- + \text{AlCl}_3 \rightarrow [\text{AlCl}_4]^- + (n\text{-}1)\text{Cl}^- \qquad (\chi_{AlCl3} < 0.5)\ (5)$$

Upon reaction of equimolar amounts of aluminium(III) chloride with [cation]Cl (χ_{AlCl3} = 0.5), a *neutral* ionic liquid will be formed, according to Equation 6.

$$\text{Cl}^- + \text{AlCl}_3 \rightarrow [\text{AlCl}_4]^- \rightleftarrows \text{Cl}^- + [\text{Al}_2\text{Cl}_7]^- \qquad (\chi_{AlCl3} = 0.5)\ (6)$$
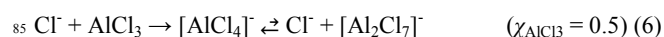
It is worth noting that, in practice, attaining a perfectly neutral composition is challenging; very small excess of either of the reactants gives rise to either acidic or basic compositions, which result in a dramatic narrowing of an electrochemical window. Reaction of excess of aluminium(III) chloride with [cation]Cl (χ_{AlCl3} > 0.5) results in the formation of Lewis acidic, oligomeric anions: [Al$_2$Cl$_7$]$^-$ and [Al$_3$Cl$_{10}$]$^-$, according to Equation 7.

$$\text{Cl}^- + 2\text{AlCl}_3 \rightarrow [\text{Al}_2\text{Cl}_7]^- \rightleftarrows [\text{AlCl}_4]^- + [\text{Al}_3\text{Cl}_{10}]^-\ (\chi_{AlCl3} > 0.5)\ (7)$$

In the presence of a base, these anions dissociate into a neutral anion and a free Lewis acid, which complexes the base (Equation 8).

$$[\text{Al}_2\text{Cl}_7]^- + \text{B} \rightarrow [\text{AlCl}_4]^- + [\text{AlCl}_3\text{B}] \qquad (8)$$
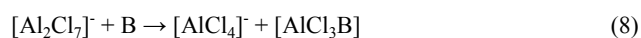
3.1. Acidity in different chlorometallate systems

The ability to act as a Lewis acid depends on the electrophilicity of the metal centre and availability of its LUMO orbital. Hence, naturally, ionic liquids based on zinc(II) will be weaker acids

than those based on aluminium(III). However, it is very important to remember that the *neutral* point depends on the coordination chemistry of the metal in question, and does not have to be at $\chi_{MCln} = 0.5$.

For example, a neutral chlorozincate(II) anion is formed at $\chi_{ZnCl_2} = 0.33$ from $ZnCl_2 + 2Cl^- \rightarrow [ZnCl_4]^{2-}$, hence all compositions $\chi_{ZnCl_2} > 0.33$ contain oligomeric $[Zn_xCl_{(2x+2)}]^{2-}$ species and are Lewis acidic. In contrast, oligomeric anions are not formed in chloroindate(III) systems, which are typically not considered as Lewis acidic. However, In(III) can expand its coordination number to 6 much more readily than Al(III). Consequently, chloroindate(III) ionic liquids are absolutely neutral at $\chi_{InCl_3} = 0.25$, where the only chloroindate(III) anion present is $[InCl_6]^{3-}$, whilst for higher χ_{InCl_3} values, where $[InCl_5]^{2-}$ and $[InCl_4]^-$ exist, they display mild Lewis acidity, reacting with bases according to the Equations (9 and 10):

$$[InCl_4]^- + nB \rightarrow [InCl_4B_n]^-, (n = 1 \text{ or } 2) \qquad (9)$$

$$[InCl_5]^{2-} + B \rightarrow [InCl_5B]^{2-} \qquad (10)$$
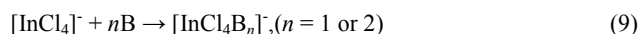
Once again, these species only result in very mild acidity due to the nature of the In(III) centre, as shown in comparison of chloroindate(III) ionic liquids to analogous systems based on Al(III) and Ga(III) in Figure 26.[156]
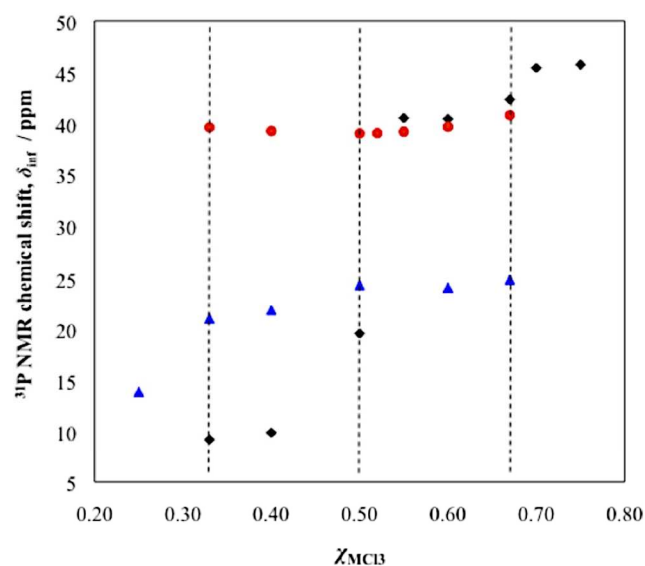

Figure 26. Plot of ^{31}P NMR shifts of tepo solutions at infinite dilution, $\delta_{inf,}$ in chlorometallate(III) ionic liquids based on indium(III), ▲, gallium(III), ◆, and aluminium(III), ●. Dashed lines at $\chi_{MCl_3} = 0.33$, 0.50 and 0.67 facilitate comparison of the crucial compositions reproduced from Ref. 156.

The upper limit of the acidity achievable for any chlorometallate ionic liquid is the solubility of metal halide in the [cation]Cl of interest. Chloroferrate(III) ionic liquids are relatively moisture-stable and hydrophobic, and taking into account high Lewis acidity of iron(III) chloride, they appear to be great candidates for Lewis acidic systems. However, this is restrained by the limited ability of Fe(III) to form dimeric $[Fe_2Cl_7]^-$ anions – the most acidic, homogenous composition achievable in these systems is *ca.* $\chi_{FeCl_3} = 0.60$,[157,158] as shown in Table 2.

Following on from this discussion, it should also be clear that merely ***dissolving a Lewis acidic salt in an ionic liquid does not guarantee a Lewis acidic system***. At low concentrations, the Lewis acid will be neutralised by the excess of basic anions, as exemplified by Equation 5. This appears obvious, but the literature features numerous examples, predominantly from the realm of organic chemistry, where several mol % of metal chloride or triflate is solubilised in to an ionic liquid, and systems with more basic (stronger coordinating) anions are rendered as bad for the particular type of reaction, because the authors perceive ionic liquids as an inert solvent

3.2. Buffering and latent acidity

As mentioned previously, preparation of ideally neutral chloroaluminate(III) systems is technically difficult, simply due to experimental error involved in weighing out the starting materials. However, it is possible to achieve a perfectly neutral compositions by buffering a slightly acidic ionic liquid, $0.50 < \chi_{AlCl_3} < 0.55$, to neutrality with an excess of NaCl. This results in precipitation of sodium tetrachloroaluminate(III) and a shift in the equilibrium from acidic $[Al_2Cl_7]^-$ to neutral $[AlCl_4]^-$, as shown in Equation 11.

$$[C_2mim][Al_2Cl_7] + NaCl \rightarrow [C_2mim][AlCl_4] + Na[AlCl_4]\downarrow \quad (11)$$
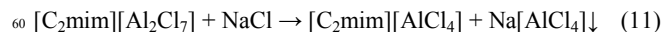
The same effect can be achieved using a range of organic bases, such as pyridine, although this also results in the introduction of additional protic-cations.

Buffered chloroaluminate systems have wide electrochemical window of a neutral composition. Also the ^{27}Al NMR signal is identical with that of neutral system. At the same time, they do display behaviour called ***latent acidity***. Unlike the 'truly' neutral systems, they can interact with bases and catalyse reactions, although their acidity is mitigated to a certain extent by the buffer.[159] This phenomenon was used in catalytic applications, where unbuffered chloroaluminate(III) systems were too active, yielding unwanted by-products, and buffered systems offered moderate acidity and improved selectivity.

As emphasised a number of times, the behaviour observed for chloroaluminate(III) systems cannot be directly extrapolated to other systems. For example, it was demonstrated that chlorogallate(III) systems also can be buffered with NaCl, but in this case the buffered composition remains slightly acidic. [71]Ga NMR signal resembles that of unbuffered $\chi_{AlCl_3} = 0.51$ composition. Moreover, electrodeposition from the buffered system is possible, giving deposits with superior morphology. The buffering to mild acidity can be attributed to higher tendency of Ga(III) to form oligomeric chlorogallate(III) anions; in the equation analogous to Equation with Al, the equilibrium is shifted more to the left, with some $[Ga_2Cl_7]^-$ still present in the buffered system.

3.3. Measurement of Lewis acidity

3.3.1. Stoichiometric probes

We all know that sulphuric acid is stronger than acetic acid. This is because their acidity – Brønsted acidity – has been long measured and quantified in a variety of scales: pH, pKa, Hamett acidity – to mention just the most common ones. The situation is fundamentally different with Lewis acids – and for a fundamental

reason. In Brønsted acids, proton is the agent of acidity. The freedom of proton, the ability of acid to protonate a base, is the universal measure. In contrast, Lewis acids are characterised by having a free LUMO, available to interact with HOMO of a base.
5 Each Lewis acid has different size of LUMO, hence the strength of interaction with base will be different. As a simple example, the affinity of Al(III)-based acids to O-donors and S-donors is different to the affinity of Ga(III)-based acids to the same donors, due to the differences in the orbital sizes, both on the HOMO and
10 LUMO sides.

Lacking the universal probe, methods to measure Lewis acidity are based mainly on choosing an arbitrary one, and measuring the strength of its interaction with different acids by spectroscopic means.

15 Yang and Kou[160] adapted techniques used to characterise solid acids, based on changes in the vibrational spectra of surface condensed basic probes such as pyridine or acetonitrile,[161] to determine the Lewis acidity of chlorometallate ionic liquids containing $CuCl$, $FeCl_3$, $ZnCl_2$, and $AlCl_3$. The authors reported
20 that the acidity followed the order Cu(I) < Fe(III) < Zn(II) < Al(III) for $\chi_{MCln} = 0.66$. Moreover, at the compositions where neutrality could be expected based on stoichiometry ($\chi_{MCln} = 0.50$ for M = Cu, Fe, Al, and $\chi_{ZnCl2} = 0.33$), a free pyridine signal was observed for each sample, indicative of the lack of acidity. The
25 same methodology as been employed using acetonitrile for other ionic liquids[162] including cholinium chlorozincates(II).[163]

Xin et al[164] demonstrated that, unsurprisingly, replacing chlorides coordinating to the metal centre with bromides or iodides enhances Lewis acidity of the chlorometallate ionic
30 liquids, which for $\chi_{AlCl3} = 0.67$ was demonstrated to increase in the following order: $[C_4mim]Cl\text{-}AlCl_3$ < $[C_4mim]Br\text{-}AlCl_3$ < $[C_4mim]I\text{-}AlCl_3$.

Although these measurements are simple, the molecular probes (pyridine, acetonitrile etc.) are used at levels approaching
35 stoichiometric which can significantly perturb the anion equilibrium and consequentially do not report on the acidity of 'pure' ionic liquids.

3.3.2. Gutmann Acceptor Number

A much less invasive approach is to measure the Gutmann
40 Acceptor Number (AN).[165] The strength of interaction of a Lewis basic probe, triethylphosphine oxide (tepo), with the ionic liquid environment can be determined using ^{31}P NMR spectroscopy. The change in ^{31}P NMR chemical shift, extrapolated to infinite dilution, reports directly on the AN. Crucially, since typically
45 three small quantities of tepo are solubilised in ionic liquid to extrapolate to infinite dilution, the bulk equilibria are assumed to remain unaffected. Moreover, since data for a wide range of molecular acids (both Brønsted and Lewis) have been measured, this approach also allows the acidities of ionic liquids to be
50 compared directly to 'traditional' acids.

AN values for neat and buffered chloroaluminate(III) ionic liquids were initially measured by Osteryoung and co-workers.[159,166] This studies were recently expanded to other systems, including Group 13 metals,[156] Zn(II)[167] and Sn(II)[48,168]
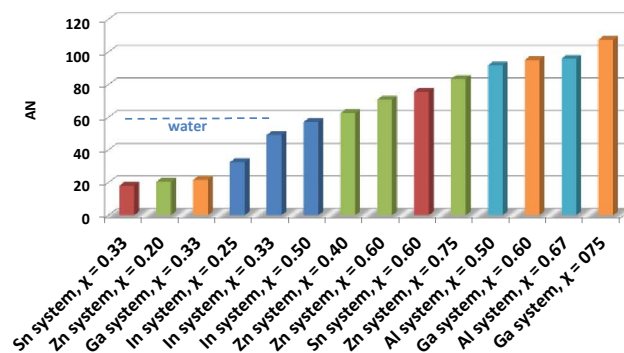55 (Figure 27).

Figure 27. Comparison of AN values for several chlorometallate systems based on 1-octyl-3-methylimidazolium cation reproduced from Ref. 156.

3.3.3. XPS measurements

60 Licence and co-workers[58] studied changes in Zn $2p_{3/2}$ binding energies of various compositions of the $[C_8mim]Cl\text{-}ZnCl_2$ system as a probe of Lewis acidity. These were in a very good correlation with AN values measured for the corresponding system by Estager et al.[27] (Figure 28).
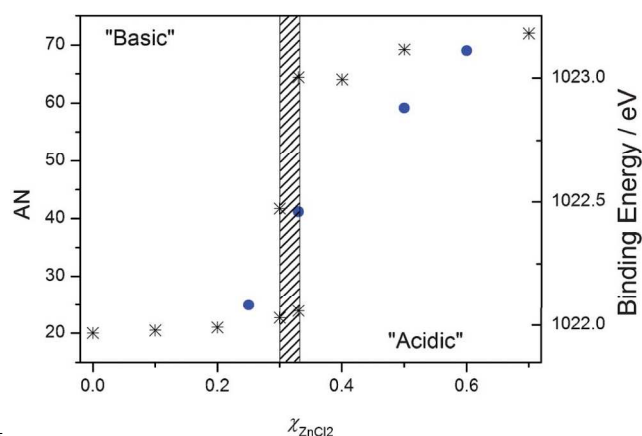

65 Figure 28. Plots of AN values calculated by Estager et al.[27] (black stars) and Zn $2p_{3/2}$ binding energies (blue circles) against composition, χ_{ZnCl2}, of the $[C_8mim]Cl\text{-}ZnCl_2$ system. The neutral zone is shown as a shaded region between $\chi_{ZnCl2} = 0.3$ and 0.33 (reproduced from Ref. 58).

70 XPS appears to be a powerful and elegant tool to obtain information about speciation, simultaneously investigating acid-base interactions in the neat ionic liquid, without the requirement for a spectroscopic probe. The main drawback is that the method is less universal than Gutmann AN measurements,
75 because it is tied to the binding energy of the studied metal, making comparison between different systems difficult. Furthermore, as already mentioned, data acquisition and analysis requires XPS machine and expert training. In conclusion, it appears that the two approaches: XPS studies and AN
80 measurements are very compatible, the former offering breadth of information on the neat system, the latter benefiting of the simplicity of use and possibility of comparison across the range of known acids of any kind.

3.4. Brønsted acidity

85 As described in the section on hydrolysis, the presence of water or other protic species (i.e. Brønsted acid) can have a profound influence on the properties of chlorometallate ionic liquids.

Dissolving HCl in basic chloroaluminate(III) systems leads to

formation of $[HCl_2]^-$ anions through complexation of HCl with excess Cl^-.[169] Adding HCl to acidic compositions leads to coordination of the Cl^- with $[Al_2Cl_7]^-$ anions and formation of 'free' superacidic protons[170] following Equation 12.

$$HCl + [Al_2Cl_7]^- \rightarrow H^+ + 2[AlCl_4]^- \qquad (12)]^-$$
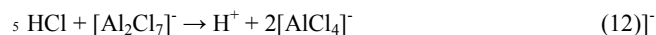
As a matter of fact, a small amount of adventitious protons arising from residual moisture is always present in chloroaluminate(III) ionic liquids, unless removed using strong bases and handled with utmost care.

Smith et al[171] measured Hammett constants for protons in chloroaluminate(III) ionic liquids, obtaining values as low as -18 when HCl was dissolved in acidic the $[C_2mim]Cl-AlCl_3$ ($\chi_{AlCl3} = 0.66$). It is this Brønsted acidity that is responsible for a many of the acid-catalysed processes reported for chloroaluminate(III) systems as solvent (*viz.* isomerisation of hydrocarbons[172]). For a comprehensive review of Brønsted acidic ionic liquids see Johnson, Pagni and Bartmess.[173]

4. Applications

4.1. Catalysis

The three key features of chlorometallate ionic liquids which lend them to catalysis are (i) controllable acidity, (ii) ability to dissolve metal complexes and act as ligands/co-catalyst and (iii) the potential to engineer simple separations of heterogeneous liquid catalysts from product streams. This is particularly valid within the petrochemical sector since most aliphatic hydrocarbon oligomers and polymers are typically poorly soluble in the ionic liquids.
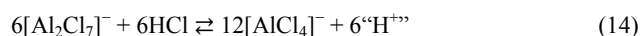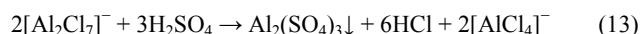
4.1.1. Acid Catalysis

Chloroaluminate(III) ionic liquids. The primary area of interest has been the use of acidic chloroaluminate(III) systems for industrial Friedel-Crafts alkylations and acylations, as well as oligomerisation and isomerisation reactions of olefins and aromatics. These transformations provide routes to upgrade light hydrocarbon feedstocks to fuels (octane enhancement, dimerisation and isomerisation), surfactant intermediates (linear alkyl benzenes for sulfonation, alkylation) and lubricants (polyalphaolefins, oligomerisation).

The most interesting new developments come from promoting and controlling the Brønsted superacidity in these Lewis acidic ionic liquids. For example, a pilot-scale oligomerisation of olefins process at BP[174] and an alkylation of benzene process by Akzo-Nobel[175] use acidic chloroaluminate(III) ionic liquids with protic cations, $[HN_{1\,1\,1}]Cl-AlCl_3$, $\chi_{AlCl3} = 0.66$, as catalysts. Zhang *et al.*[176] have also reported isomerisation of *n*-pentane with $[HN_{2\,2\,2}]Cl-AlCl_3$, $\chi_{AlCl3} = 0.67$. Huang *et al.*[177] and Wang *et al.*[178] have explored the isomerisation of dicyclopentadienes, which is a valuable route to high energy density hydrocarbons. The authors report near quantitative endo- to exo- isomerisation of tetrahydrodicyclopentadiene (THTCPD), with total selectivity,

when using heterogenised acidic chloroaluminate(III) ionic liquids in montmorillonite clays.[179] In contrast, the use of $[Hpy]Cl-AlCl_3$ system, $\chi_{AlCl3} = 0.65$,[180] led to further internal cyclisation to diamondoids, including adamantane (tricyclo[3.3.1.13.7]decane) and tetramethyleneadamantane (Figure **29**). Exo-THTCPD is a valuable compound used in JP-10 aviation fuel, and the authors note that the endo-cyclopropyl fragment of THTCPD cannot be isomerised by $AlCl_3$. The differences in selectivity result probably from the changes in Brønsted superacidity arising from the use of protonated cations addition to Lewis acidity.

Jess and co-workers[181,182] explored the influence of various proton sources: water, acidic cation exchange resins, or 1-(4-sulfobutyl)-3-methylimidazolium hydrogensulfate, on the alkylation of but-2-ene with butane in acidic chloroaluminate ionic liquids ($\chi_{AlCl3} = 0.55 - 0.66$). They report that incorporating Brønsted acidic protons in the Lewis acidic chloroaluminate(III) ionic liquids promoted the formation of branched oligomers, especially trimethylpentane, giving research octane numbers comparable, or greater than, those obtained using concentrated H_2SO_4 as a catalyst. Meyer and Wasserscheid[183] also showed that a Brønsted superacidic ionic liquid capable of catalysing isomerisation of *n*-octane to isooctanes could be prepared by adding sulphuric acid to Lewis acidic chloroaluminate(III). They proposed that Brønsted superacidity was promoted the through the precipitation of aluminium sulfate which displaces the anion equilibria generating 'naked' protons (Equations 13 and 14).

$$2[Al_2Cl_7]^- + 3H_2SO_4 \rightarrow Al_2(SO_4)_3\downarrow + 6HCl + 2[AlCl_4]^- \qquad (13)$$

$$6[Al_2Cl_7]^- + 6HCl \rightleftarrows 12[AlCl_4]^- + 6\text{``}H^+\text{''} \qquad (14)$$

Overall, this is equivalent to the addition of HCl, as described in Section 3.4.

Other chlorometallate systems. Although many chlorometallate systems are known, and have been described in earlier sections, there are comparatively few examples where the differences in their performance as acid catalysts have been assessed, beyond yes/no stage-gates for reactivity. Where comparisons have been made, these are usually found under the pretext of forming empirical "acidity scales", or aiming to alleviate some of the problems arising from the hydrolysis of chloroaluminates(III) ionic liquids. It is worth pointing out that as AN measurements have shown,[156] most chlorometallate ionic liquids (irrespective of metal type, or mole fraction metal chloride present) present lower Lewis acidity than that of 'acidic' chloroaluminate(III) systems. This is exemplified by the alkylation of benzene using *p*-formaldehyde[184] and dichloromethane[185] as C1 fragments catalysed by acidic chlorometallate ionic liquids (with Al(III), Fe(III), Cu(II), Zn(II), Sn(II) and Sn(IV) based anions) where the greatest activity was observed with chloroaluminate(III) ionic liquids.

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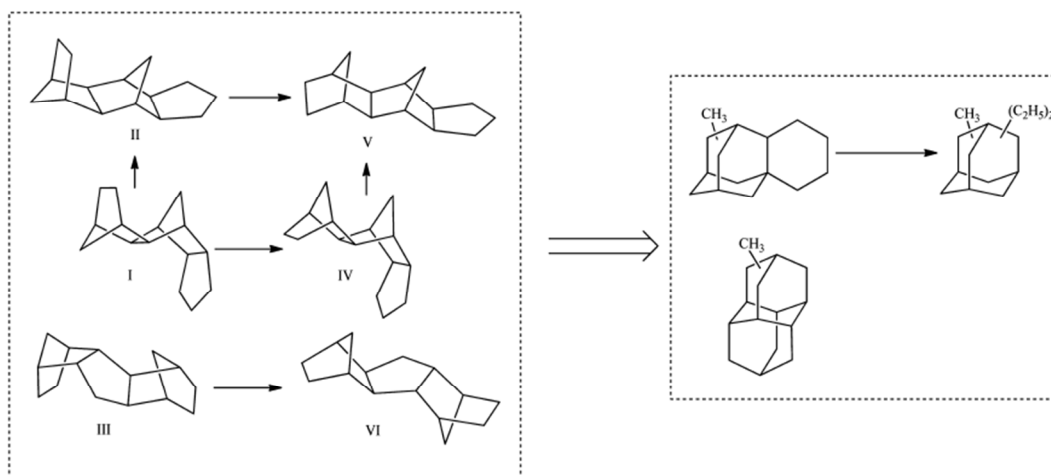Dynamic Article Links ▶

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Figure 29. Isomerisation and rearrangement pathways of tetrahydrodicyclopentadiene (THTCPD) leading to diamondoids reproduced from Ref. 180 with permission from Elsevier.

However, despite (or because of) the extreme activity of chloroaluminate(III) systems, it is often beneficial to move onto milder catalysts. Gunaratne et al.[186] showed how phenols and catechols could be alkylated in weakly acidic chloroindate(III) ionic liquids, with good control over selectivity, preventing polyalkylation that would occur using stronger acids. Moreover, chloroindate(III) did not react with hydroxo groups of the reactants, which is a major impediment for using chloroaluminate(III) systems in such reactions. Atkins et al.[187] used acidic chlorogallate(III) ionic liquids to oligomerise 1-pentene, producing lubricant base oils with high yields of desirable C20-C50 hydrocarbons. Again, this was in contrast to chloroaluminate(III) analogues, which under the same conditions yielded high-MW polymers. Oligomerisation of isobutene catalysed with chloroferrate(III) ionic liquids has been studied by Yang and co-workers.[188] When a protic cation, $[HN_{222}]^+$, which provided a source of Brønsted acidic species, was combined with acidic chloroferrate(III) compositions, high selectivities to di- and tri-isobutene oligomers were reported, and when Cu(I)Cl was added, producing mixed metallate $[HN_{222}]Cl$-$FeCl_3$-CuCl (1 : 1.5 : 0.1-0.3) systems, both conversion and selectivities to di- and tri- (C8 and C12) products were enhanced.

Kim and Varma[189] reported that chlorogallate(III) ionic liquids were better than the chloroindate(III) equivalents for the acetalysation of benzaldehyde. Since GaCl₃ is a stronger Lewis acid than InCl₃, this is as anticipated. However, the experiments were performed at $\chi_{MCl3} = 0.49$ (i.e. in the basic regime of the chlorogallate(III) phase diagram), where no Lewis acidity from the chlorogallate(III) system would be expected.. It is possible that the higher activity of chlorogallates(III) could be attributed to the higher activity of adventitious protons, i.e. to the partial hydrolysis of ionic liquids (which would be occurring for Ga(III) to a much greater extent). Furthermore, neutral chloroferrate(III) ionic liquids, containing [FeCl₄]⁻ anions, have been reported to be mildly acidic. This may be due to the latent acidity, the amphoteric nature of Fe(III), or to the presence of water which causes shifts in anion equilibrium comparable to those with chloroaluminates. Taking advantage of the acidity and water stability, chloroferrate(III) systems have been used to prepare 4-aryl-dihydropyrimidinones through Biginelli condensation reactions,[190] to convert trimethylsilyl ethers to acetates,[191] as mild acids for the deprotection of aryl aldehyde bisulfite adducts[192] and ethers to aldehydes and ketones.[193] Gao[194] and Wang[195] have both reported that $[C_4mim][FeCl_4]$ can be used as a mild Lewis acidic catalyst for the benzylation of various arenes to form diarylmethane derivatives. It is worth noting that the water-tolerant (cf. anhydrous FeCl₃) and magnetic characteristics[196] of chloroferrate(III) systems present interesting opportunities for novel reaction and separation processes. The material properties of chloroferrate(III) ionic liquids are discussed in the appropriate section of this review.

Mixed metal Lewis acidic systems. Liu et al.[126] have used the $[HN_{111}]Cl$-$AlCl_3$-CuCl (1:1:1) system, containing the $[CuCl(AlCl_4)]^-$ anion, for the alkylation of isobutane with 2-butene, forming trimethylpentane. Zinurov et al.[197] describe using the acidic $[HN_{111}]Cl$-$AlCl_3$ ionic liquid doped with copper(II) salts as catalysts for the oligomerisation and isomerisation of n-pentane. The authors report that oligomers are formed when copper(II) chloride was added, whereas addition of copper(II)sulphate increased isomerisation (to isopentane).

Stenzel[198] et al. examined olefin oligomerisation in slightly acidic $[C_4mim]Cl$-$AlCl_3$ ionic liquids. Adding ethylaluminium dichloride did not influence the oligomerisation reaction, whereas adding titanium tetrachloride led to the formation of high yields of branched, atactic polymers with narrow monomodal polydispersities. This contrasts with the polymerisation of ethene by titanium tetrachloride in toluene where mainly linear polyethene with broad polydispersity and a higher molar mass are

obtained. Azizov *et al.*[199] also describe the use of titanium compounds as modifiers in chloroaluminate ionic liquids; saturated oligoalkylnaphthenes were obtained with a narrow molecular mass distribution (M_w/M_n = 1.03-1.55) from hex-1-ene.

4.1.2. Chlorometallate anions as ligands

Adding metal salts to chlorometallate ionic liquids can either lead to changes in the chlorometallate anion activity through extraction or chloride ligands as described above, or to coordination of the added metal ions by chlorometallate anions. This 'feature' was one of the key advantages highlighted by Parshall in 1972,[9] for using $PtCl_2$ dissolved in chlorogermanate(II) and chlorostanate(II) ionic liquids as catalysts for the carbonylation and hydrogenation of olefins. Based on the isolation and identification of different species from the reaction media including $[(C_2H_5)_4N]_3[Pt(SnCl_3)_5]$ and $[(C_2H_5)_4N]_3[HPt(SnCl_3)_4]$ after hydrogenation, the catalytic cycle shown in Figure 30 was proposed for the hydrogenation of ethylene, in which the platinum catalyst remains coordinated and stabilised by nucleophilic chlorostanate(II) anions as an anionic complex within the ionic liquid.
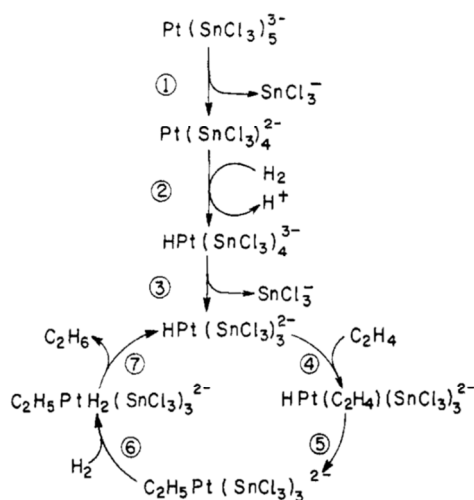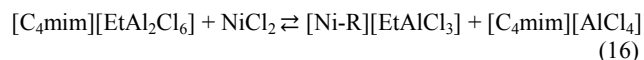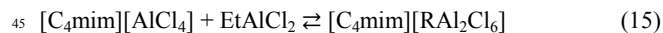

Figure 30. Mechanism proposed by Parshall for Pt-catalysed hydrogenation of ethane in $[SnCl_3]^-$ ionic liquids, showing the reversible steps (1-6) around the chlorostannate coordinated Pt catalyst (reproduced with permission from Ref. 9).

The ability of trichlorostannate(II) and trichlorogermanate(II) anions to coordinate to metal centres is a consequence of the stereochemically active lone-pair present in tin(II) and germanium(II). Formation of active catalytic species through complexation of nickel(II) centres in chloroaluminate(III) ionic liquids provides the key improvement within the IFP Difasol process for olefin dimerisation, as highlighted by Chauvin in his Nobel prize lecture.[16]

The best known example of catalysis in mixed-metal ionic liquids is the Difasol process developed by Chauvin and co-workers at the IFP[15,200,201] as an advance over their conventional, commercial Dimersol olefin oligomerisation technology. Dimersol makes use of trialkylaluminium and nickel(II) complexes to generate a Ziegler-Natta catalyst. In the Difasol modification, trialkylaluminium reagents are substituted by 1,3-dialkylimidazolium alkylchloroaluminate(III) ionic liquid. The ionic liquid acts as a Lewis acidic co-catalyst, forming and maintaining the Ziegler-Natta catalytic species within the ionic liquid, as shown in Equations 15 and 16.

$$[C_4mim][AlCl_4] + EtAlCl_2 \rightleftarrows [C_4mim][RAl_2Cl_6] \quad (15)$$

$$[C_4mim][EtAl_2Cl_6] + NiCl_2 \rightleftarrows [Ni-R][EtAlCl_3] + [C_4mim][AlCl_4] \quad (16)$$

'Basic' compositions (χ_{AlCl3} < 0.5) of the ionic liquid are not catalytically active due to the formation of anionic $[NiCl_4]^{2-}$ species, whereas in the acidic compositions it is presumed that active Ni-sites are coordinated by $[AlCl_4]^-$. Moreover, as the feed and oligomeric products are both poorly soluble in the ionic liquid catalyst (*cf* homogeneous reaction with the Dimersol catalysts) the process can be run in a semi-continuous batch operation with simple separation of products and recovery of the active liquid catalyst (see Figure 31). The Difasol process is reported to give C8 yields 10% higher than for homogeneous systems with lower consumption of nickel and with no ionic or metal contamination in the products, simplifying the unit operation.

Subsequently, oligomerisation reactions have been investigated in [cation]Cl-AlCl$_3$-Ni(II) ionic liquid systems by many groups. For example, Pei *et al.*[202] performed biphasic oligomerisation of ethylene. Thiele and de Souza[203] and Eichmann *et al.*[204] have examined the effects of different aluminium species and ligands respectively.

Addition of secondary metal components to chlorometallate ionic liquids in order to modify or moderate their activity has not been limited to Al/Ni systems. Building on the $PtCl_2/[SnCl_3]^-$ catalytic system described by Parshall,[9] Wasserscheid and Waffenschmidt[205] suggested that methyl-3-pentenoate could be hydroformylated over a $(PPh_3)_2PtCl_2$ catalyst precursor dissolved in a 'slightly acidic' chlorostannate(II) ionic liquid (χ_{SnCl2} = 0.51). The change in the acidity of the ionic liquid, on adding the $(PPh_3)_2PtCl_2$ was monitored from the ^{119}Sn NMR chemical shifts and demonstrated the interaction between the chlorostannate(II) anions and platinum centre. The mechanism for this reaction[206] reveals that first there is rapid exchange of one coordinated chloride on the platinum centre by $[SnCl_3]^-$, followed by a second slow substitution forming $Pt(PPh_3)_2(SnCl_3)_2$.

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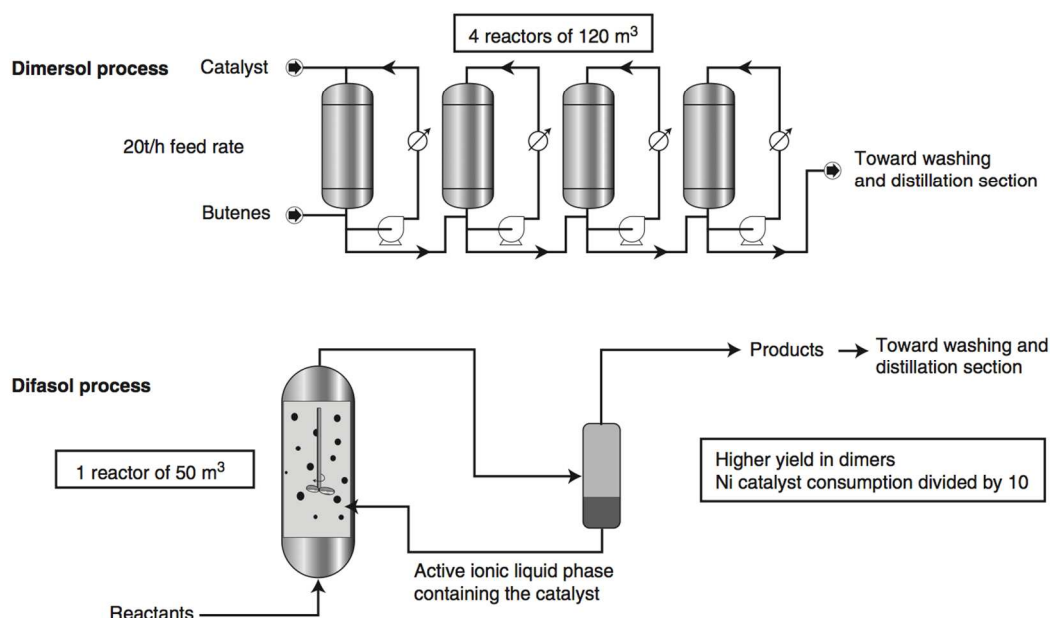**Chemical Society Reviews**

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Figure 31. Comparison of Dimersol and Difasol processes as an example of the process intensification possible using catalytic biphasic ionic liquid systems (reproduced from Ref. 15).

4.1.3. Basic catalysis

As discussed earlier, *basic* chlorometallate ionic liquid compositions contain an excess of free chloride anions. Under such conditions, the metal ions present may be coordinatively saturated and so will not behave (typically) as Lewis acids.

The most prominent developments in recent years have focussed on the isomerisation and dehydration of sugars in ionic liquids. The transformation of C5 and C6 sugars (mainly fructose and glucose) to 5-hydroxymethylfurfural (HMF) has been proposed as a key step in the generation of liquid hydrocarbon fuels from biomass resources (see Figure 32).
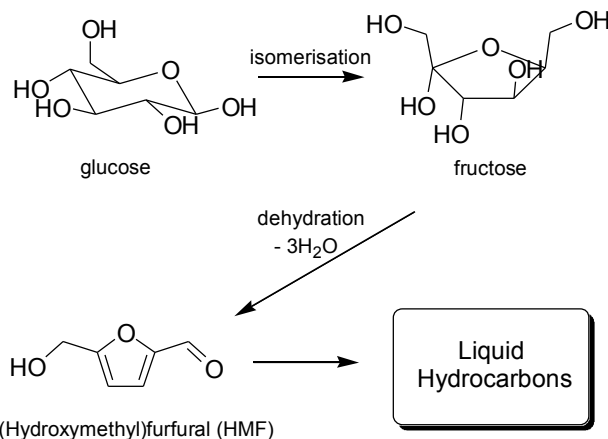

Figure 32. Glucose to fructose isomerisation followed by dehydration to HMF has been proposed as a route to obtain liquid hydrocarbons from biomass.

In 2007, Zhang and co-workers[207] reported that a wide range of metal chlorides ($CrCl_2$, $CrCl_3$, $FeCl_2$, $FeCl_3$, $CuCl$, $CuCl_2$, VCl_3, $MoCl_3$, $PdCl_2$, $PtCl_2$, $PtCl_4$, $RuCl_3$, or $RhCl_3$) dissolved in chloride-based ionic liquids could be used to catalyse the dehydration of fructose at 80 °C. Some metal chlorides (including alkali chlorides, $LaCl_3$ and $MnCl_2$) were noted to be ineffective. Glucose, in contrast, was found to be much more difficult to dehydrate, with only $CrCl_2$ from the range of metal chlorides screened yielding high conversions of glucose to HMF. Following on from this report, many groups have examined the same reactions with a range of chloride-based ionic liquids.[208-217]

The most challenging task appears to be in understanding the mechanism of the process and elucidation of the active chromium species. Zhang and co-workers[207] rationalised their results in terms of two separate steps; glucose isomerisation to fructose, followed by fructose dehydration. The latter step can be readily promoted by many metal salts dissolved in ionic liquids (and even by chloride-based ionic liquids containing no additives), whereas for glucose→fructose isomerisation, only $CrCl_2$ was effective from the initial screen. They proposed that $[CrCl_3]^-$, formed by dissolution of $CrCl_2$ in $[C_2mim]Cl$, coordinated to the glucose hydroxyl groups facilitatating mutarotation and effecting a formal hydride transfer to allow isomerisation of glucose to fructose. The free-energy barriers to the mechanism with four different metal chlorides (WCl_3, $MoCl_3$, $CrCl_3$ and $FeCl_3$) have been explored using DFT by Guan *et al*.[218] who suggested that WCl_3 may be a more promising catalyst for low temperature transformations.

However the mechanism for the initial aldose to ketose

transformation has been questioned by Binder *et al.*[219] who proposed, on the basis of H/D isotopic labelling studies, that this occurs *via* a different 1,2-hydride shift with the metal coordinated to the carbonyl-group of the sugar. This mechanism was
5 supported by detailed *ab initio* and EXAFS studies by Pidko *et al.*[220] who proposed the catalytic cycle shown in Figure 33.
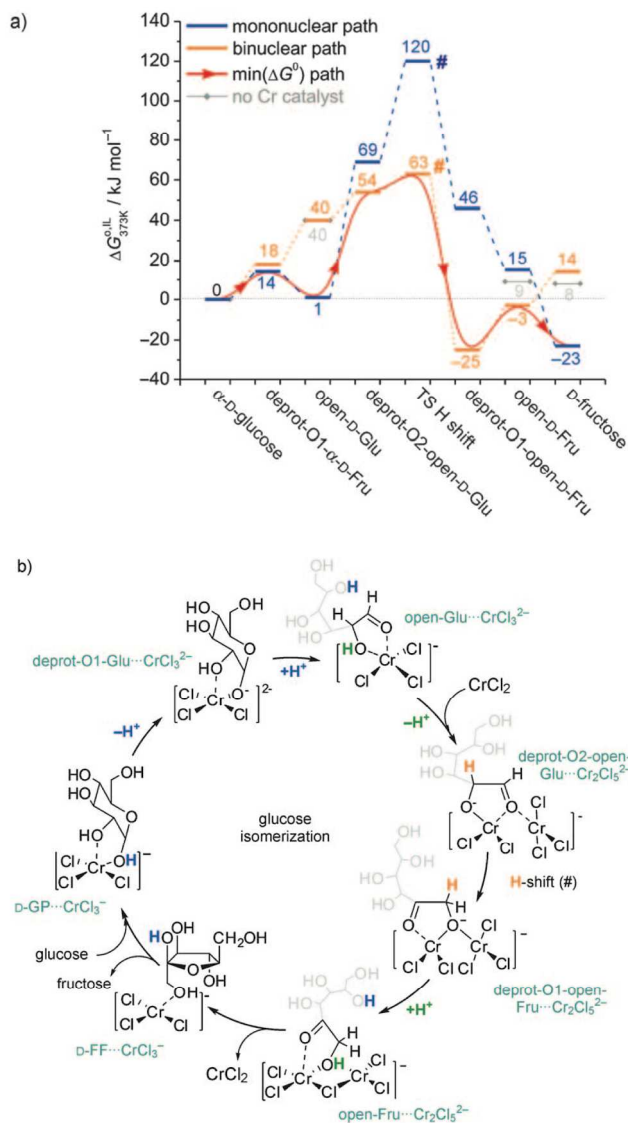

Figure 33. (a) *Ab initio* determined energy pathway for glucose
10 isomerisation involving mono- (blue) and binuclear (orange) CrII complexes with the carbohydrate in a model MMIM ionic liquid. The red line highlights the path of lowest free energy. (b) The proposed catalytic cycle corresponding catalytic cycle for the isomerisation of glucose in the presence of CrCl₂ in a model MMIM ionic liquid medium. d-FF =
15 d-fructofuranose, d-GP = d-glucopyranose (reproduced from Ref. 220 with permission from Wiley).

It is noteworthy that Pidko postulated Cr(II) to be a *transient* catalyst. Considering that Cr(II) can be readily oxidised to Cr(III) even by water, led Bali *et al.*[221] to question whether Cr(II) was
20 the active species and to propose Cr(III) instead. It is worth noting in this context that ionic liquids containing high concentrations of chlorochromate(III) anions, prepared from choline and $CrCl_3 \cdot 6H_2O$, have been described by Abbott and

co-workers.[150] Most recently, mixed metal chlorides systems
25 combining $CuCl_2$ (as the primary metal chloride) with $CrCl_2$,[222] $PdCl_2$ and $FeCl_3$,[223] or $CrCl_2/RuCl_3$[224] in [C₂mim]Cl have been reported to be effective for combined hydrolysis of cellulose and subsequent dehydration the glucose oligomers to HMF. These have been reported exhibit greater activity than corresponding
30 single metal systems, for example with enhanced yield of HMF using $CuCl_2:CrCl_2$ at ratio of 0.17:0.83 compared to either sole metal chloride (Figure 34). The nature of the cooperative effects or metal-speciation in the ionic liquids is not fully understood.

Mixed halide systems also have been reported to be more
35 effective than solely chloride-containing ionic liquids. For example, using chromium and tin chlorides in bromide ionic liquids,[225] or mixtures of CrX_3 (X = F, Cl, Br) in chloride ionic liquids.[226]

Buxing Han and co-workers[227] found that $SnCl_4$ in a range of
40 ionic liquids could also catalyse conversion of glucose to HMF. Conversion was poorer in ionic liquids containing coordinating anions, such as Cl⁻, compared to those based on weakly coordinating anions, *e.g.* [BF₄]⁻. The reaction was proposed to take place *via* the formation of a five-membered ring chelate
45 complex of Sn(IV), and coordinating anions compete with glucose for the metal centre, inhibiting the catalytic cycle.
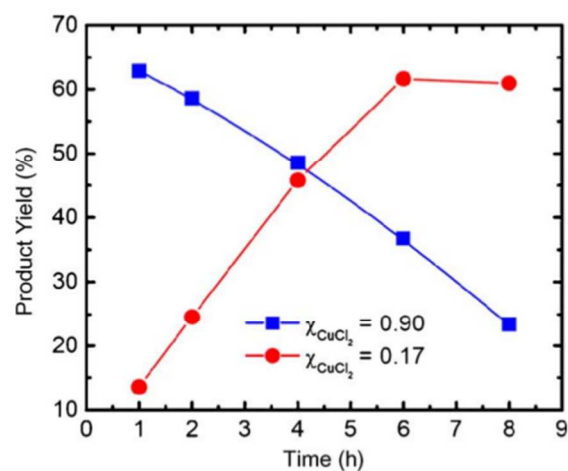

Figure 34. Changes in yield of cellulose hydrolysis products generated using mixed $CuCl_2/CrCl_2$ catalyst precursors at 120 °C at different Cu:Cr
50 ratios (reproduced from Ref. 222 with permission from Elsevier).

4.2. Separations

4.2.1. Extraction of aromatics and olefins from hydrocarbons

Huang and co-workers[228] have examined the use of acidic chloroaluminate(III) ionic liquids with [C₄mim]⁺, [(CH₃)₃NH]⁺,
55 and [(CH₃CH₂)₃NH]⁺ cations for the extraction of aromatics from aromatic/alkane mixtures and report good extraction (selectivity) and high solvent capacities. Enhanced selectivity (higher aromatic solubility and lower aliphatic solubility) was observed with imidazolium-based ionic liquids compared to the
60 corresponding protic ammonium systems, and with increasing acidity (from $\chi_{AlCl_3} = 0.55$ to 0.66). Although the imidazolium system showed better performance, the protic ammonium systems were favoured due to lower cost and the ability to recycle the ionic liquids by vacuum distillation.
65 However, the feasibility of using chloroaluminate(III) systems for such separations remains questionable. Their main drawbacks

are the lack of hydrolytic stability and the possibility of undesired acid-catalysed reactions, such as cracking, oligomerisation or alkylation. On the other hand, such reactions may be beneficial. For example, Shi and co-workers[229,230] reported that the olefin
5 content of fuels can be reduced by contacting with acidic chloroaluminate(III) ionic liquids. It is likely that, in addition to physical extraction, alkylation reactions could account for the net reduction in the number of olefinic compounds in the feeds.

4.2.2 Desulfurisation of fuels

10 Physical and chemical (oxidative) extraction of N- and S-compounds from liquid fuels has been extensively studied. Jess *et al.*[231] were the first to use ionic liquids for the deep desulfurisation of fuels, *i.e.* removing polyaromatic sulfur (PAS) compounds, which are not removed in standard HDS processes
15 and found that chloroaluminate(III) systems gave the best performance in terms of both separation and selectivity.[232] Meindersma and co-workers[233] found similar results, , but concluded that chloroaluminate(III) systems were not suitable for industrial practice due to their sensitivity to moisture and
20 competing acid-catalysed reactions as discussed above.

The use of chlorometallate ionic liquids for oxidative desulfurisation (ODS), where PAS compounds are oxidised with hydrogen peroxide to sulfones and sulfoxides (Figure 35), was considered as more feasible. In ODS, the ionic liquid acts a
25 reservoir for the oxidant (hydrogen peroxide), as an acid catalyst to promote the formation of the reactive peroxyacids needed for oxidation, as the initial extracting phase for PAS compounds (exemplified by dibenzothiophene), and finally as an extracting phase for the resultant oxidised products.
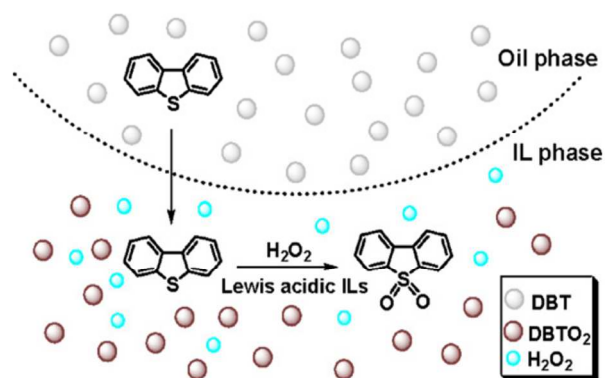

30
Figure 35. Schematic oxidative desulfurisation (ODS) with hydrogen peroxide using an ionic liquid as both the extractant phase and oxidation catalyst (Reproduced from Ref. 235 with permission from Elsevier).

ODS studies using numerous water-tolerant metallate ionic
35 liquids, such as chloroferrates(III), $\chi_{FeCl3} = 0.50$,[234] have been reported. Recently Chen *et al.*[235] has compared the performance of different chlorometallate ionic liquids of the general formula [C$_4$mim]Cl-MCl$_2$, where M = Zn, Fe, Cu, Mg, Sn and Co, in a range of compositions. At $\chi_{MCl2} = 0.50$, the chlorozincate(II)
40 system showed enhanced oxidative extraction, whereas little difference between pure extractive and oxidative extraction was observed with the remainder of the systems (Figure 36). This reflects on the importance of the speciation. It is known that Zn(II)-based systems form Lewis-acidic [Zn$_2$Cl$_6$]$^{2-}$ anions, hence
45 are active. Among other metals, Sn(II) forms a neutral [SnCl$_3$]$^-$

anion, Co(II) contains [CoCl$_4$]$^{2-}$ and precipitation of unreacted CoCl$_2$, *etc.* – which explains their poor activity. Furthermore, the S-removal efficiency of the chlorozincate(II) systems increased markedly with increasing χ_{ZnCl2}, and reached 99.9% S-removal in
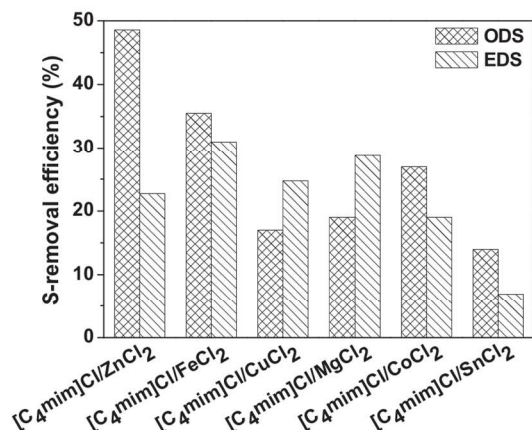50 the most Lewis acidic system when $\chi_{ZnCl2} = 0.75$, as shown in Figure 37.

Figure 36. Comparison of extractive (EDS) and oxidative (ODS) desulfurisation of model diesel oils using [C$_4$mim]Cl-MCl$_2$ ($\chi_{MCl2} = 0.5$)
55 ionic liquids with H$_2$O$_2$ as oxidant reproduced from Ref. 235 with permission from Elsevier. ODS shows pronounced enhancement with acidic chlorozincate(II) compared to other (neutral) chlorometallate(II) ionic liquids.
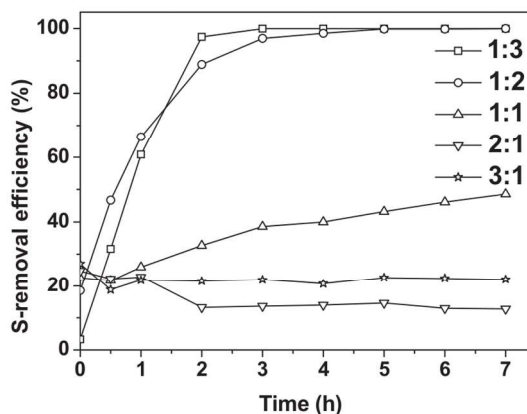

60   Figure 37. The efficiency of oxidative desulfurisation efficiency using H$_2$O$_2$ in [C$_4$mim]Cl-ZnCl$_2$ ionic liquids depends markedly on the presence of acidic chlorozincate(II) anions at [C$_4$mim]Cl:ZnCl$_2$ ratios > 1:1 as acid catalysts (reproduced from Ref. 235 with permission from Elsevier).

4.2.3. Metal ion extraction

65 In order to extract metal ions from aqueous solutions using ionic liquids, two requirements must be met: (i) hydrophobicity – that is, formation of a biphase with water, and (ii) ability to extract metal ions. These two appear initially to be at odds with each other, since the perfluorinated anions such as [PF$_6$]$^-$ and [NTf$_2$]$^-$
70 typically used to generate hydrophobic ionic liquids are poorly coordinating. Indeed, Rogers and co-workers,[236] and later Prausnitz and co-workers,[237] reported that most metal ions did not partition from aqueous (acidic) solutions to hydrophobic ionic liquids containing perfluorinated anions in the absence of specific
75 complexants.

However, for an ionic liquid where hydrophobicity is

conferred through the cationic moiety, rather than by using perfluorinated anions, then anions capable of coordinating metals – such as chloride – can be introduced. Extraction can then be driven by the transformation of typically hydrated $M^{n+}_{(aq)}$ ions to more hydrophobic metallate $[MX_m]^{(n-m)-}$ anions, which associate with the hydrophobic cations of the ionic liquid.

Of course, this is not a new concept, as solvent extraction processes using hydrophobic organic salts such as Aliquat-336^{TM} (trioctylmethylammonium chloride, from Cognis/BASF) and Cyphos-101^{TM} (trihexytetradecylphosphonium chloride, from Cytec) are routinely used in hydrometallurgy.[238] Traditionally they have been used as the active agents in supported separations membranes, or in conjunction with organic solvents to lower their viscosity. However, more recently these materials have been explored as ionic liquids, that is, as bulk liquid extractants rather than as additives.

The key features of these extraction systems are that: (i) soft metal ions, which readily expand their coordination spheres, are most effectively extracted and (ii) extraction is enhanced from solutions containing high concentrations of coordinating anions (strong electrolyte or acid). For example, Regel-Rosocka and co-workers[239],[240] compared the efficiency of removal of Zn(II) from hydrochloric acid using $[P_{6\,6\,6\,14}]Cl$ (Cyphos 101) and $[P_{6\,6\,6\,14}][NTf_2]$ (Cyphos 109) as shown in Figure 38. It illustrates the importance of the coordinating chloride anions in Cyphos 101 compared to non-coordinating $[NTf_2]^-$ in Cyphos 109 in order to facilitate the extraction of Zn(II) through the formation of chlorozincate(II) anions. Heterogenised Cyphos 101, impregnated into amberlite XAD-7 resins,[241] and PVC membranes[242] has also been used for Zn(II) extraction. Moreover, alginate beads incorporating Cyphos 101 were studied for the extraction of Zn(II), Hg(II),[243] Au(III)[244] and Cd(II) from acidic media.[245]
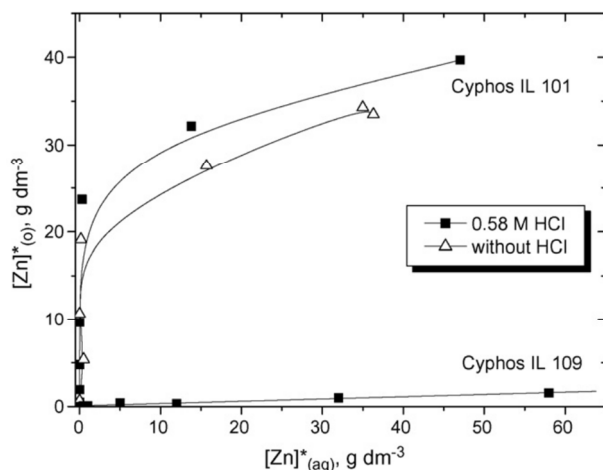

Figure 38. Comparison of the extraction of Zn(II) with Cyphos 101 and 109 showing the importance of the chloride anions present in Cyphos 101 to enable extraction (reproduced from Ref. 239 with permission from Elsevier).

Cieszynska and Wisniewski[246] used Cyphos 101 diluted with toluene to selectively extract of Pd(II) from different hydrochloric acid solutions. In the case of 0.1 M HCl solution, Pd(II) was extracted over Ni(II), Cu(II), Pb(II), Fe(III), Rh(III) and Ru(III), however, from 3 M HCl solution, the selectivity with respect to

Pb(II) and Fe(III) decreased. The results were rationalised in terms of the relative speciation of the different metals at 0.1 and 3 M HCl. At low acidity, Fe(II), Ni(II), Cu(II) and Pb(II) are present mostly as cationic and neutral species, whereas Pd(II) forms the $[PdCl_4]^{2-}$ anion. At higher acidity, all the metals form chlorometallate anions, reducing extraction selectivity. Similar results have been reported using mixed trioctylammonium-based ionic liquids to recover platinum and palladium.[247],[248]

Kebiche-Senhadji and co-workers[249] achieved selective extraction of Cr(VI) over other metal ions using Aliquat-336 bound in polymer inclusion membranes, while Goyal et al.[250] similarly reported chromium ion extraction using liquid emulsion membranes containing tetraoctylammonium chloride, with $[C_4mim][NTf_2]$ as a stabiliser.

The enhanced extraction of soft metals enabled selective Co(II)/Ni(II)[251] and Fe(III)/Ni(II)[252] separations using immobilised Cyphos-101. In both cases, the softer metal ions (cobalt or iron) was extracted in preference to nickel. Following the same principle, selective separation of transition metals (Cu, Co, Mn, Fe) from rare earths was achieved, with the transition metal ions selectively extracted to Cyphos 101.[253] Wellens et al.,[74] reported the Co(II)/Ni(II) separation using the neat Cyphos 101 ionic liquid as the extracting phase, and most recently developed this concept to a lab-scale continuous process, potentially superior to the current industrial system, one both in terms of cost and sustainability.[254] Finally, the same group accomplished the Co(II)/Ni(II) separation using a biphasic system based entirely on ionic liquids.[255] 'Hydrophilic' $[C_2mim]Cl$ phase solubilised Ni(II) in the form of $[NiCl_4]^{2-}$, and dialkylphosphinate anions in 'hydrophobic' $[P_{6\,6\,6\,14}][R_2POO]$ coordinated to softer Co(II).

4.3. Syntheses of inorganic materials

Among many reviews on inorganic chemistry in ionic liquids, Freudenmann et al.[256] have examined syntheses involving chlorometallate, mainly chloroaluminate(III), ionic liquid systems, with an emphasis on their ability to solubilise elemental metals and chalcogens. The main materials types that have been prepared from chlorometallate ionic liquids, along with typical synthetic routes, are listed in Table 3.

Table 3. Materials prepared in chlorometallate ionic liquids along with typical synthetic routes.

Type of material	Synthetic method
Metal clusters and Zintl phases	Reduction, ionothermal
NLO and semiconductors	Oxidation, ionothermal
MOFs	Ionothermal
Nanostructures	Reduction, ionothermal, electrochemical
Alloys	Electrochemical

4.3.1. Inorganic syntheses involving *in-situ* formation of halometallate ionic liquid

In a number of publications, inorganic syntheses have been performed in [cation]X (X = Cl or Br) ionic liquids, where metal halides were dissolved (often along with other reactants, such as elemental metals or chalcogens). It should be recognised that the first step of such syntheses is the formation of halometallate anions in the ionic liquid, which can then act in multiple roles as solvents, reactants and templating agents.

In 1998, Marin and Leafblad[257] reacted diethylammonium

chloride, aluminium(III) chloride and copper(I) chloride under ionothermal conditions (neat reactants, 250 °C, sealed ampoule under vacuum), to prepare microcrystalline material, $[\{(H_2N_2{}_2)_2\}_2(Cu^ICl_4)][AlCl_4]$. They named this an 'anti-zeolite'

5 because the strongly hydrogen-bonding diethylammonium cation connected tetrahedral chlorocuprate(I) anions, while the weakly-coordinating $[AlCl_4]^-$ acted as the templating agent (in contrast to zeolites, where the cation would be a template, and the anion would be the linker). It is worth highlighting the deliberate

10 choice of each reactant: the chlorocuprate(I) anion providing the tetrahedral building blocks, diethylammonium as a donor of two hydrogen bonds, and the $[AlCl_4]^-$ anion selected as it is non-coordinating, and so would not compete with $[CuCl_4]^{3-}$ as a hydrogen bonds acceptor, thus make a good template.

15   Using an analogous approach, Freudenmann and Feldmann[258] reported the preparation of $[Te_8]_2[Ta_4O_4Cl_{16}]$ from a solution of tellurium and $TaOCl_3$ dissolved in the $[C_4mim]Cl\text{-}TeCl_4\text{-}TaCl_5$ system. The same authors also prepared $[Bi_3GaS_5]_2[Ga_3Cl_{10}]_2[GaCl_4]_2 \cdot S_8$ (Figure 39) which was

20 crystallised from a solution of elemental bismuth and sulphur in $[C_4mim]Cl\text{-}GaCl_3\text{-}BiCl_3$.[259] Ionic liquids provide the ability to dissolve reactants under relatively mild conditions (*cf.* strong mineral acids) combined with good thermal stability which permits the syntheses of thermodynamically metastable

25 complexes. However, writing clearly from a solid-state chemist perspective, the authors state that the ionic liquid, $[C_4mim]Cl$, neither reacts, nor coordinates to the reactants, whereas it should be evident from the context of this review that $[C_4mim]Cl$ mixed with the metal halide salts will generate halometallate anions,

30 such as $[GaCl_4]^-$. Chlorogallate(III) anions are incorporated in the crystalline structure, balancing the charge of chalcogenide heterocubane cation.

4.3.2. Multifunctional chlorometallates for the syntheses of inorganic materials

35   Taubert and Li in their Frontiers article[260] provide a valuable discussion on the benefits of 'all-in-one' approaches to inorganic materials syntheses with ionic liquids, where metal-containing ionic liquids can have multiple roles, *e.g.* acting as solvents, precursors and templating agents.

40   Ruck and co-workers used Lewis acidic $[C_4mim]Cl\text{-}AlCl_3$ ionic liquids as both solvents and reactants in a range of room-temperature inorganic syntheses.[261] For example, the dissolution of elemental bismuth and $BiCl_3$ in $[C_4mim]Cl\text{-}AlCl_3$ (χ_{AlCl3} = 0.57) resulted in the formation of a range of bismuth

45 polycations which were identified by Raman spectroscopy. From this solution, single crystals of $Bi_5[AlCl_4]_3$ were grown. The Lewis acidic chloroaluminate(III) anions were used to abstract chloride from the bismuth salt, and the authors point out that neutral or basic compositions did not promote the formation of

50 bismuth clusters. Compared to traditional routes, using ionic liquid solvents enabled these reactions to take place rapidly under very mild conditions, and offered good stabilisation of the ionic species. They suggested that this methodology could be expanded to other systems and, indeed, a number of other metal clusters

55 have been accesses in this way. These include: $[Mo_2Te_{12}]I_6$, $Te_6[WOCl_4]_2$, $Te_4[AlCl_4]_2$,[262] $Sn[SnCl][W_3Cl_{13}]$,[263] $[Sb_{10}Se_{10}][AlCl_4]_2$[264] and two polymorphs of $[Ru_2Bi_{14}Br_4][AlCl_4]_4$ (see Figure 40).[265]
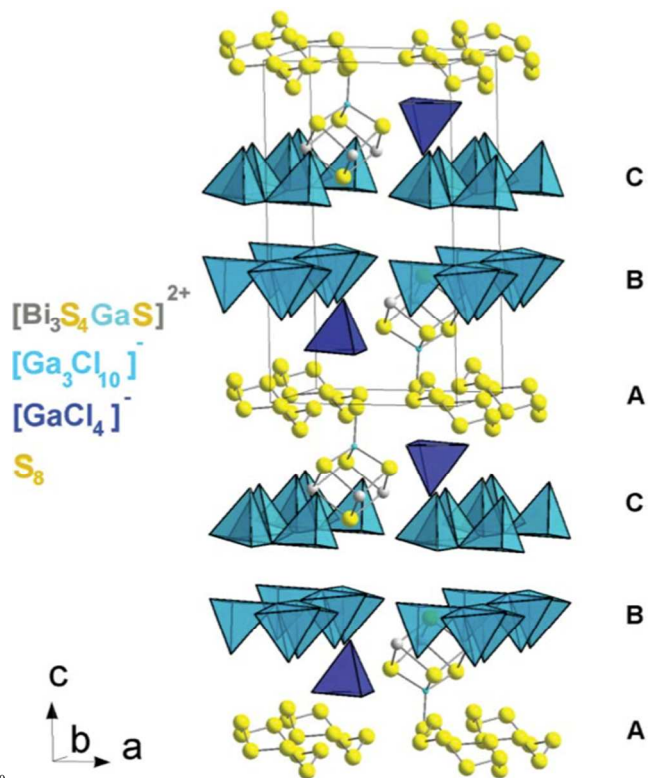
60   Figure 39. Unit cell and layer-like packing of $[Bi_3GaC_5]^{2+}$, star-shaped☐$[Ga_3Cl_{10}]^-$ (light blue), monomeric $[GaCl_4]^-$ (dark blue) and S_8 in $[Bi_3GaS_5]_2[Ga_3Cl_{10}]_2[GaCl_4]_2 \cdot S_8$. (reproduced from Ref. 259).
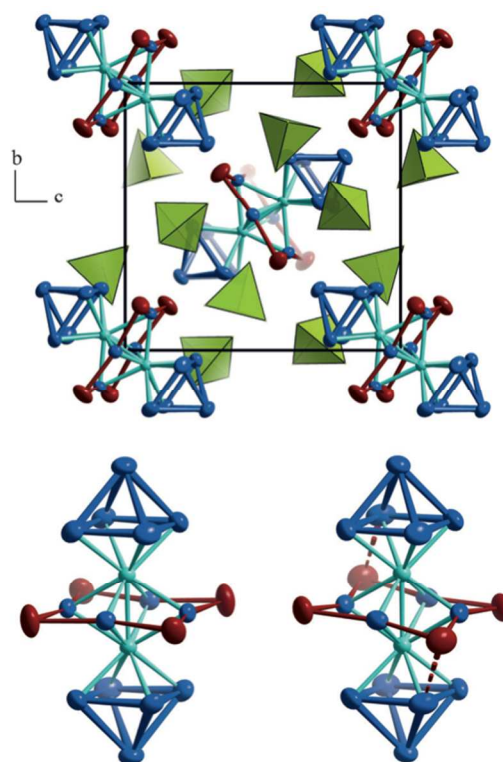
65   Figure 40. Crystal structure of β-$[Ru_2Bi_{14}Br_4][AlCl_4]$ (top) and the $[Ru_2Bi_{14}Br_4]$+ clusters in the β form (bottom left) and α form (bottom right). Bi – blue, Ru – cyan, Br – ted, $[AlCl_4]^-$ - yellow tetrahedra; thermal ellipsoids are at 70% probability level, reproduced from Ref. 265 with permission from Wiley.

A solution of elemental sulphur and antimony dissolved in neutral [C$_2$mim]Br-AlCl$_3$ was used to prepare red crystals of [Sb$_7$S$_8$Br$_2$][AlCl$_4$]$_3$ (Figure 41) *via* ionothermal syntheses (165 °C, 10 days).[266] The product exhibited non-linear optic (NLO) properties, and the authors emphasised that this was the first example of a cationic chalcogenide cluster prepared from an ionic liquid rather than the more typical anionic structures previously synthesized from molten salts.
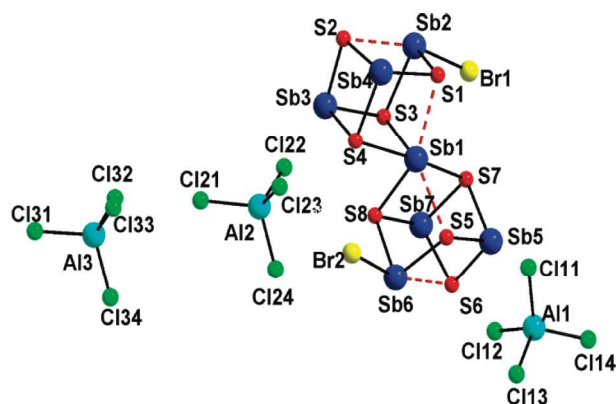

Figure 41. Structure of [Sb$_7$S$_8$Br$_2$][AlCl$_4$]$_3$ (**1**). The red dashed lines show weak Sb-S bonds (2.938-3.136 Å), reproduced with permission from Ref. 266.

Biswas *et al.*[267] prepared a direct band semiconductor material, [Bi$_2$Te$_2$Br][AlCl$_4$], using an analogous procedure, taking advantage from the ability of chloroaluminate(III) ionic liquids to enhance the reactivity of normally inert reactants such as Bi, Sb, and Te. Building on this synthetic strategy, the group subsequently reported the preparation of [(Bi$_4$Te$_4$Br$_2$)(Al$_2$Cl$_{(6-x)}$Br$_x$)]Cl$_2$ and [Bi$_2$Se$_2$Br][AlCl$_4$] semiconductors.[268]

Crystals of [C$_2$mim]$_4$[(Zr$_6$Be)Br$_{18}$] and [C$_2$mim][(Zr$_6$Fe)Br$_{18}$] have been obtained[269] after dissolution of Na$_4$[(Zr$_6$Be)Cl$_{16}$] and K[(Zr$_6$Fe)Cl$_{15}$] clusters respectively, in Lewis basic [C$_2$mim]Br-AlBr$_3$ ionic liquids. Demonstrably, both outer and inner chlorides were displaced with bromides, and since the reverse reaction had been previously been reported,[270] the authors state that such exchange is reversible, and depends on the free halide concentration.

4.3.3. Chlorometallates as precursors to inorganic nanostructures

Taubert[271] prepared CuCl nanoplatelets from [C$_{12}$py]Cl-CuCl$_2$ (χ_{CuCl2} = 0.33) systems by ionothermal reduction of Cu(II) to Cu(I) using 6-*O*-palmitoyl ascorbic acid as reductant and liquid crystalline co-templating agent. The use of ionic liquid as a solvent, precursor and a templating agent is an example of the 'all-in-one' approach, and this system has been thoroughly analysed in the subsequent publications of Taubert and co-workers.[272] However, among many factors influencing the formation and morphology of the nanoplatelets, the composition of chlorocuprate(II) anions present in the ionic liquid has not been explored, and has always been maintained at χ_{CuCl2} = 0.33.

Two-step, one-pot syntheses of indium(0) nanoparticles[41] have been achieved from haloindate(III) ionic liquid systems, χ_{InCl3} = 0.50, with three different cations. In the first step, the In(III)-containing anion was electrochemically reduced to an In(I)-anion which, after diffusion from the electrode, underwent disproportion to In(III) and In(0) in the bulk ionic liquid electrolyte. The morphology of the In(0) nanoparticles formed depended strongly on the nature of the cation used (as shown in Figure 42) with the ionic liquid acting as a templating and stabilising agent in addition to a metal source and electrolyte.
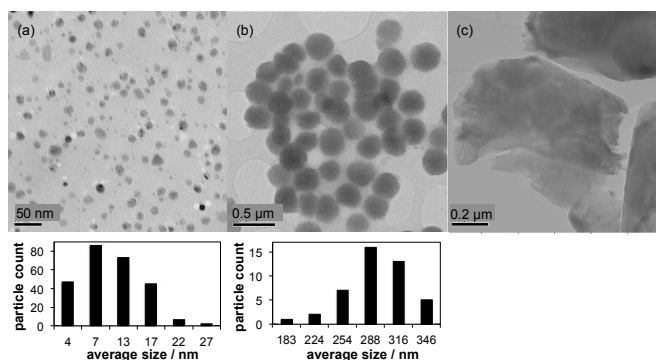
Figure 42. TEM bright field images and size distribution of indium(0) particles prepared in: (a) [C$_8$mim][InCl$_4$], (b) [N$_{1 1 1 16}$][InCl$_4$], and (c) [P$_{6 6 6 14}$][InCl$_4$] reproduced from Ref. 41 with permission from Wiley.

Serpell *et al.*[110] have synthesised gold and palladium nanoparticles using 1,3-dialkylimidazolium ionic liquids with [AuCl$_4$]$^-$ and [PdCl$_4$]$^{2-}$ anions combined with chemical reduction (Figure 43). It was demonstrated that Pd(0), but not Au(0), nanoparticles were stabilised by the imidazolium cations of the ionic liquids. However, when a strong base was added prior to metal reduction, the generation of N-heterocyclic carbenes lead to stabilisation of both Pd(0) and Au(0) nanoparticles.

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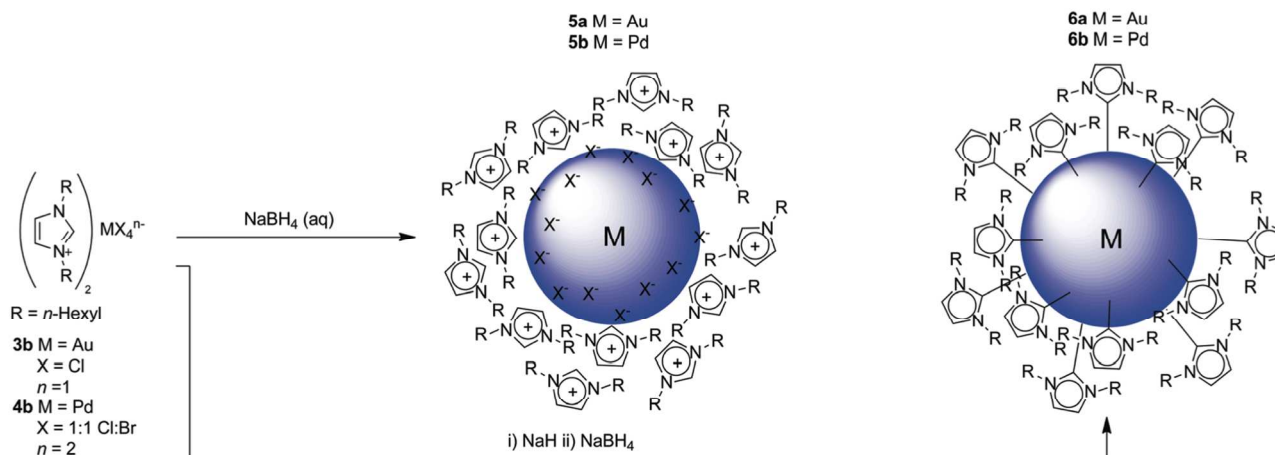
Figure 43. Synthesis of imidazolium and NHC stabilised metal nanoparticles (reproduced from Ref. 110).

4.4. Soft and composite materials

A variety of 'metal-centred' characteristics can be introduced into
5 ionic liquid materials through the incorporation of specific chlorometallate anions; for example, iron(III) or copper(II) systems can be paramagnetic, introducing lanthanides can lead to both luminescence and paramagnetism, and when combined with cations may lead to the formation of liquid crystalline
10 metallomesogens. Finally, some material properties are system-specific, such as reactive gas absorption by chlorocuprate(I) systems.

4.4.1. Paramagnetic chlorometallates ionic liquids

'Magnetic ionic liquids' can be prepared by introducing
15 paramagnetic chlorometallate anions. Yoshida and Saito[273] have recently reviewed the development of these materials, providing a comprehensive table of MPMS SQUID magnetic data.

Fe(III)-based magnetic ionic liquids have been the most popular subjects for study, largely as a result of their low cost,
20 relative abundance, and ease of preparation;[274] Examples incorporating a variety of cations including 1-alkyl-3-methylimidazolium,[275,276] tetraalkylphosphonium,[276] pyrrolidinium,[274] and amino acid-based systems[277] have been reported. In 2004, Hamaguchi and co-workers[278] measured the
25 magnetic susceptibility of the room temperature ionic liquid, $[C_4mim][FeCl_4]$ (with molar magnetic susceptibility $1.37\pm0.70\cdot10^{-2}$ emu mol^{-1}) using magnetic property measurement system on superconducting quantum interference device (MPMS SQUID). Subsequently, a range of haloferrate(III) systems, based
30 on typical cations have been tested. Magnetic susceptibility values are very similar for all haloferrate(III) ionic liquids, marginally lower for $[FeBr_4]^-$ compared to $[FeCl_4]^-$ based salts, which can be justified in terms of lower ligand field for the former anion.[275]

35 An interesting system has been prepared by appending TEMPO functionality to an imidazolium cation, which in

combination with $[FeCl_4]^-$ yielded an ionic liquid with dual sources of paramagnetism: from the anion and from the stable radical functional group (Figure 44).[279] Molar magnetic
40 susceptibility of this ionic liquid was slightly higher than that of chloroferrates(III) with non-magnetic cations, and the effective magnetic moment was found to bear contributions from both the anion and the cation.

[Imim-TEMPO][FeCl₄]
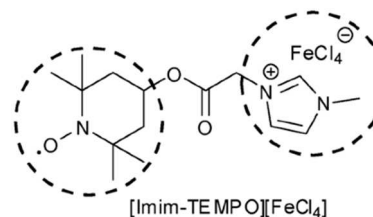
45 Figure 44. TEMPO-functionalised ionic liquid with dual source of paramagnetism: a chloroferrate(III) anion and a stable TEMPO free radical (reproduced from Ref. 279).

Dilution of $[C_2mim][FeCl_4]$ with an equimolar amount of a non-magnetic ionic liquid, $[C_2mim][GaCl_4]$ resulted in both
50 magnetic susceptibility and Curie constant values decreasing by *ca*. 50%.[125] Xie *et al*.[280] were able to incorporate $[C_4mim][FeCl_4]$ into flexible, transparent ionogels prepared from PMMA (Figure 45). The materials were reported to be both conducting and paramagnetic.
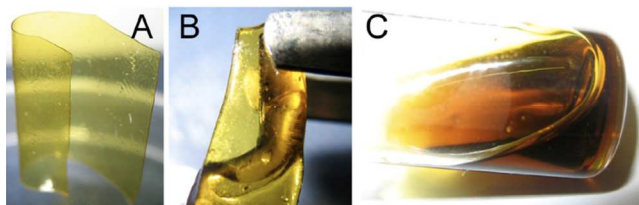
Figure 45. Images of free standing and soft ionogel materials incorporating paramagnetic chloroferrate(III) ionic liquids (Reproduced from Ref. 280).

Several unusual phenomena have been studied in chloroferrate(III) systems. When an inert gas was bubbled through a chloroferrate(III) ionic liquid, the bubbles were observed to be 'repulsed' by the neodymium magnet.[281] Arguably, this might be explained in terms of paramagnetic liquid being attracted to magnet, while the diamagnetic gas was not.

Akitsu and Einaga[282] reported alternating irradiation with UV and visible light (in 5 min periods for each wavelength) of an equimolar mixture of $[C_4mim][FeCl_4]$ with azobenzene caused reversible isomerisation between *cis* and *trans* isomers of azobenzene and a permanent monotonous increase in the magnetic susceptibility of the mixture; the increase was observed both after the exposure to UV and to visible light. The authors justify these observations in terms of the formation of supramolecular, ordered structures containing aggregates of paramagnetic anions.

Similarly, it has been claimed that chemical reactions carried out in paramagnetic ionic liquids can be influenced by a strong magnetic field as a result of the induction of structure within the liquids. The morphology of conducting polymers (polypyrrole, N-methylpolypyrrole, polythiophene,[283] and poly(3-methylthiophene)[284]) prepared in $[C_4mim][FeCl_4]$, differs depending upon whether a magnetic field is applied.[285] However, radical polymerisation reactions can be affected directly by the presence of magnetic fields[286] so it is not possible to assess whether it is the combination of magnetic field and ionic liquid, or solely the magnetic field, that induced the differences in polymer morphology.

Warner and co-workers[277] have reported the synthesis of magnetic ionic liquids incorporating amino acid derived cations and chloroferrate(III) anions. These ionic liquids were miscible with water, contrasting with the typical behaviour of dialkylimidazolium chloroferrate(III) systems that are hydrophobic, or display thermomorphic behaviour.[287] However, Warner and co-workers suggest that the combination of chirality and the strong response to magnetic fields could provide a method to manipulate their phase separation behaviour and that this might lead to applications in the field of chiral extraction and enrichment of chiral compounds.[277]

Ionic liquids prepared by combining $[P_{6\,6\,6\,14}]^+$ cations with $[CoCl_4]^{2-}$, $[MnCl_4]^{2-}$ and a *pseudo*-halometallate $[Co(NCS)_4]^{2-}$ anions have been reported.[276] All compounds were hydrophobic, and those prepared from hydrates separated from aqueous phase, *e.g.* a blue ionic liquid containing tetrahedral $[CoCl_4]^{2-}$ anion was prepared from purple (octahedral) hydrate salt, $CoCl_2 \cdot 4H_2O$. In addition to simple paramagnetic behaviour over a wide temperature range (50-350 K), only very weak antiferromagnetic interactions was detected which indicates that the magnetic

centres (anions) in the ionic liquids were not aggregating and forming clusters.

4.4.2. Ionic liquid crystals based on transition metals

Ionic liquid crystals (ILCs) have been reviewed comprehensively in 2005 by Binnemans,[288] and more recently by Axenov and Laschat.[289] The formation of transition metal halometallate ILCs is governed by two general conditions: the presence of surfactant-like cation with a long alkyl chain, and a doubly charged anion, $[MCl_4]^{2-}$.

In the majority of publications, phase behaviour has been studied as a function of temperature, metal and chain length of the cation alkyl chain, but the composition of ionic liquid was constant ($\chi_{MCl2} = 0.33$).[290] ILC behaviour is typically observed with carbon-chains of 12-18 atoms appended to 1-alkyl-3-methylimidazolium or 1-alkylpyridinium cations and the predominant LC phase found is a lamellar smectic A. This approach seems a bit restricting since, as Martin *et al*. demonstrated, ILC behaviour depends strongly on the composition of the chlorometallate system.[78] The authors studied $[N_{1\,1\,1\,n}]Cl\text{-}MCl_2$ salts ($n = 12$ or 16, $M = Zn$, Cu or Cd) as a function of χ_{MCl2}, and identified a variety of ILC phases in each system, their presence depending on metal, temperature and χ_{MCl2}. Example of such complex phase behaviour for the $[N_{1\,1\,1\,16}]Cl\text{-}ZnCl_2$ system was shown in Figure 16.

Aside of interesting phase behaviour and visually appealing images, only a few uses chlorometallate ILCs based on transition metals have been reported. Taubert and co-workers used ILC-forming chlorocuprate(II) system ($\chi_{CuCl2} = 0.33$) for the syntheses of copper(I) chloride nanoplatelets.[291] Templating of inorganic materials with liquid crystals is a known synthetic strategy; hence future development in this direction appears to be open. Another field of application, yet to be properly explored, is catalysis. For example, Wasserscheid and co-workers[292] demonstrated recently that ILCs containing dissolved metal complexes and supported sillica (SILPs) have different activity from 'anisotropic' ionic liquids containing analogous complexes. It is probable, that chlorometallate SILPs[293] could display similar behaviour, but this area is yet to be explored.

4.4.3. Halolanthanide ionic liquids

Lanthanide-containing chlorometallate systems typically combine several interesting material properties, such as magnetism and luminescence, and may display liquid crystalline behaviour. Luminescent and/or paramagnetic ionic liquids were recently shortly reviewed by Yoshida and Saito.**Error! Bookmark not defined.**

Research on lanthanide-containing ionic liquids is relatively new; it developed from the field of ionic liquids rather than from traditional molten salts pathway. Rather than being studied in electrochemistry or Lewis acid catalysis, chlorolanthanide systems were studied predominantly as materials. Furthermore, non-halide ligands, such as thiocyanate[294] or bistriflamide ligands were typically used.

The first lanthanide-containing halometallate ionic liquid, $[P_{6\,6\,6\,14}][GdCl_6]$, was studied from the materials perspective, in comparison to transition metals-based systems, with the focus on hydrophobic and paramagnetic properties.[294] The incentive to include a lanthanide in this study was that a higher spin moment of certain f-block elements can produce ionic liquids with stronger magnetism.[295] The research was further pursued by

Getsis *et al*.[296-299] and produced a series of papers on bromolanthanide(III) ionic liquid crystals, using long-chain [C$_{12}$mim]$^+$ and [C$_{12}$C$_1$pyrr]+ cations. Bromide salts of the cations were either only doped with lanthanide(III) bromide (low χ_{LnBr3} values) or prepared from stoichiometric quantities of the reactants to form [cation]$_3$[LnBr$_6$] (χ_{LnCl3} = 0.25). In all cases, they displayed mesomorphic behaviour, forming smectic liquid crystalline phases (see Figure 46).
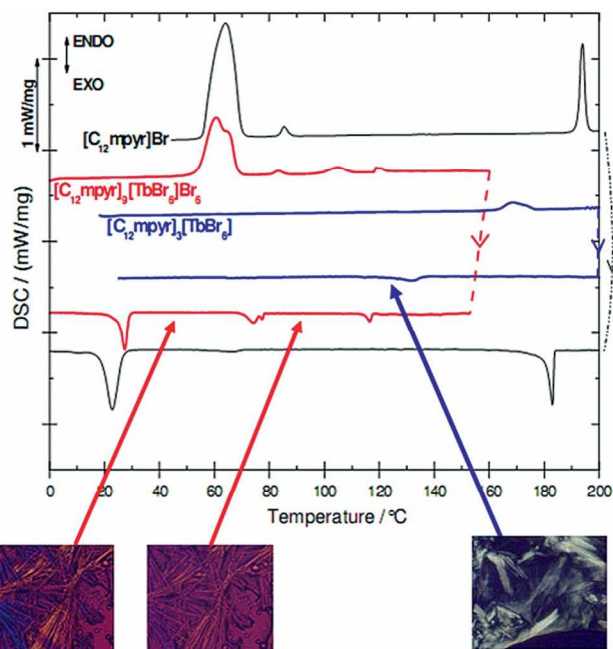

Figure 46. DSC-thermograms of [C$_{12}$mpyr]Br-TbBr$_3$ system, χ_{TbBr3} = 0.10 (in red) and χ_{TbBr3} = 0.25 (in blue) with corresponding POM micrographs, compared to the thermogram of neat [C$_{12}$mpyr]Br (reproduced from Ref. 299 with permission from Wiley).

All materials, irrespective of their χ_{LnBr3} value were luminescent (Figure 47). For the systems based on Tb(III) and Dy(III), the emission colour could be tuned by changing the excitation wavelength.[296,297]
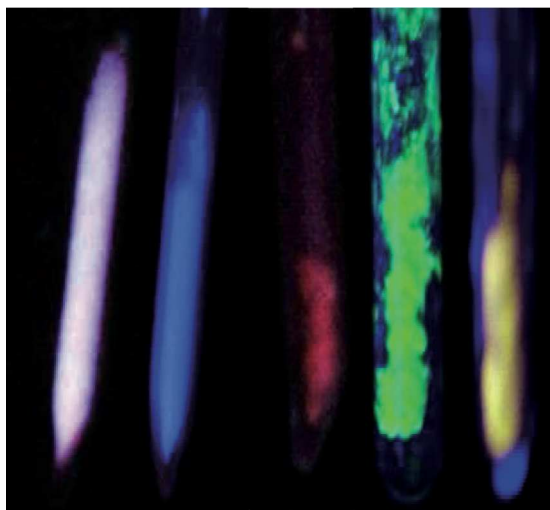

Figure 47. Neat [C$_{12}$mim]Br (left) doped with various lanthanide bromides under UV light (reproduced from Ref. 297 with permission form Wiley).

Magnetic behaviour was studied only for [C$_{12}$mim]$_3$[DyBr$_6$], system,[296] which showed superparamgnetic properties at room temperature (300 K) and exhibited signs of soft-magnetic ferromagnetic behaviour, albeit with dominant paramagnetic component, at 5 K. The compound could be manipulated by an external magnetic field due to large anisotropic magnetic moment of Dy(III).

4.4.4. Gas storage media

Air Products have developed ionic liquid-based approaches to transport reactive gases[300] such as trifluoroborane, phosphine, and arsine. Combining computational studies (see Figure 48) and absorption experiments, Tempel *et al*.[301] demonstrated that [C$_4$mim][Cu$_2$Cl$_3$] could be used to capture, store and reversibly release reactive and toxic gas, PH$_3$, under controlled conditions. Each binuclear anion is able to bind two moles of PH$_3$ by formation of covalent Cu-P bonds. This provides very high storage capacity (2 moles gas per mole of ionic liquid) and stores the gas at ambient atmospheric pressure which neatly eliminates the implicit risk associated with high pressure storage of such reactive gasses.
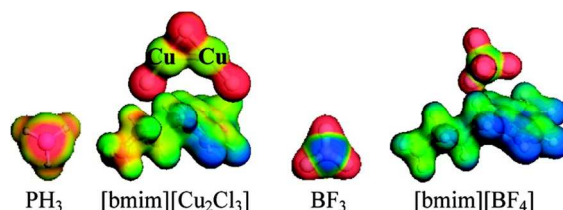

Figure 48. Calculated electrostatic potentials surfaces for 1-butyl-3-methylimidazolium chlorocuprate(I) and tetrafluroroborate ion pairs, and the corresponding electrostatic potential surfaces of the reactive gases PH$_3$ and BF$_3$, that are selectively complexes by the two ionic liquids respectively (reproduced with permission from Ref. 301).

The ionic liquid, as used, can be considered as a truly 'designer' material. Speciation of the chlorocuprate(I) anion was controlled through selection of the metal oxidation state and χ_{CuCl} in order to match Lewis acidity to the basicity of PH$_3$ and enable selective and reversible binding.

4.4.5. Pharmaceutical ionic liquids (PILs)

Lovejoy *et al*.[302] reported a route to prepare amorphous pharmaceutically active materials by converting their chloride salts to chlorometallate ionic liquids based on metal chlorides generally recognised as safe (GRAS), predominantly on zinc(II) chloride. These salts were found to retain antibiofilm activity, and significantly improved shelf life was predicted (Figure 49). This system exemplifies the use of complex anionic speciation to control material properties; chlorozincate(II) anions were purposefully chosen due to their ability to suppress crystallisation, forming glassy rather than crystalline active pharmaceutical intermediates..

5. Concluding remarks

Modern ionic liquids emerged as a direct consequence of the evolutionary development of low temperature chloroaluminate(III) 'molten salt' electrolytes[11] which, when combined with the ubiquity of aluminium chloride as a Lewis acid catalyst,[303] provided the springboard for investigation of both catalysis and electrochemistry. The properties of the chloroaluminate(III) ionic liquids (low viscosity, wide liquid

ranges *etc*) are very favourable, however they are not the only chlorometallate ionic liquids and, importantly, the properties of other systems cannot be implied by comparison or analogy.
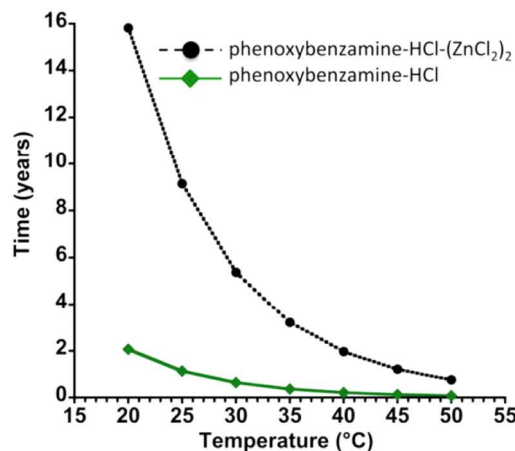

Figure 49. Estimation of shelf life shown in terms of time to reach 5.0% decomposition at different isothermal temperatures for phenoxybenzamine-HCl and phenoxybenzamine-HCl-$(ZnCl_2)_2$ reproduced with permission from Ref. 302.

The periodic table contains over fifty metals that can readily form chlorometallate anions. However whether an ionic liquid can be prepared depends on the choice of metal, oxidation state, and on the composition, χ_{MCln}. In turn, these variables define the anion speciation and the resultant properties of the ionic liquid (if produced). The fact that robust, reliable speciation data, reported in Table 2, can only be found for less than half of these metals demonstrates one of the limits of current knowledge.

This review summarises the key ways in which the speciation of chlorometallate ionic liquids and their resulting properties can be investigated. Most of these methods are complementary, and the use of multi-technique approaches can be used effectively to obtain robust and unambiguous data. Of particular merit are the use of Raman[37-41] and X-ray (XPS[57] and XAFS[61]) spectroscopy to study neat liquids. These data, supported by high level *ab initio* calculations, are revealing unprecedented levels of detail and allowing mistakes or ambiguities from the past to be corrected.

Speciation studies are not a simple data-logging exercise; in fact, the knowledge of speciation, and thus properties, is necessary to guide the informed selection of appropriate ionic liquids for investigation or screening in any given application. For example, when considering acidic systems, limiting solubility and so acidity of $FeCl_3$ in chloroferrate(III) ionic liquids,[157,158] relative acidities of ionic liquids containing Al(III), Ga(III) and In(III), and the recognition that $\chi_{ZnCl2} = 0.5$ compositions of chlorozincate(II) ionic liquids are acidic,[156,167] can all help to clarify experimental observations. It can not be over-emphasised that this detailed level of understanding for *all* ionic liquids is extremely important and this represents an on-going challenge.

It is hoped that the survey of some of the new and emerging areas of chlorometallate ionic liquids research presented here will be of use to many researchers in the fields of catalysis, separations, and materials chemistry (both soft and hard matter). It seems obvious that chlorometallate species will continue to have a major influence on ionic liquid science, where the ability to selectively introduce new combinations of characteristics – for example; magnetism, hydrophobicity, luminescence, variable (and controllable) catalytic activity *etc*, will define the properties of new and emerging materials. Unexpected applications will continue to emerge, as exemplified with Zn(II)-based pharmaceutical ionic liquids, where the desired property of the material (glass formation rather than crystallisation)[302] is a direct consequence of complex anion speciation in the ionic liquid.

In addition, we hope that it will encourage groups to further explore, and design new metallate-based ionic liquid systems and fully characterise their properties using the techniques described here, so that their relationships to the existing body of chlorometallate data can be quantitatively assessed.

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[a] *CERTECH asbl, Rue Jules Bordet, Zone Industrielle C, B-7180 Seneffe, Belgium; E-mail: julien.estager@certech.be*
[b] *QUILL, School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, United Kingdom; E-mail: j.holbrey@qub.ac.uk, m.swadzba-kwasny@qub.ac.uk*

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