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Lanthanides and Actinides in Ionic Liquids

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Contents

1. Introduction

Koen Binnemans was born in Geel, Belgium, in 1970. He obtained his M.Sc. degree (1992) and Ph.D. degree (1996) in Chemistry at the Catholic University of Leuven, under the direction of Prof. C. Görller-Walrand. In the period 1999–2005, he was a postdoctoral fellow of the Fund for Scientific Research Flanders (Belgium). He did postdoctoral work with Prof. Jacques Lucas (Rennes, France) and Prof. Duncan W. Bruce (Exeter, U.K.). In 2000, he received the first ERES Junior Award (ERES, European Rare-Earth and Actinide Society). From 2002 until 2005, he was (part-time) associate professor. Presently, he is professor of chemistry at the Catholic University of Leuven. His current research interests are metal-containing liquid crystals (metallomesogens), lanthanide-mediated organic reactions, lanthanide spectroscopy, supramolecular coordination chemistry, and ionic liquids.

Ionic liquids are salts with a low melting point (below 100 °C).[1−6] Several types of ionic liquids are liquid at room temperature (*room-temperature ionic liquids* or RTILs). The cations of ionic liquids are often large organic cations, like imidazolium,[1] pyridinium,[1] pyrrolidinium,[7] quaternary ammonium,[8] or phosphonium ions[9,10] (Figure 1). Especially the 1-alkyl-3-methylimidazolium ions are often used as the cationic part of ionic liquids.[1,4] Whereas Cl^- and Br^- yield hydrophilic ionic liquids (miscible with water), fluorinated anions like $[PF_6]^-$ allow preparation of hydrophobic ionic liquids (immiscible with water).[4] The hydrophobicity of ionic liquids containing $[BF_4]^-$ depends on the alkyl chain length of the associated cation.[4] Recently, the bis(trifluoromethylsulfonyl)imide anion, $[(CF_3SO_2)_2N]^-$ (abbreviated to $[Tf_2N]^-$), has become a popular anion for synthesizing hydrophobic

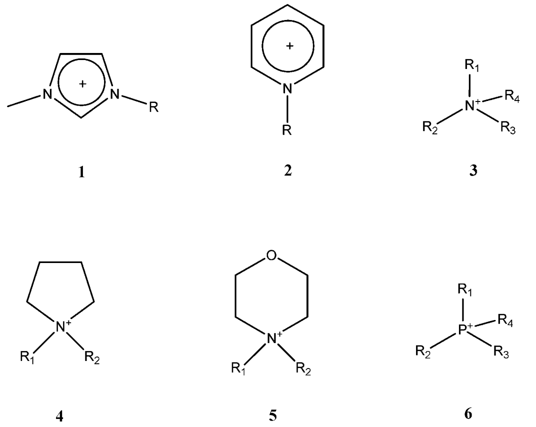

Figure 1. Examples of cations commonly used in ionic liquids: (**1**) 1-alkyl-3-methylimidazolium; (**2**) 1-alkylpyridinium; (**3**) quaternary ammonium; (**4**) 1,1′-dialkylpyrrolidinium; (**5**) 1,1′-dialkylmorpholinium; (**6**) phosphonium.

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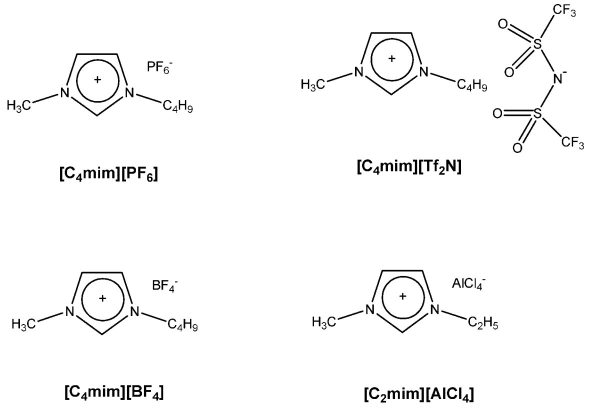


Figure 2. Commonly used imidazolium ionic liquids.

ionic liquids, because the resulting ionic liquids are chemically and thermally more robust than ionic liquids with $[BF_4]^-$ and $[PF_6]^-$ anions (Figure 2).[11−14] $[Tf_2N]^-$-containing ionic liquids have relatively low viscosities and high electrical conductivities. Due to their hydrophobicity, they can be dried to very low final water contents. Metal-containing species (anions or cations) can be an integral part of ionic liquids, not only in the chloroaluminate ionic liquids but in other types of ionic liquids as well.[15] Because the properties of ionic liquids (miscibility with water and other solvents, dissolving ability for metal salts, polarity, viscosity, density, etc.) can be tuned by an appropriate choice of the anion and the cation, ionic liquids can be considered as *designer solvents*.

The use of room-temperature ionic liquids in synthesis, catalysis, separations, and electrochemistry has become very common in recent years.[1,4] The vapor pressure of an ionic liquid is very low, so ionic liquids are nonvolatile and do not evaporate. However, ionic liquids can be distilled under high vacuum.[16] It has been proposed to use ionic liquids as environmentally friendly alternatives for volatile organic solvents.[2,17−19] Ionic liquids are fluid over a broad temperature range, from the melting point to the onset of thermal decomposition. Because many ionic liquids are nonflammable and nonexplosive, they are much safer to work with in the lab than the conventional organic solvents. However, one should keep in mind that only a limited number of in-depth toxicological studies have been performed on ionic liquids, so one cannot state that ionic liquids are intrinsically “green solvents”.[20] Ionic liquids with fluorinated anions, and especially those containing the hexafluorophosphate anion, are prone to hydrolysis.[21] This can lead to the formation of toxic and corrosive products like hydrogen fluoride. Due to their ionic nature, ionic liquids conduct electricity by ion migration. Ionic liquids have a very wide “electrochemical window”, so they are very resistant to oxidation and reduction processes.[22] By dissolution of metal salts in ionic liquids, reactive metals can be deposited and purified by electrolysis.[23] Ionic liquids are polar solvents, and their polarity is comparable with that of the lower alcohols (*n*-propanol, *n*-butanol, *n*-pentanol).[24,25] In contrast to other polar organic solvents, ionic liquids are weakly coordinating and weakly solvating solvents. Ionic liquids are good solvents for many organic and inorganic compounds.[26−29] Higher rates and better selectivity in selected ionic liquids than in classical solvents have been observed in the case of Friedel−Crafts reactions,[30,31] Diels−Alder reactions,[32] Heck reactions[33] and radical polymerizations.[34] Catalysis in ionic liquids is a very popular research theme.[5,18,35−37] Ionic liquids can be applied as extraction solvent in liquid−liquid solvent extraction processes for the separation of metal ions[38−41] and as electrolytes in batteries[42,43] or in photovoltaic devices.[44−46]

The chloroaluminate ionic liquids should be mentioned here as well, because they are early examples of room-temperature ionic liquids.[1,47,48] They can be prepared by combination of anhydrous aluminum chloride ($AlCl_3$) with 1-ethyl-3-methylimidazolium chloride, $[C_2mim]Cl$,[49] or with 1-butylpyridinium chloride, [BuPy]Cl.[50] Although they suffer from an extreme sensitivity to even small amounts of water, these systems exhibit a very interesting chemistry. The Lewis acid−base properties of chloroaluminate ionic liquids depend on their composition or more particularly on the molar fraction of aluminum chloride. Melts with a molar excess of aluminum chloride are acidic because they contain coordinatively unsaturated species like $[Al_2Cl_7]^-$ that exhibit Lewis acidity. Melts with a molar excess of the organic salt are basic, because they contain chloride ions that are not coordinated to aluminum (“free” chloride ions). In acidic ionic liquid systems, the molar fraction of aluminum chloride is larger than 0.5, that is, $X(AlCl_3) > 0.5$, whereas in basic melts, $X(AlCl_3) < 0.5$. The composition with $X(AlCl_3) = 0.5$ is called neutral. In chloroaluminate ionic liquids, species like Cl^-, $[AlCl_4]^-$, $[Al_2Cl_7]^-$, $[Al_3Cl_{10}]^-$, and $[Al_2Cl_6]$ can be detected. When metal salts are dissolved in basic chloroaluminate ionic liquids, anionic species tend to be formed (due to the presence of chloride ions), whereas cationic species dominate in acidic chloroaluminate ionic liquids.

This review on lanthanides and actinides in ionic liquids intends to give an overview of the properties and applications of f-elements in room-temperature ionic liquids. Although many studies have been devoted to ionic liquids and their applications, only few researchers have explored the combination of ionic liquids with the coordination chemistry of lanthanides and actinides. However, this research field is emerging, and a review could be helpful to draw attention to the potential of incorporation of the f-elements in ionic liquid media. First, theoretical and experimental studies of the solvation of f-elements in ionic liquids are considered. The spectroscopic properties of lanthanide and actinide ions in ionic liquids are discussed with special emphasis on the luminescence properties. Due to their ionic nature and redox stability, ionic liquids can be used as solvents for lanthanide ions in unusual oxidation states. Metals of the f-elements and their alloys can be deposited for these solvents. The behavior of ionic liquids in solvent extraction of metal ions is compared with that of molecular solvents. The application of ionic liquids for the processing of spent nuclear fuel rods is considered. In this context, the stability of these solvents against radiation damage is an important issue. An overview of lanthanide-mediated organic reactions in ionic liquids is given. Finally, some applications in materials sciences are discussed. The behavior of lanthanides and actinides in high-temperature molten salts is outside the scope of this review. The literature has been covered until early January 2007.

The term f-elements (or f-block elements) is used to designate the lanthanides and actinides, because in this series of elements the 4f shell (lanthanides) or the 5f shell (actinides) is gradually filled. The lanthanides are the elements with an atomic number between 57 (lanthanum) and 71 (lutetium), whereas the actinides are the elements with an atomic number between 89 (actinium) and 103 (lawrencium). The term *rare earths* is used for the lanthanides in combination with scandium and yttrium. The coordination chemistry of the f-block elements quite differs from that of the (middle and late) d-block elements.[51] Although their exotic names might suggest that these elements are as toxic as other heavy metals, rare-earth salts have in fact a low acute and chronic toxicity.[52]

The use of ionic liquids as solvents for organic reactions is in accordance with the *Twelve Principles of Green Chemistry*,[53] but there are several reasons why the combinations of lanthanides and actinides with ionic liquids are relevant to green chemistry. Ionic liquids can replace the volatile and flammable kerosene fraction in solvent extraction processes that are used for the separation of rare-earth elements (fifth principle of green chemistry: safer solvents and auxiliaries). The production of rare-earth elements in their metallic state presently relies on high-temperature molten salt technology. Molten salt technology is also of importance for some steps in the processing of spent nuclear fuel rods. When the molten salts in these processes can be replaced by room-temperature ionic liquids, a huge saving in energy costs can be achieved (sixth principle of green chemistry: design for energy efficiency). Boron-containing ionic liquids have a large cross-section for neutron capture. The use of this type of ionic liquid for processing of spent nuclear fuel rods can greatly reduce the risk of criticality accidents (12th principle of green chemistry: inherently safer chemistry for accident prevention). In several classes of organic reactions where at least stoichiometric amounts of strong Lewis acids (e.g., $AlCl_3$ or $FeCl_3$) are required, catalytic amounts of lanthanide salts can give the same yields. This results in the generation of much less acidic waste (ninth principle of green chemistry: catalysis; first principle of green chemistry: prevention). Cerium(IV) salts are much safer selective oxidants than transition metal salts like chromium(VI) salts and osmium tetroxide (third principle of green chemistry: less hazardous chemical syntheses).

2. Solvation and Solubility

2.1. Solvation

Solvation of ions by solvent molecules is an important issue in the coordination chemistry of f-elements.[54,55] For instance, the stability of the trivalent lanthanide ions in aqueous solution can be attributed to the high hydration energy, which compensates for the energy that has to be invested to triply ionize these elements.[56] Solvation is also of importance to understand the behavior of f-elements under solvent extraction conditions. Chaumont and Wipff published detailed theoretical studies on this topic.[57−62] Their molecular dynamics calculations explicitly represent the solvent. Interesting conclusions were made on the basis of quantum mechanics and molecular dynamics calculations on trivalent lanthanide ions in the ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate, $[C_4mim][PF_6]$, and 1-ethyl-3-methylimidazolium tetrachloroaluminate(III), $[C_2mim][AlCl_4]$. The latter ionic liquid is a neutral chloroaluminate ionic liquid, $AlCl_3$ and $[C_2mim]Cl$ in 1:1 molar ratio. The calculations predict that the trivalent lanthanide ions, Ln^{3+} (Ln = La, Eu, Yb), are surrounded by six $[PF_6]^-$ anions in $[C_4mim][PF_6]$ and by 11−13 imidazolium ions in the second ionic sphere.[57] It is also predicted that the “naked” lanthanide cations are poorly soluble in $[C_4mim][PF_6]$. In $[C_2mim][AlCl_4]$, the trivalent lanthanide ions are surrounded by eight $[AlCl_4]^-$ anions. The actual coordination number of the lanthanide ions in these two ionic liquids depends on the ionic radius of the lanthanide and decreases with decreasing ionic radius. The $[PF_6]^-$ and $[AlCl_4]^-$ ions tend to be bidentate ligands for the large lanthanide ions and monodentate for the smaller metal ions, but both anions are weakly coordinating. Molecular dynamics calculations show that the $[PF_6]^-$ anions rotate rapidly in the first ionic shell, but the $[AlCl_4]^-$ anions do not. A subsequent study focused on the behavior of $LnCl_3$ and the charged $[LnCl_n]^{3-n}$ species in ionic liquids (Ln = La, Eu, Yb).[61] The simulations reveal that the octahedral $[LnCl_6]^{3-}$ complexes are important species in the $[C_4mim][PF_6]$ and $[C_2mim][AlCl_4]$ ionic liquids. The $[LnCl_6]^{3-}$ anions are surrounded by nine to ten imidazolium cations (Figure 3). The $[LnCl_6]^{3-}$ complexes are unstable in the gas phase towards dissociation of one or two chloride ligands, but the complex is stabilized by solvation in an ionic liquid. The $LnCl_3$, $[LnCl_4]^-$, and $[LnCl_5]^{2-}$ species do not dissociate in the ionic liquids, and their first ionic shell is completed by, respectively, three, two, and one $[PF_6]^-$ ions and four, three, or one $[AlCl_4]^-$ ions for Ln = Eu. The $[LnCl_8]^{5-}$ species tends to lose two chloride anions and to be transformed to the $[LnCl_6]^{3-}$ species. However, the $[LaCl_7]^{4-}$ species seems stable in $[C_2mim][AlCl_4]$. In basic $AlCl_3$−$[C_2mim]Cl$ ionic liquids (i.e., a chloroaluminate ionic liquid with an excess of chloride ions), calculations predict the existence of different chloro complexes for Eu^{3+} and Eu^{2+}.[60] Lipsztajn and Osteryoung studied the solvation behavior of

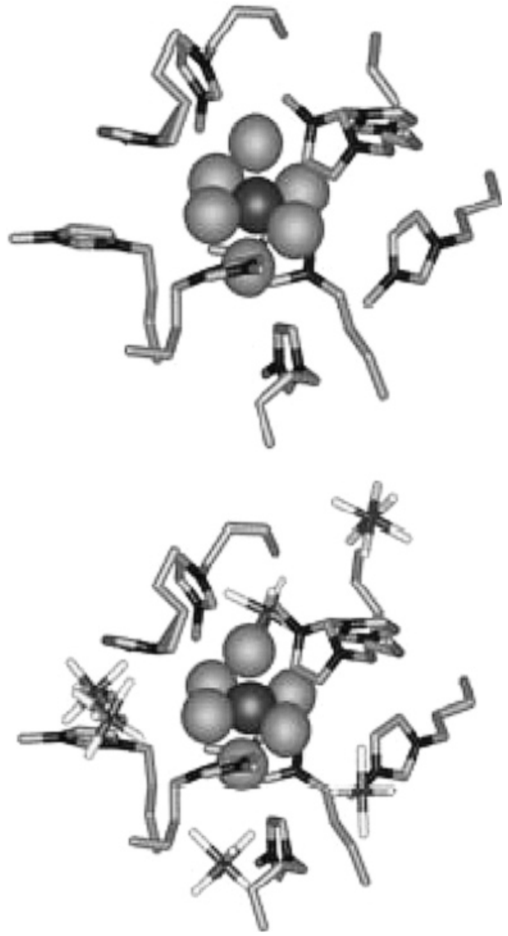


Figure 3. $[YbCl_6]^{3-}$ complex in $[C_4mim][PF_6]$. Snapshot of the first solvation shell of cations only (top) and of anions + cations (bottom). Adapted from Figure S3 in the Supporting Information of ref 59. Copyright 2004 American Chemical Society.

$NdCl_3$ in $AlCl_3$−[C_2mim]Cl ionic liquids.[63] In a “neutral basic” $AlCl_3$−[C_2mim]Cl ionic liquid (i.e., a 1:1 molar ratio, with a slight excess of the organic salt), the $[NdCl_6]^{3-}$ species could be identified. In a “neutral acidic” $AlCl_3$−[C_2mim]Cl ionic liquid (i.e., a 1:1 molar ration, with a slight excess of $AlCl_3$), no $[NdCl_6]^{3-}$ complexes are present, but here the neodymium(III) ion is solvated by either $[AlCl_4]^-$ or $[Al_2Cl_7]^-$. Unfortunately, $NdCl_3$ has a very low solubility in these “neutral acidic” melts, so a detailed study was difficult.

Simulations show differences in solvation behavior in wet and dry ionic liquids.[59] As indicated above, the Eu^{3+} is coordinated by $[PF_6]^-$ anions in dry [C_4mim][PF_6]. In a wet [C_4mim][PF_6], the Eu^{3+} ion is surrounded by water molecules only, whereas the $[PF_6]^-$ ions are in the second ionic shell and H-bonded to the coordinated water molecules. The $[Eu(H_2O)_9]^{3+}$ complexes are embedded in a shell of seven or eight $[PF_6]^-$ anions. In the case of the $[EuCl_6]^{3-}$ complex in wet [C_4mim][PF_6], water molecules are in the first ionic shell, but $[C_4mim]^+$ cations are not. Water can coordinate to $[EuCl_6]^{3-}$, so mixed aquo−chloro species are formed. Because the chloro species have a stronger tendency to interact with the water molecules present in the ionic liquid than with the ionic liquid molecules themselves, the chloro complexes are more soluble in wet than in dry ionic liquids. A molecular dynamics study of the solvation of the fluoro complexes $[EuF_n]^{3-n}$ in the ionic liquid [C_4mim][PF_6] revealed that the species with the highest fluorine content in the ionic liquid should be $[EuF_6]^{3-}$.[62] Complexes like $[EuF_{10}]^{7-}$ and $[EuF_7]^{4-}$ tend to lose fluoride ligands in ionic liquid solutions with the formation of the $[EuF_6]^{3-}$ species. Fluoro species with less than six fluoro ligands bonded to the europium(III) ion contain $[PF_6]^-$ anions in the first coordination sphere. The anionic complexes are surrounded by six to nine $[C_4mim]^+$ cations. The calculations show that the hexafluoro complexes are more stable than the corresponding hexachloro complexes. The crystal structure of tris(1-ethyl-3methylimidazolium) hexachlorolanthanate(III), [C_2mim][$LaCl_6$], clearly shows the hydrogen bonding between the chloro atoms of the octahedral $[LaCl_6]^{3-}$ moiety and the hydrogen atoms of the imidazolium ring (Figure 4).[64]

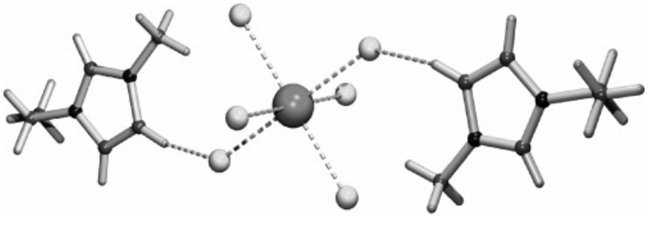


Figure 4. Molecular structure of tris(1-ethyl-3-methylimidazolium) hexachlorolanthanate(III). The atomic coordinates were taken from ref 64.

A luminescence study of Eu^{3+} in the ionic liquid [C_4mim][Tf_2N] indicates that water molecules instead of $[Tf_2N]^-$ anions coordinate to the europium(III) ion.[65] Addition of chloride ligands resulted in the formation of different chloro species. The luminescence spectrum of the complex formed at high chloride concentrations is similar to the spectrum of $[EuCl_6]^{3-}$ in ethanol.[66] Gaillard and co-workers investigated by time-resolved luminescence spectroscopy and by EXAFS the influence of the anion in $[C_4mim]^+$ ionic liquids on the first coordination sphere of the trivalent europium(III) ion, which was dissolved in the ionic liquids in the form of europium(III) triflate, $Eu(OTf)_3$.[67] The experiments were supported by molecular dynamics calculations. EXAFS data indicate that the coordination number of the europium(III) ion is between eight and nine in the ionic liquids [C_4mim][PF_6], [C_4mim][BF_4], [C_4mim][OTf], and [C_4mim][Tf_2N]. The molecular dynamics simulations on both the “naked” Eu^{3+} ion and on nondissociated $Eu(OTf)_3$ gave similar results. The calculations suggest that the triflate anions are coordinated to europium(III) in [C_4mim][PF_6] and dissociated in [C_4mim][BF_4] and [C_4mim][Tf_2N]. In contrast to the theoretical predictions, addition of chloride and fluoride ions to the europium(III)-containing [C_4mim][PF_6] ionic liquid did not result in the formation of chloro or fluoro complexes. Trichloro complexes are formed in [C_4mim][BF_4] and hexachloro complexes in [C_4mim][Tf_2N]. Complex formation between Eu^{3+} and chloride ligands could be observed in [C_4mim][OTf], but it was not possible to determine the exact stoichiometry. This study shows that kinetic effects are very important for complex formation between europium(III) and chloride ligands in ionic liquids. A correlation could be found between the viscosity of the ionic liquid and the number of chloride ligands bound to europium(III). In viscous ionic liquids, complex formation is slow, and it takes several days before thermodynamic equilibrium is reached. Probably for this reason no complex formation was observed during the experiments in [C_4mim][PF_6], the most viscous ionic liquid studied.

The coordination chemistry of actinides in ionic liquids has recently been reviewed by Rogers and co-workers.[68] Uranium(VI) oxide solubilizes in basic chloroaluminate ionic liquids to form a series of uranyl chloro complexes that can be formulated as $[UO_2Cl_{4+x}]^{(2x+1)-}$, where $x = 0-2$.[69] The research groups of Seddon and Hussey studied the structure of the uranium salts 1-ethyl-3-methylimidazolium hexachlorouranate(IV), $[C_2mim]_2[UCl_6]$, and tetrachlorodioxouranium(VI), $[C_2mim]_2[UO_2Cl_4]$.[70] The crystal structures of these compounds have been reported. A recent hydrogen bonding analysis of these complexes revealed that donor hydrogen atoms of low acidity, like the methylene protons of the ethyl group and the protons of the methyl group form C−H···Cl hydrogen bonds, whereas the much more acidic C2 proton of the imidazolium ring is not involved in hydrogen bonding.[71,72] In the $[UO_2Cl_4]^{2-}$ group, the negative charge is concentrated on the four equatorial chloro ligands, rather than on the axial oxygen ligands.

The behavior of the $[UO_2]^{2+}$, $UO_2(NO_3)_2$, UO_2Cl_2, and $[UO_2Cl_4]^{2-}$ species in the ionic liquids [C_4mim][PF_6] and [C_2mim][$AlCl_4$] were compared by using molecular dynamics calculations.[58] The calculations predict that the free uranyl ion in [C_4mim][PF_6] is surrounded on average by six $[PF_6]^-$ anions and that these $[PF_6]^-$ groups freely rotate. The free uranyl ion in [C_2mim][$AlCl_4$] is surrounded by a fairly rigid shell of $[AlCl_4]^-$ anions that shield the uranyl ion from the $[C_2mim]^+$ cations in the second shell. The first ionic shell of the neutral species $UO_2(NO_3)_2$ and UO_2Cl_2 consists mainly of $[PF_6]^-$ or $[AlCl_4]^-$ anions. The imidazolium cations efficiently solvate the $[UO_2Cl_4]^{2-}$ complexes: each $[UO_2Cl_4]^{2-}$ ion is surrounded by six to nine imidazolium cations. According to the molecular dynamics calculations, the solvation of the uranyl ion is different in dry and wet ionic liquids. In wet [C_4mim][PF_6], the uranyl ion forms $[UO_2(H_2O)_5]^{2+}$ complexes that are surrounded by eight $[PF_6]^-$ anions.[59] In the same wet ionic liquid, $[UO_2Cl_4]^{2-}$ complexes are surrounded by a shell of water molecules, followed by a shell of $[C_4mim]^+$ cations. Simulations show that the $[UO_2Cl_4]^{2-}$ complex is the dominating species in basic

$AlCl_3$−[C_2mim]Cl ionic liquids.[60] Mizuoka and Ikeda assume that the uranyl ion exists in the dehydrated 1-butyl-3-methylimidazolium nonafluorobutanesulfonate ionic liquid as a naked cation, with no ligands in its equatorial plane.[73] Experimental and theoretical studies on the interaction between the uranyl ion and fluorinated anions in acidic aqueous solutions have been performed to get insight in the ability of these ligands to coordinate to the uranyl ion in wet ionic liquids.[74] It was found that the $[Tf_2N]^-$ ion does not coordinate to the uranyl ion so that uranyl will be coordinated by water molecules in wet [C_4mim][Tf_2N]. However, $[PF_6]^-$ and $[BF_4]^-$ are able to compete with water molecules for coordination to the uranyl ion. $[UO_2(PF_6)]^+$ and $[UO_2(BF_4)]^+$ can be formed.

Schurhammer and Wipff have investigated by molecular dynamics the solvation of the uranium hexachloro complexes $[UCl_6]^{n-}$ (n = 1, 2, 3) in the hydrophobic ionic liquids [C_4mim][Tf_2N] and [$(CH_3)(C_4H_9)_3N$][Tf_2N].[75] The solvation of the complexes depends both on the uranium oxidation state and on the nature of the ionic liquid. The first coordination shell of $[UCl_6]^{3-}$ contains only solvent cations. The first solvation shell is surrounded by a second shell that is mainly anionic in nature. The first solvation shell of the less charged $[UCl_6]^-$ complex is also positively charged but consists of a mixture of solvent cations and anions. The solvation behavior of $[UCl_6]^{2-}$ is intermediate between that of $[UCl_6]^{3-}$ and $[UCl_6]^-$. Notice that $[UCl_6]^{2-}$ with uranium in its tetravalent state is chemically the most stable hexachloro complex of uranium. The calculations indicate that the hexachloro complexes are better solvated by [C_4mim][Tf_2N] than by [$(CH_3)(C_4H_9)_3N$][Tf_2N]. The presence of water molecules has only little effect on the solvation of the $[UCl_6]^{n-}$ species.

Upon dissolution of [C_4mim]$_2$[$NpCl_6$] and [C_4mim]$_2$[$PuCl_6$] in the ionic liquid [C_4mim][Tf_2N], the octahedral hexachloro complexes $[NpCl_6]^{2-}$ and $[PuCl_6]^{2-}$ are preserved in solution.[76] These complexes are stable against hydrolysis in water in wet [C_4mim][Tf_2N]. However, when [C_4mim]Cl is added to the [C_4mim][Tf_2N] ionic liquid, precipitation of solid compounds is observed. Although these solid compounds were not characterized in detail, it can be assumed that oligomeric or polymeric species with a chloride-to-metal ratio higher than six are formed. Time-resolved laser fluorescence spectroscopy data show that the coordination of curium(III) in the ionic liquid [C_4mim][Tf_2N] is very similar to that of europium(III) in the same ionic liquid.[77]

2.2. Solubility

Contrary to common belief, most ionic liquids are not “supersolvents” in which all kinds of materials including rocks can be dissolved without any problem. In fact, the solubility of common inorganic ionic compounds like sodium chloride in the classic imidazolium ionic liquids is very low.[78] This low solubility is due to the poor solvating power of ionic liquids with weakly coordinating anions like $[BF_4]^-$, $[PF_6]^-$, or $[Tf_2N]^-$ and to the modest polarity of ionic liquids, which is comparable to that of the lower alcohols. The solubility of metal salts is better in ionic liquids with coordinating anions, like chloride ions. Chloroaluminate ionic liquids are good solvents for a range of transition metal salts, including lanthanide and actinide salts. The solubility of metal salts in so-called *task-specific ionic liquids* can be higher than that in the common types of ionic liquids, because the task-specific ionic liquids can be designed to exhibit excellent metal-salt solubilizing power.[79−82] When assessing the solubility of metal salts in hydrophilic ionic liquids, one has to realize that these solvents tend to retain even after drying a non-negligible amount of water. High solubilities of ionic compounds in hydrophilic ionic liquids can often be attributed to the solubilizing properties of the water present and not to the ionic liquid itself. On the other hand, coordination complexes can be solubilized in ionic liquids, especially hydrophobic or anionic complexes. A trick to solubilize metal salts in an ionic liquid is to dissolve both the metal salt and the ionic liquid first in an organic solvent (or water), followed by evaporation of the solvent. Finally, it should not be forgotten that many ionic liquids have a high viscosity. The slow mass transfer in viscous ionic liquids can slow down the dissolution process of metal salts.

Afonso and co-workers investigated the solubility of $LaCl_3$ in different imidazolium ionic liquids, and the results show that the solubilities are very low.[83] For instance, in 100 g of 1-butyl-3-methylimidazolium hexafluorophosphate, [C_4mim][PF_6], only 0.658 mg of $LaCl_3$ can be dissolved at room temperature. The solubility of $LaCl_3$ in tetrafluoroborate ionic liquids is higher than that in the corresponding hexafluorophosphate ionic liquids. The presence of ether or hydroxyl functional groups in the alkyl chains of the cationic part of the ionic liquids enhances the solubility of salts, but in none of the cases the solubility of $LaCl_3$ is higher than 29 mg per 100 g of ionic liquid. This stands in contrast to the high solubility of $LaCl_3$ in water, 49.2 g per 100 g of water (at 25 °C)! Addition of poly(ethylene glycol) (PEG) to an ionic liquid[6] can also increase the solubility of inorganic salts, but this has not been tested for lanthanide salts yet.

Tsuda and co-workers determined the solubility of $LaCl_3$ in $AlCl_3$−[C_2mim]Cl ionic liquids.[84] They observed the highest solubility of $LaCl_3$ in acidic chloroaluminate ionic liquids, that is, systems where a high concentration of the $[Al_2Cl_7]^-$ anion is present. The highest solubility of $LaCl_3$ at 25 °C is 45 ± 5 mmol/kg, which corresponds to 1.1 g per 100 g of ionic liquid. The dissolution reaction is thought to be

$$LaCl_3 + 3[Al_2Cl_7]^- \rightleftarrows La^{3+} + 6[AlCl_4]^- \qquad (1)$$

Scandium(III) triflate is only slightly soluble in [C_4mim][PF_6], but it is well soluble in [C_4mim][BF_4] and [C_4mim][OTf].[85] The same solubility behavior was reported for dysprosium(III) triflate.[86] Mehdi et al. investigated the solubility of cerium(IV) salts in imidazolium ionic liquids.[87] The following cerium(IV) salts were selected: ammonium hexanitratocerate(IV), cerium(IV) sulfate dihydrate, cerium(IV) ammonium sulfate, cerium(IV) ammonium sulfate dihydrate, cerium(IV) hydroxide, cerium(IV) triflate, and hydrated cerium(IV) triflate. A general observation is that cerium(IV) salts can only with difficulty be dissolved in imidazolium ionic liquids. Among the cerium(IV) salts that were investigated, only ammonium hexanitratocerate(IV) (CAN) and cerium(IV) triflate (anhydrous and hydrated) were well soluble. The triflate ionic liquids are the best choice to solubilize cerium(IV) salts.

There are only a limited number of data on the temperature dependence of the solubility of lanthanide salts in ionic liquids available, but there are indications that the solubility increases with increasing temperature (as is the case for the solubility in many other solvents). Mudring took advantage of this property to crystallize [mppyr]$_2$[$Yb(Tf_2N)_4$] from a solution of the ionic liquid 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [mppyr][Tf_2N].[96] Notice that this compound contains divalent ytterbium. The solubility of EuI_2 in [C_4mim][PF_6] was estimated to be 2 mmol L^{-1}.[88]

Very high solubilities of rare-earth oxides were observed in the task-specific ionic liquid protonated betaine bis(trifluoromethylsulfonyl)imide, [Hbet][Tf_2N].[89] Hbet stands for $(CH_3)_3N^+CH_2COOH$. The high solubility is due to the acid−base reaction between protonated betaine and the rare-earth oxide Ln_2O_3 so that complexes of the type [Ln(bet)$_3$][Tf_2N] are formed.

For $LaCl_3$ and Cs_2UCl_6, solutions of at least 0.05 mol L^{-1} can be prepared in ethylammonium nitrate at 25 °C.[90] The tetravalent uranium in Cs_2UCl_6 can be oxidized in this ionic liquid to uranyl by an oxygen flow:

$$U^{4+} + O_{2(g)} + 2\,Cl^- \rightarrow UO_2^{\;2+} + Cl_{2(g)} \tag{2}$$

Upon addition of Li_2O to these solutions, both La_2O_3 and UO_3 precipitate. Interestingly, the precipitate obtained from solutions that have originally a U/La ratio of 1 were found to have a U/La ratio of 4. The solid phase is thus enriched in uranium in comparison to the solution. This can be explained by the higher solubility of UO_3 than La_2O_3 in the ionic liquid.

2.3. Lanthanide Complexes as Major Ionic Liquid Components

In most of the ionic liquid systems described in this review, lanthanide and actinide salts are dissolved in an ionic liquid. However, there are also ionic liquids that contain f-elements as a main component. Examples are the inorganic ionic liquids that are based on lanthanide-containing polyoxometalate anions with the Keggin structure, $Na_{13}[Ln(TiW_{11}O_{39})_2]\cdot xH_2O$. ($x$ varies between 27 and 44).[91] Water is a necessary component in these ionic liquids; upon loss of the constituent water molecules, the ionic liquids are transformed into “mudlike” solids. The ionic liquids are immiscible with all common organic solvents and water at room temperature. However, at higher temperatures, they are miscible with water. Nockemann et al. reported on room-temperature ionic liquids based on anionic rare-earth thiocyanate complexes.[92] Different stoichiometries have been observed, and the complexes can be represented by the general formula $[C_4mim]_{x-3}[Ln(NCS)_x(H_2O)_y]$ ($x = 6-8$; $y = 0-2$; $x + y < 10$; Ln = Y, La−Yb) (Figure 5). These ionic liquids are miscible with hydrophobic ionic liquids like [C_4mim][Tf_2N]. However, the rare-earth-containing ionic liquids are completely hydrolyzed in aqueous solutions.

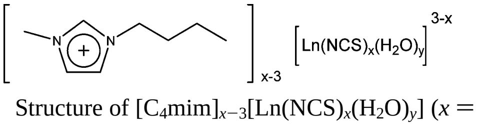


Figure 5. Structure of $[C_4mim]_{x-3}[Ln(NCS)_x(H_2O)_y]$ ($x = 6-8$; $y = 0-2$; $x + y < 10$; Ln = Y, La−Yb).

2.4. Bis(trifluoromethylsulfonyl)imide Complexes

Given the omnipresence of the bis(trifluoromethylsulfonyl)imide ion, [Tf_2N]$^-$, as anion in different classes of ionic liquids,[11−13,14] it is of importance to get insight in the coordination behavior of this anion. Because the [Tf_2N]$^-$ ion is a weakly coordinating anion, it can be expected that this ion will not coordinate to lanthanide ions in wet ionic liquids and that in this case the first coordination sphere contains only water molecules. However, in dry ionic liquids or in ionic liquids with a low water content, the situation is different, and the [Tf_2N]$^-$ ion can no longer be considered as a noncoordinating anion. The interaction of [Tf_2N]$^-$ with lanthanide ions can be studied by different spectroscopic methods such as absorption spectroscopy, luminescence spectroscopy, and EXAFS. Direct information on the coordination modes can be obtained from crystal structures of the metal complexes. Although the compounds that crystallize from a solution do not necessarily have the same stoichiometry as the complexes dissolved in the solution, single-crystal X-ray data can give valuable information. A few examples of crystal structures of lanthanide(III) bis(trifluoromethylsulfonyl)imide complexes have been published. $[La(Tf_2N)_3(H_2O)_3]$ crystallizes in the cubic space group $P2_13$ (Figure 6). The [Tf_2N]$^-$ ligand acts as a bidentate ligand, and coordination occurs through an oxygen atom of each sulfonyl group.[93] Because of the additional coordination of three water molecules, the coordination number of the lanthanum(III) ion is nine. The coordination polyhedron can be described as a tricapped trigonal prism, and the three water molecules form the bottom triangular face of the trigonal prism. The three [Tf_2N]$^-$ ligands bind to the central metal ion in a propeller-like arrangement, which makes the complexes chiral. Of the eight coordinating units in the unit cell, four have the Λ absolute configuration and four have the Δ absolute configuration. The fact that [Tf_2N]$^-$ is a weakly coordinating anion towards trivalent lanthanide ions is nicely illustrated in recent work by Babai and Mudring.[94] By reaction of anhydrous praseodymium(III) iodide with the ionic liquid [bmpyr][Tf_2N] (where bmpyr is 1-butyl-1-methylpyrrolidinium), crystals of [bmpyr]$_4$[PrI_6][Tf_2N] were obtained. Above each face of the [PrI_6]$^{3-}$ octahedra, one 1-butyl-1-methylpyrrolidinium cation is tangentially located. [Tf_2N]$^-$ anions fill the remaining space. To force the bis(trifluoromethylsulfonyl)imide anion to coordinate to the

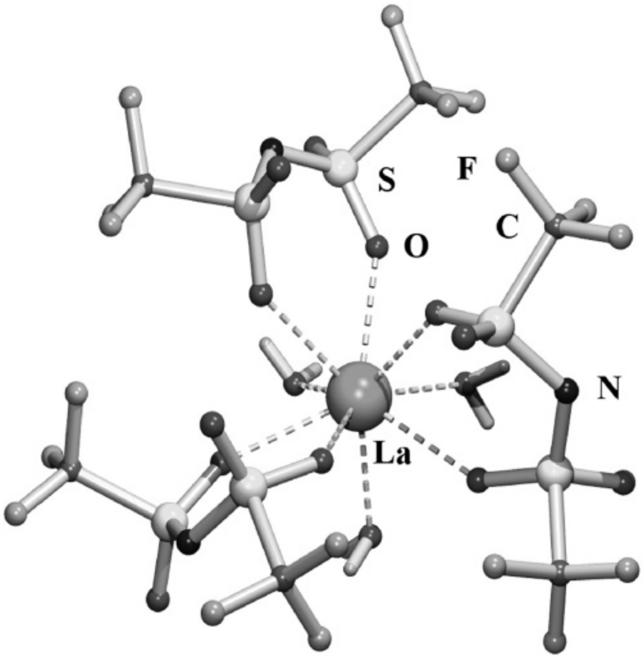


Figure 6. Molecular structure of $[La(Tf_2N)_3(H_2O)_3]$. The atomic coordinates were taken from ref 93.

lanthanide ion, the authors reacted $Pr(Tf_2N)_3$ with the ionic liquid [bmpyr][Tf_2N]. In this case, a crystalline compound with the composition $[bmpyr]_2[Pr(Tf_2N)_5]$ was obtained. In the crystal structure, sheets formed by $[Pr(Tf_2N)_5]^{2-}$, which are separated by layers of $[bmpyr]^+$ cations. The crystal structures of $[bmpyr]_4[LaI_6][Tf_2N]$ and $[bmpyr]_4[ErI_6][Tf_2N]$ have been reported later on.[95] With divalent ytterbium, $[Tf_2N]^-$ forms the complex $[mppyr]_2[Yb(Tf_2N)_4]$, where mppyr is 1-methyl-1-propylpyrrolidinium (Figure 7).[96] Here, the coordinating unit is an anionic tetrakis complex, which shows similarities with the well-known tetrakis β-diketonate complexes.[97] A subsequent study described the crystal structures of $[bmpyr]_2[Ln(Tf_2N)_5]$ (Ln = Nd, Tb) and $[bmpyr][Ln(Tf_2N)_4]$ (Ln = Tm, Lu).[98] In these compounds, only coordination via the oxygen atoms of the $[Tf_2N]^-$ anion is observed and discrete anionic complexes of the types $[Ln(Tf_2N)_5]^{2-}$ and $[Ln(Tf_2N)_4]^-$ are built. In the $[Ln(Tf_2N)_5]^{2-}$ unit formed by the larger lanthanide(III) ions, four $[Tf_2N]^-$ anions are bidentate, and one $[Tf_2N]^-$ anion is monodentate, so the coordination number of the lanthanide ion is nine. The coordination polyhedron can be described as a monocapped square antiprism. In the $[Ln(Tf_2N)_4]^-$ unit formed by the smaller lanthanide ions, four bidentate $[Tf_2N]^-$ anions result in coordination number eight. The coordination polyhedron is in this case a dodecahedron. This study also points to the conformational flexibility of $[Tf_2N]^-$ anions, with the presence of both *cisoid* and *transoid* conformations of the anions. This can be an explanation for why it is so difficult to obtain bis(trifluoromethylsulfonyl)imide complex crystals of good quality. The influence of the alkyl chain length of the pyrrolidinium ionic liquids on the type of complexes that can be crystallized from this type of ionic liquid is shown by the fact that after dissolution of NdI_3 in [bmpyr][Tf_2N] or in [mppyr][Tf_2N], the complex $[bmpyr]_4[NdI_6][Tf_2N]$ precipitated from [bmpyr][Tf_2N] and the complex $[mppyr]_3[NdI_6]$ from [mmpyr][Tf_2N].[99]

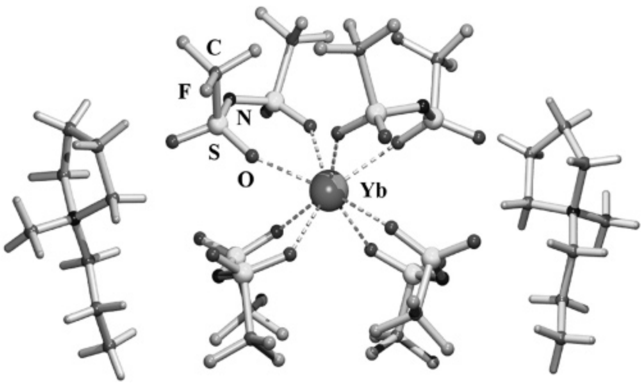


Figure 7. Molecular structure of $[mppyr]_2[Yb(Tf_2N)_4]$. The atomic coordinates were taken from ref 96.

The divalent lanthanide iodides SmI_2 and NdI_2 were found to react with the ionic liquid triethylsulfonium bis(trifluoromethylsulfonyl)imide, [SEt_3][Tf_2N], and single crystals of $[SEt_3]_3[NdI_6]$ and $[SEt_3]_3[SmI_6]$ could be obtained.[100] The octahedral building units $[LnI_6]^{3-}$ are surrounded by eight triethylsulfonium cation in a distorted cubic arrangement. The octanuclear europium(III) cluster $[bmpyr]_6[Eu_8(\mu_4\text{-O})(\mu_3\text{-OH})12(\mu_2\text{-OTf})_{14}(\mu_1\text{-OTf})][HOTf]_{1.5}$ has been synthesized by reaction of acidic europium(III) triflate with the ionic liquid [bmpyr][OTf] in a sealed silica tube at 120 °C.[101]

3. Spectroscopic Properties

3.1. Trivalent Lanthanide Ions

The trivalent lanthanide ions have special spectroscopic properties because the 4f valence shell is shielded from the environment around the lanthanide ion by higher lying closed shells.[102,103] Therefore the weak intraconfigurational f−f transitions show sharp line transitions. A lanthanide spectrum resembles more an atomic spectrum than a transition metal spectrum. In addition, some lanthanide ions exhibit a strong photoluminescence, so the lanthanides are of interest for luminescence applications. The luminescence can be in the visible (e.g., Eu^{3+}, Tb^{3+}) or in the near-infrared part of the spectrum (e.g., Nd^{3+}, Er^{3+}, Yb^{3+}). The spectroscopic properties of the lanthanide and actinide ions are somewhat similar, although the absorption bands of actinide ions are in general more intense than those of the lanthanide ions. This can be explained by the less effective shielding of the 5f valence shell from its environment (in contrast to the 4f shell of the lanthanide ions).

The luminescence of the Eu^{3+} ion can be used to probe the local environment of lanthanide ions in ionic liquids. Changes in the crystal-field fine structure observed in high-resolution emission spectra reflect small changes in the first coordination sphere of the Eu^{3+} ion. For instance, the interaction between Eu^{3+} and halides (chloride/fluoride) in anhydrous 1-butyl-3-methylimidazolium ionic liquids with different anions ($[BF_4]^-$, $[PF_6]^-$, $[OTf]^-$, $[Tf_2N]^-$) has been investigated.[67] The effects of water and added chloride ions on the spectra of Eu^{3+} in the ionic liquid [C_4mim][Tf_2N] were studied.[65] Besides the crystal-field fine structure of the spectra, also the luminescence decay time can provide valuable information. For instance, the decay time of the excited state $^5D_0$ of the Eu^{3+} ion can be used to determine the number of water molecules that is directly coordinated to the Eu^{3+} ion.[104] Monitoring the luminescence intensity and the luminescence decay time as a function of the temperature allowed detection of phase transitions in europium(III)-containing ionic liquid crystals. Bünzli and coworkers investigated the spectroscopic properties of different europium(III) salts dissolved in 1-alkyl-3-methylimidazolium chloride and nitrate ionic liquid crystals.[105] The neat ionic liquid crystals showed blue fluorescence (ligand emission) upon irradiation by ultraviolet radiation. Addition of a europium(III) salt partially quenched this blue fluorescence, but at the same time, red europium(III)-centered luminescence was observed. This is due to energy transfer of the excitation energy from the organic chromophores to the europium(III) ion. By a proper choice of the excitation wavelength and counterion, the emission color could be tuned from blue to red. Ionic liquids have a beneficial effect on the photostability of lanthanide β-diketonate complexes.[106] The β-diketonate complexes are being intensively studied as molecular luminescent materials.[97] Although the lanthanide β-diketonates exhibit intense photoluminescence intensities, they suffer from a low photochemical stability. Irradiation of solutions of lanthanide β-diketonate by ultraviolet radiation often leads to fast decomposition of the complexes and of the ligands. It was shown that a europium(III) tetrakis(2-thenoyltrifluoroacetonate) complex dissolved in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_6mim][Tf_2N], has a much higher photostability than when dissolved in acetonitrile.[106] The authors also showed the crystal structure of the europium tetrakis β-diketonate complex with $[C_6mim]^+$ counterions (Figure 8).

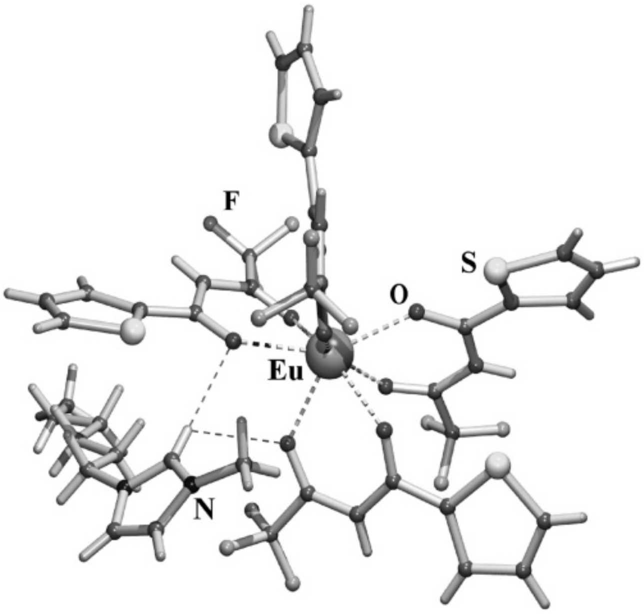


Figure 8. Molecular structure of [C_6mim][Eu(tta)$_4$], where C_6mim is 1-hexyl-3-methylimidazolium and tta is 2-thenoyltrifluoroacetonate. The atomic coordinates were taken from ref 106.

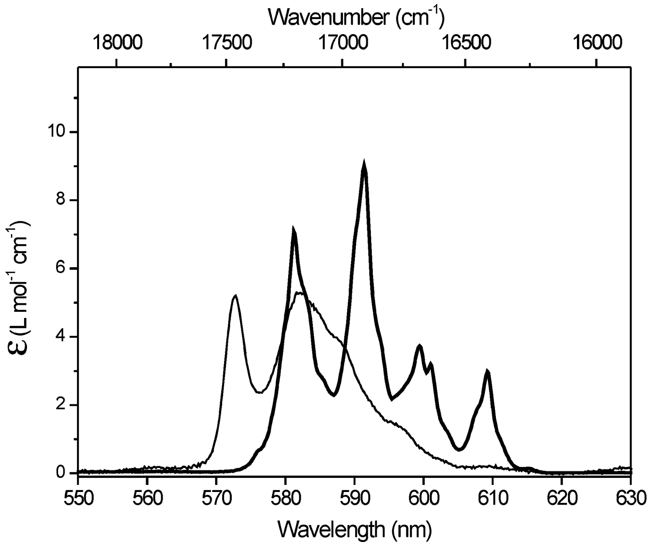


Figure 9. Absorption spectra of the hypersensitive transition $^4G_{5/2} \leftarrow {}^4I_{9/2}$ at 586 nm of [Nd(nta)$_4$]$^-$ in [C_6mim]Br (thin line) and of $NdBr_3$ in [C_6mim]Br (thick line) Here, nta is naphthoyltrifluoroacetonate and C_6mim is 1-hexyl-3-methylimidazolium.

Ionic liquids are good solvents to study the infrared luminescence of lanthanide complexes in solution, as was illustrated by the infrared luminescence of Nd^{3+} ions in different imidazolium ionic liquids.[107] This study shows that the band shape and the intensity of the hypersensitive $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition (observable in the absorption spectrum at ca. 586 nm) depends very much on the type of anion in the ionic liquid (Figure 9). The dramatic effect of the water content of the ionic liquid on the infrared emission was evident for neodymium(III) iodide and erbium(III) iodide dissolved in carefully dried 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.[108] Exposure of the samples to atmospheric moisture lead to a rapid decrease of the luminescence intensity to nearly zero intensity. Bünzli and co-workers studied the visible and near-infrared luminescence of lanthanide β-diketonate complexes [Ln(tta)$_3$(phen)] (Ln = Nd, Eu, Er, Yb; tta = 2-thenoyltrifluoroacetonate; phen = 1,10-phenanthroline) dissolved in the ionic liquid crystal 1-dodecyl-3-methylimidazolium chloride.[109] An interesting observation is that the quantum efficiency of the [Yb(tta)$_3$(phen)] complex dissolved in the ionic liquid is higher than that for the complex in the solid state. This indicates that nonradiative relaxation processes are less important in the ionic liquid solution than in the solid state. On the other hand, the quantum efficiency of [Yb(tta)$_3$(phen)] dissolved in toluene is smaller than that in the solid state. For [Nd(tta)$_3$(phen)], [Er(tta)$_3$(phen)], and [Yb(tta)$_3$(phen)] the luminescence decay times are slightly longer in the ionic liquid than in the solid state. Once again, this illustrates the reduction of the nonradiative relaxation processes in the ionic liquid compared to these processes in the solid state. A spectroscopic study of PrI_3 and Pr(Tf_2N)$_3$ in the ionic liquid [bmpyr][Tf_2N] (where bmpyr is 1-butyl-1-methylpyrrolidinium) revealed that after excitation in the $^3P_2$ level emission takes place not only from the $^1D_2$ level but also from the $^3P_0$ and $^3P_1$ levels.[94] This is one of the few cases where luminescence starting from the $^3P_1$ level was observed in the liquid state. This unusual behavior can be attributed to the reduced radiationless deactivation of the excited states of the Pr^{3+} ion in the ionic liquid. Also dysprosium(III) iodide and terbium(III) iodide show a strong photoluminescence when dissolved in an imidazolium ionic liquid.[110]

3.2. Divalent Lanthanide Ions

The spectroscopic behavior of divalent europium differs very much from that of trivalent europium. Whereas the absorption and luminescence spectra of the Eu^{3+} exhibit the typical line transitions due to the forbidden intraconfigurational f−f transitions, the spectra of Eu^{2+} contain intense broad bands due to the allowed interconfigurational f−d transitions. Billard and co-workers studied the absorption and luminescence spectra of EuI_2 dissolved in [C_4mim][PF_6].[88]

3.3. Uranium

UV−vis spectroscopy is a useful technique for the speciation of uranium complexes, because each oxidation state of uranium gives a typical spectrum. Although the uranyl ion (dioxouranium(VI) ion) has no f-electrons, electronic transitions are possible between the molecular orbitals formed by interaction between ligand and uranyl atomic orbitals. The absorption and luminescence spectra of uranyl compounds exhibit a characteristic vibrational fine structure.[111] Absorption spectra of uranium(VI) (uranyl), uranium(V), uranium(IV), and uranium(III) in ionic liquids have been reported.[112] Most of those studied have been performed in chloroaluminate ionic liquids. The vibrational fine structure in the absorption and luminescence spectra of the dioxouranium (uranyl) ion can be used to probe the local environment of this ion. Anderson and co-workers used spectroscopic methods to monitor the decomposition of UO_2Cl_2 in an acidic $AlCl_3$−[C_2mim]Cl melt.[113] Also in studies on the mechanism of solvent extraction in ionic liquids, the absorption spectra of the uranyl ions were useful. The spectra of the octahedral hexachlorouranate(IV) complex [UCl_6]$^{2-}$ in the ionic liquids [C_4mim][Tf_2N] and [(CH_3)(C_4H_9)$_3$N][Tf_2N] have been presented.[114] The intensities of the complex in ionic liquids were higher than those in acetonitrile, which was attributed to the stronger solvation in ionic liquids. The [UCl_6]$^{2-}$ is stable against hydrolysis in the ionic liquids.

Addition of ≥4 equiv of chloride ions to a solution of $[UO_2][OTf]_2$ in the ionic liquids $[C_4mim][Tf_2N]$ and $[(CH_3)(C_4H_9)_3N][Tf_2N]$ leads to the formation of the tetrachlorouranyl complex $[UO_2Cl_4]^{2-}$.[115] This complex has a very typical absorption spectrum.[116,117] The photoluminescence of uranyl complexes is barely detectable in imidazolium ionic liquids due to the background luminescence of the imidazolium cation. The $[UO_2Cl_4]^{2-}$ complex shows an intense luminescence in the quaternary ammonium ionic liquid.

3.4. Other Actinides

Schoebrechts and Gilbert reported the absorption spectra of neptunium(III) and neptunium(IV) in different chloroaluminate ionic liquids.[118] This work shows that $[NpCl_6]^{3-}$ and $[NpCl_6]^{2-}$ occur in basic chloroaluminate melts, whereas $[NpCl_x]^{(4-x)+}$ (with $1 \leq x \leq 3$) species are present in acidic chloroaluminate ionic liquids. Nikitenko and Moisy studied the absorption and diffuse reflectance spectra of $[NpCl_6]^{2-}$ and $[PuCl_6]^{2-}$ complexes in the ionic liquid $[C_4mim][Tf_2N]$.[76] These studies revealed that these hexachloro complexes are stable against hydrolysis but not stable against addition of chloride ions. Although time-resolved laser fluorescence spectroscopy measurements indicate that the coordination sphere of curium(III) is very similar to that of europium(III) in the ionic liquids $[C_4mim][Tf_2N]$, the two ions show a different behavior with respect to luminescence quenching by copper(II) ions.[77] Copper(II) does not quench the luminescence of curium(III) in $[C_4mim][Tf_2N]$ whereas the luminescence decay time of europium(III) decreases with increasing copper(II) concentration.

4. Redox Behavior and Electrodeposition of Metals

4.1. Redox Behavior of Lanthanides

Lanthanide chemistry is dominated by the trivalent oxidation state in aqueous solution (with the exception of Eu^{2+} and Ce^{4+}), but other lanthanide ions in other oxidation states than +3 can occur in the solid state and in nonaqueous solutions.[56,119,120] It is therefore not a surprise that lanthanide ions in different oxidation states can occur in ionic liquids. Several ionic liquids have a wide electrochemical window, which means that they are stable over a large potential range.[6] The electrochemical properties of lanthanide ions in chloroaluminate ionic liquids have been reviewed by O'Donell.[112] Acidic chloroaluminate ionic liquids are good solvents for the stabilization of divalent lanthanide ions, partially due to the weakly solvating power of the ionic liquid solvent. The divalent lanthanide ions Sm^{2+}, Eu^{2+}, Tm^{2+}, and Yb^{2+} were prepared from the trivalent lanthanide ion by electrolytic reduction of trivalent lanthanide salts dissolved in $AlCl_3-[Bupy]Cl$ ionic liquids.[121,122] However, the divalent ions are much less stable in basic chloroaluminate ionic liquids. It was suggested by O'Donnell that divalent lanthanide ions could undergo disproportionation in chloroaluminate ionic liquids if the acidity of the ionic liquid is reduced to neutrality and the ionic liquids are progressively more basic.[112] The disproportionation involves decomposition of Ln^{2+} species into Ln^{3+} and Ln^0 species. The presence of dispersed lanthanide metal particles renders the basic ionic liquids containing divalent lanthanides to strongly reducing mixtures. The largest electrochemical window is observed for chloroaluminate ionic liquids with a neutral or close to neutral composition ("neutral basic" and "neutral acidic" melts). This extended electrochemical window allows the investigation of redox systems that are inaccessible in acidic and basic chloroaluminate melts. The redox behavior of europium[123] and ytterbium[124] has been investigated by Gua and Sun in $AlCl_3-[C_2mim]Cl$ ionic liquids. Billard and co-workers report that the divalent europium ion is unusually stable in the 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid.[88] Trials to oxidize Eu^{2+} in Eu^{3+} in $[C_4mim][PF_6]$ by $K_2Cr_2O_7$, $Ce(SO_4)_2$, or O_2 were unsuccessful. A solution of Eu^{2+} in $[C_4mim][PF_6]$, left in a container without special care, is stable for months. Europium(III) is easier to reduce to europium(II) in imidazolium and ammonium ionic liquids than in aqueous solutions.[125] Mudring et al. reported that the divalent ytterbium ion is a stable species in a pyrrolidinium ionic liquid.[96] The redox behavior of the lanthanide complexes $[Ln(Tf_2N)_3(H_2O)_3]$ (where Ln = La, Sm, Eu) in the ionic liquid $[(n\text{-}C_4H_9)(CH_3)_3N][Tf_2N]$ has been investigated by cyclic voltammetry.[93] Whereas only one cathodic reduction peak could be observed for the lanthanum system, two reduction peaks could be observed for the samarium and europium systems. This is consistent with the occurrence of the La^{3+}/La^0 redox couple for lanthanum, with the redox couples Sm^{3+}/Sm^{2+} and Sm^{2+}/Sm^0 for samarium, and with the redox couples Eu^{3+}/Eu^{2+} and Eu^{2+}/Eu^0 for europium. However, all these redox reactions are irreversible, and as a consequence, no anodic oxidation peak (stripping peak) could be observed. Yamagata and co-workers investigated the electrochemical behavior of samarium, europium, and ytterbium in the ionic liquids $[C_2mim][Tf_2N]$ and $[C_4mim][Tf_2N]$.[126] Tetravalent cerium is not stable in LiCl−KCl eutectic melts, because cerium(IV) is reduced by chloride ions.[127] Cerium(IV) has a higher kinetic stability in $AlCl_3-[C_2mim]Cl$ ionic liquids, but it is eventually reduced to cerium(III).[128] The half-life of cerium(IV) in this ionic liquid is 8 days at room temperature. Both cerium(III) and cerium(IV) form hexachloro complexes, $[CeCl_6]^{2-}$ and $[CeCl_6]^{3-}$. This study also shows that cerium(IV) can be generated by electrolysis in basic chloroaluminate ionic liquids.

4.2. Redox Behavior of Uranium

The redox behavior of uranium species has been studied in detail in chloroaluminate ionic liquids.[112] Major differences were found between the behavior in acidic and in basic melts. Surprisingly, UO_2Cl_2 is not stable in an acidic chloroaluminate melt.[113] The decomposition of uranyl is characterized by a relatively rapid disappearance of $[UO_2]^{2+}$ to form an intermediate that slowly reacts further to the uranium(V) species $[UCl_6]^-$ as the final product. The solvent acts as the reducing agent, in which the species $[AlCl_4]^-$ and $[Al_2Cl_7]^-$ are oxidized to form chlorine gas. A detailed study of the reaction mechanism has been performed in acidic $AlCl_3-[C_2mim]Cl$ room-temperature ionic liquids. The first steps are probably two rapid acid−base equilibria:

$$UO_2^{\ 2+} + Al_2Cl_7^{\ -} \rightleftarrows UO^{4+} + AlCl_4^{\ -} + AlOCl_3^{\ 2-} \quad (3)$$

and

$$UO^{4+} + Al_2Cl_7^{\ -} \rightleftarrows U^{6+} + AlCl_4^{\ -} + AlOCl_3^{\ 2-} \quad (4)$$

By these reactions two oxide ions are transferred from uranyl to the solvent so that the U^{6+} ion is formed in solution. U^{6+} and possibly also UO^{4+} are then slowly reduced to U^{5+}. The uranyl ion can be reduced electrolytically in the acidic chloroaluminate ionic liquid by bulk coulometry to U^{4+}. Due to the reducing capability of the solvent, this electrolytic reaction is on average only a 1.7-electron process and not a two-electron process. In acidic $AlCl_3-[BuPy]Cl$, uranium(IV) is stable over the entire acidic composition range.[129] $[UCl_3]^+$ is the dominant species in a 2:1 $AlCl_3-[BuPy]Cl$ melt, but with decreasing acidity of the melt (i.e., increase of Cl^- content), $[UCl_2]^{2+}$ and $[UCl_3]^+$ become the dominant species. When the acidity of the melt is decreased further, UCl_4 will start to precipitate. Uranium(IV) can be reduced electrolytically in this ionic liquid to uranium(III), and it can be oxidized electrolytically to uranium(V) and uranium(VI). Uranium(III) occurs in the melt as U^{3+} and not as a chloro complex like uranium(IV) but as solvated cations.[130] Solvation probably occurs by $[UCl_4]^-$, except in the more acidic ionic liquids, where $[Al_2Cl_7]^-$ is most probably the counterion. On the other hand, uranium(V) occurs as the $[UCl_6]^-$ complex, which has approximately an octahedral symmetry.[131] The oxidation of uranium(V) to uranium(VI) takes place at potentials more positive than the thermodynamic potential limit of the solvent (chlorine gas formation). Because of the reaction of uranium(VI) with the solvent, pure solutions of uranium(VI) cannot be prepared by bulk coulometry. Dissolution of either $[C_2mim]_2[UBr_6]$ or $[C_2mim]_2[UO_2Br_4]$ in an acidic $AlBr_3-[C_2mim]Br$ ionic liquid results in the formation of the same electroactive species, which is very likely the solvated uranium(IV) ion, $[U(AlBr_4)_3]^+$.[71,72] The $[AlBr_4]^-$ species present in the acidic ionic liquid thus replaces the ligands that were originally bonded to the uranium center. The electroactive $[U(AlBr_4)_3]^+$ complex can be reduced to $[U(AlBr_4)_3]$ in a quasi-reversible reaction:

$$[U(AlBr_4)_3]^+ + e^- \rightleftarrows [U(AlBr_4)_3] \qquad (5)$$

In contrast to its behavior in acidic chloroaluminate ionic liquids, the uranyl ion is stable in basic ionic liquids.[113] The uranium(VI) ion can be reduced electrolytically to uranium(IV) with the formation of the $[UCl_6]^{2-}$ species. Uranium(III) is not a stable species in $AlCl_3-[BuPy]Cl$ ionic liquids; it is oxidized by the 1-butylpyridinium cation. It is stated that U^{3+} undergoes disproportionation into U^{4+} and U^0.[112] This disproportionation reaction leads to the formation of finely dispersed uranium metal, which can reduce the 1-butylpyridinium cation rather easily. The electrolytic reduction of U^{4+} to U^{3+} is not observed in $AlCl_3-[BuPy]Cl$ ionic liquids. Because the 1-ethyl-3-methylimidazolium cation is more difficult to reduce than the 1-butylpyridinium cation, U^{4+} reduction can be studied in basic $AlCl_3-[C_2mim]Cl$ ionic liquids.[113] Seddon, Hussey, and co-workers reported the cyclic voltammograms of the uranium salts $[C_2mim]_2[UCl_6]$ and $[C_2mim]_2[UO_2Cl_4]$ in a basic $AlCl_3-[C_2mim]Cl$ ionic liquid.[70] A two-electron reduction process of $[UO_2Cl_4]^{2-}$ involves a fast transfer of the oxygen ligands to the ionic liquid, followed by the formation of the hexachlorouranate(IV) ion, $[UCl_6]^{2-}$. In a second step, the reversible reduction of $[UCl_6]^{2-}$ to $[UCl_6]^{3-}$ takes place:

$$[UO_2Cl_4]^{2-} + 2[AlCl_4]^- + 2e^- \rightleftarrows 2\text{“}\{AlOCl_2\}^-\text{”} + [UCl_6]^{2-} + 2Cl^- \qquad (6)$$

$$[UCl_6]^{2-} + e^- \rightleftarrows [UCl_6]^{3-} \qquad (7)$$

In the case of the $[C_2mim]_2[UCl_6]$ salt, only the second step, the one-electron reversible redox process, occurs. The redox behavior of $[C_2mim]_2[UBr_6]$ and $[C_2mim]_2[UO_2Br_4]$ in basic $AlBr_3-[C_2mim]Br$ bromoaluminate ionic liquids is very similar to the redox behavior of the corresponding chloroaluminate systems.[71,72] The uranium(V) hexachloro complex $[UCl_6]^-$ undergoes spontaneous reduction in a basic $AlCl_3-[C_2mim]Cl$ ionic liquid to the uranium(IV) hexachloro complex $[UCl_6]^{2-}$.[131] This reduction is not due to disproportionation of uranium(V) but rather to the oxidation of ionic liquid components by uranium(V).

The electrochemistry of the hexachloro uranate(IV) complex $[UCl_6]^{2-}$ in the ionic liquids $[C_4mim][Tf_2N]$ and $[(CH_3)(C_4H_9)_3N][Tf_2N]$ has been discussed by Nikitenko and co-workers.[114] The study shows that the uranium redox potential is sensitive to the cation of the ionic liquid. The highest sensitivity was found for the uranium(IV)/uranium(III) redox couple. The reduction of uranium(III) to metallic uranium could be observed, but this process is irreversible. Martinot et al. studied the electrochemical reduction of uranium(VI) and uranium(IV) in the protic ionic liquid ethylammonium nitrate at 25 °C.[132] Uranium(VI) in the form of uranyl is stable in this ionic liquid, but it can be electrolytically reduced to the uranium(V) species UO_2^+. This reduction is an irreversible process, and UO_2^+ is unstable in the ionic liquid. Tetravalent uranium is unstable in ethylammonium nitrate, but when one works fast, it can be electrolytically reduced in a one-electron step to an unstable uranium(III) species.

4.3. Redox Behavior of the Other Actinides

Bhatt et al. demonstrated by cyclic voltammetry that thorium(IV) can be reduced in a single reduction step to the zero-valent state in the ionic liquid $[(n\text{-}C_4H_9)(CH_3)_3N][Tf_2N]$.[133] They also noticed that it is easier to reduce thorium(IV) in this ionic liquid than in other solvents like water, nonaqueous solvents, or high-temperature molten salts. These results can be explained by the weak coordinating ability of the $[Tf_2N]^-$ anion so that reduction is facilitated. The $E°$ value of the Th^{4+}/Th^0 redox couple in the ionic liquid is -1.80 V (versus SHE), whereas this value is -1.899 V in aqueous solutions at 25 °C and -2.359 V in the LiCl−KCl eutectic at 450 °C. The electrochemical studies suffered from the deposition of a nonconductive oxide layer on the electrode, so that no stripping or anodic peak was observed in the voltammogram. Possibly, thorium(IV) oxide was formed by reaction of thorium metal with water present in the ionic liquid. Nikitenko and Moisy investigated the electrochemical behavior of neptunium and plutonium complexes in the ionic liquid $[C_4mim][Tf_2N]$.[76] The $[NpCl_6]^{2-}$ and $[PuCl_6]^{2-}$ complexes are electrochemically inert in this ionic liquid. Irreversible redox processes were observed by cyclic voltammetry after addition of chloride ions in the form of $[C_4mim]Cl$. By steady-state linear sweep voltammetry, it was demonstrated that in these chloride-containing ionic liquids, neptunium(IV) can be reduced to neptunium(III), and that plutonium(IV) can be reduced to plutonium(III). The electrochemical behavior of neptunium(III) and neptunium(IV) in chloroaluminate ionic liquids is very similar to that of, respectively, uranium(III) and uranium(IV).[118]

4.4. Electrodeposition

The lanthanides and actinides are very electropositive elements. The standard reduction potentials of the lanthanides and actinides are more negative than those of aluminum and are comparable to that of magnesium. The metallic f-elements react with water to give hydrogen and metal hydroxides or oxides.[56] Therefore, the pure metals cannot be deposited electrochemically from an aqueous solution. Electrodeposition or electrorefining of lanthanides and actinides requires the use of anhydrous molten salt baths. Ionic liquids could be an alternative to the high-temperature molten salts for electroprocessing of metallic f-elements. Not only does the use of ionic liquids allow working at lower temperatures, but ionic liquids are in addition less corrosive than high-temperature molten salts.

The strongly electropositive character of the lanthanides and actinides makes the cathodic stability of many types of ionic liquids too low to allow electrodeposition of the f-elements. Attempts to reduce lanthanide or actinide ions in imidazolium ionic liquids result in decomposition of the ionic liquid by reduction of the imidazolium ring.[134] Quaternary ammonium salts have a better cathodic stability than imidazolium ionic liquids, but many quaternary ammonium salts suffer from the disadvantage that their viscosity is often too high to be useful for electrochemical processes. The viscosity can be reduced by a proper choice for the anion, for instance, $[Tf_2N]^-$, and by making the alkyl chain not too long (six or less carbon atoms).[93,134] Very large electrochemical windows were reported for the ionic liquids $[(CH_3)_4N][Tf_2N]$, $[(CH_3)_4P][Tf_2N]$, and $[(CH_3)_4As][Tf_2N]$.[135] The quaternary arsonium salt showed the highest stability (from −3.4 to 2.6 V versus ferrocenium/ferrocene), followed by the phosphonium salt. It was shown by cyclic voltammetry that europium metal can be electrodeposited from these ionic liquids.

There are only a few studies available on the electrodeposition of bulk samples of lanthanide metals from ionic liquids. Tsuda and co-workers were not able to obtain lanthanum metal by electrodeposition from a $LaCl_3$-saturated $AlCl_3$−$[C_2mim]Cl$ melt but obtained rather aluminum metal. It was suggested that electrodeposits of aluminum metal were obtained from a $LaCl_3$ saturated $AlCl_3$−$[C_2mim]Cl$ melt at −1.95 V after addition of an excess of LiCl and 50 mmol kg^{-1} of thionyl chloride. However, the deposition could only be observed by cyclic voltammetry; no bulk samples could be obtained.[84] Aluminum−lanthanum alloys electrodeposited from an $AlCl_3$−$[C_2mim]Cl$ ionic liquid saturated with $LaCl_3$ contained no more than 0.12 atom % La (and in most samples even considerably less).[136] However, it was observed that these aluminum deposits had a smoother surface than those obtained in absence of $LaCl_3$. Hsu and Yang obtained Co−Zn−Dy alloys with a quite high dysprosium content (up to 24.5 wt %) by electrodeposition on nickel or copper electrodes from a $ZnCl_2$−$[C_2mim]Cl$ ionic liquid with dissolved $CoCl_2$ and $DyCl_3$.[137] The authors state that no zero-valent dysprosium metal is present, but possibly dysprosium(II) is present (although it is more likely that dysprosium(III) salts is incorporated in the alloys). Lotermeyer and co-workers tried out the $[C_2mim][OTf]$ ionic liquid as solvent for electroplating of dysprosium, but no dysprosium deposits could be obtained.[138] The authors could prepare thick, adhesive, and uniform dysprosium coatings from an electroplating bath consisting of dysprosium(III) triflate and dimethylpyrrolidinium triflate dissolved in DMF.

Studies on the purification of uranium and plutonium metal by the electrorefining process in ionic liquids have been reported.[139,140] This work is of importance for the processing of spent nuclear fuel elements (see section 6). In the electrorefining process, the spent fuel elements act as the anode and pure metal acts as the cathode in a molten salt or ionic liquid. By application of an electric field between the anode and cathode, the anode is partially dissolved and pure metal is deposited on the cathode. Because of the instability of the imidazolium cation against reduction, the electrodeposition of uranium and plutonium metal in imidazolium ionic liquids was not successful. Contact of plutonium metal with the $[C_2mim]Cl$ ionic liquid resulted in a spontaneous reaction, being the oxidation of the $[C_2mim]^+$ cation by plutonium. A problem experienced during the electrorefining of uranium was that the uranium(III) species formed upon the dissolution of uranium at the anode are not stable in $[C_2mim]Cl$. Controlled potential electrolysis of uranium(VI) in $[C_4mim]Cl$ did not lead to the formation of uranium metal but rather to a deposit of UO_2.[141]

5. Solvent Extraction

Liquid−liquid solvent extraction is a very important process for the separation and purification of lanthanide ions.[142,143] The process is also of prime importance for the separation of fission products from reusable fissile material in spent nuclear fuel elements (see section 6). The basic principle behind solvent extraction is the difference in distribution of the species of interest over two immiscible phases, being often an aqueous phase and an organic phase: some species dissolve preferentially in the organic phase, while others dissolve preferentially in the aqueous phase.

Hydrophobic ionic liquids have been considered as an alternative for the organic phase in liquid−liquid solvent extraction systems.[38−41] Major advantages of the use of ionic liquids are their extremely low vapor pressure, so that solvent losses by evaporation during the extraction process can be greatly reduced. Most ionic liquids are also nonflammable. Because many ionic liquids contain weakly coordinating anions, it will in general not be possible to extract metal ions from an aqueous phase to the ionic liquid phase in the absence of extractants. Typical extractants for lanthanide ions are β-diketones, dialkylphosphoric acids and dialkylphosphinic acids, and octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) (Figure 10). CPMO is also often used for the extraction of uranyl ions and transuranium elements. CPMO is the extractant in the TRUEX process (TRUEX = transuranium extraction).[144] Because of the ionic nature of ionic liquids, the partitioning equilibriums in solvent extraction systems involving ionic liquids are not necessarily identical to those involving conventional organic solvents. The equilibriums often involve cation or anion exchange between the aqueous phase and the ionic liquid phase. This contamination of the aqueous phase by the components of the ionic liquid is a problem for the applicability of ionic liquids in solvent extraction systems. Moreover, the coordination environment of the metal ions in ionic liquids can differ from what is observed in other organic solvents. Another problem related to ionic liquids in solvent extraction

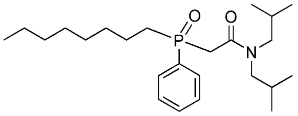


Figure 10. Structure of octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO).

processes is how to strip the metals from the ionic liquids after extraction. The possibilities to use ionic liquids for solvent extraction processes of f-elements have been discussed by Visser and Rogers.[145]

Studies of the extraction of lanthanide ions from an aqueous phase to the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [C$_4$mim][Tf$_2$N], by the extractant 2-thenoyltrifluoroacetone (Htta) revealed that the lanthanide ions are extracted as anionic tetrakis complexes of the type $[\mathrm{Ln(tta)_4}]^-$, rather than as hydrated neutral complexes of the type $[\mathrm{Ln(tta)_3(H_2O)}_n]$ ($n = 2$ or 3).[146] In the anionic complexes, no water molecules are coordinated to the lanthanide ion. Extraction of the anionic lanthanide complexes to the ionic liquid phase is made possible by the exchange of the $[\mathrm{Tf_2N}]^-$ anions into the aqueous phase for the $[\mathrm{Ln(tta)_4}]^-$ complexes. It is very likely that the lanthanide complexes exist in the ionic liquid phase as weak $[\mathrm{C_4mim}]^+[\mathrm{Ln(tta)_4}]^-$ ion pairs. The equilibrium that describes the partitioning of the lanthanide ions between the aqueous phase and the ionic liquid phase (i.e., the organic phase) can be written as

$$\mathrm{Ln}^{3+}_{\mathrm{aq}} + 4\mathrm{Htta}_{\mathrm{org}} + [\mathrm{C_4mim}][\mathrm{Tf_2N}]_{\mathrm{org}} \rightleftarrows [\mathrm{C_4mim}][\mathrm{Ln(tta)_4}]_{\mathrm{org}} + 4\mathrm{H}^+_{\mathrm{aq}} + [\mathrm{Tf_2N}]^-_{\mathrm{aq}} \quad (8)$$

It is evident from this equation that for each Ln^{3+} ion extracted to the ionic liquid, one $[\mathrm{Tf_2N}]^-$ ion is lost by transfer to the aqueous phase. This contamination of the aqueous phase by components of the ionic liquid is a serious problem that limits the applicability of these solvent extraction systems. Subsequent studies showed that the extraction equilibrium in eq 8 is valid for high Htta concentrations only and that at lower Htta concentration neutral $[\mathrm{Ln(tta)_3(H_2O)}_x]$ complexes are extracted into the ionic liquid phase.[147] The lanthanide complexes can be stripped from the ionic liquid by treatment of the ionic liquid with the acid H[Tf$_2$N]. The fact that lanthanide ions are extracted into ionic liquids as anionic complexes is in contrast to what is observed for extraction into molecular solvents with low polarity (xylene, toluene, dodecane, kerosene), where the extraction process in general takes place via hydrated neutral complexes.

On the other hand, the extraction process of $[\mathrm{UO_2}]^{2+}$, Am^{3+}, Nd^{3+}, and Eu^{3+} from an aqueous phase to the ionic liquid 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide by dialkylphosphoric acid and dialkylphosphinic acid involved the same type of metal species in the ionic liquid phase as in the case of extraction to a dodecane solution.[148] The extraction of uranyl ions by tri-*n*-butylphosphate (TBP) from an aqueous nitric acid solution to the ionic liquid [C$_4$mim][PF$_6$] is similar to the extraction behavior with dodecane as organic phase in the nitric acid concentration range between 0.01 and 4 mol L^{-1}.[149] However, extraction to the ionic liquid phase is more efficient when the nitric acid concentration is above 4 mol L^{-1}.

Because octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) is a neutral extractant, anions like $[\mathrm{NO_3}]^-$ are required to extract metal ions to the organic phase. For this reason, the aqueous phase needs to be very acidic. Nakashima et al. showed that CMPO dissolved in [C$_4$mim][PF$_6$] can extract lanthanide nitrates from deionized water (i.e., without added anionic species).[150] The presence of the ionic liquid greatly improves the extractability of lanthanide ions, as well as the selectivity of CMPO. The metal ions could be recovered from the ionic liquid by stripping with buffer solutions containing complex-forming agents (e.g., EDTA, DTPA, or citric acid). Whereas uranyl is extracted by CMPO from an aqueous nitric acid solution to dodecane as the $[\mathrm{UO_2(NO_3)_2(CMPO)_2}]$ complex, uranyl is extracted to 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C$_4$mim][Tf$_2$N], or 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C$_8$mim][Tf$_2$N], as the cationic species $[\mathrm{UO_2(NO_3)(CPMO)}]^+$.[151] The exchange process results in losses of the imidazolium cation to the aqueous phases.

Dietz and co-workers are less optimistic about the usefulness of ionic liquids as replacements for conventional organic solvents in actinide and fission product separations.[152] Ionic liquids with relatively short alkyl chains like [C$_4$mim][Tf$_2$N] exhibit a complex behavior of the distribution ratio of uranium on the nitric acid concentration and are therefore not suitable for application in extraction processes. This complex behavior indicates a shift in mechanism from cation exchange to neutral complex extraction with increasing acidity. For ionic liquids with longer alkyl chains like [C$_{10}$mim][Tf$_2$N], the acid dependencies of the distribution ratio are more favorable (i.e., increasing uranium extraction with increasing acidity), but the distribution ratios are lower than those in dodecane. No improvement in the extraction selectivity was observed.

Ouadi and co-workers designed task-specific ionic liquids for the extraction of trivalent americium.[153] The task-specific ionic liquids were prepared by attaching the 2-hydroxybenzylamine moiety to a 1-methylimidazolium core with the counterions being either $[\mathrm{PF_6}]^-$ or $[\mathrm{Tf_2N}]^-$ (Figure 11). The task-specific ionic liquids act as extractants and were used in pure form or diluted in another ionic liquid. Extraction of americium from the aqueous to the ionic liquid phase took place under basic conditions. Americium could be stripped from the ionic liquid phase by washing with an acidic aqueous solution. Problems associated with the use of ionic liquids in actinide and fission product separation are discussion in section 6.

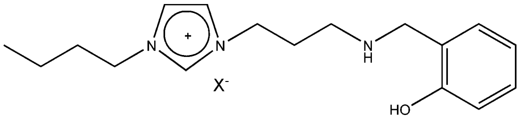


Figure 11. Task-specific ionic liquids for the extraction of americium(III); X = $[\mathrm{PF_6}]^-$ or $[\mathrm{Tf_2N}]^-$.

Solvent extraction is not the only separation method that has been tested in ionic liquids. Matsumiya and co-workers recently described electromigration experiments in the ionic liquids $[(n\text{-}\mathrm{C_6H_{13}})(\mathrm{CH_3})_3\mathrm{N}][\mathrm{OTf}]$ and $[(n\text{-}\mathrm{C_6H_{13}})(\mathrm{CH_3})_3\mathrm{N}][\mathrm{Tf_2N}]$.[154] These authors found that the trivalent rare-earth ions are efficiently enriched at the anode under high-current density conditions. By a change of the experimental parameters, it was also possible to separate the trivalent rare-earth ions from the divalent alkaline-earth ions (e.g., Ba^{2+}). This process can be of interest to remove salt impurities from ionic liquids, which is a difficult task to perform by other methods.

6. Treatment of Spent Nuclear Fuel

The processing of spent nuclear fuel elements is a very important issue in nuclear technology. Most fuel elements in commercial light water nuclear reactors consist of UO$_2$ pellets, in which uranium is enriched so that the content of the fissile ^{235}U isotope is increased to a few percent (as opposed to the natural abundance of 0.7%). During operation of the nuclear reactor, part of the nuclear fuel is burned, which means that ^{235}U is consumed by fission reactions. At the same time, higher actinides are formed by neutron capture by the different uranium isotopes in the fuel elements. The main purpose of reprocessing of the spent fuel elements is isolation of unburned ^{235}U and plutonium isotopes from fission products and from the higher actinides. The fission products ^{90}Sr and ^{137}Cs are major heat generators, and their removal from the spent nuclear fuel greatly simplifies the handling and treatment of the remaining nuclear waste. It is also possible to extract valuable byproducts (e.g., americium isotopes) from the highly radioactive waste by the reprocessing process. The first step in commercial processes like the plutonium−uranium separation by extraction (PUREX) process consists of oxidative dissolution of the UO_2 pellets in a concentrated aqueous HNO_3 solution.[155,156] After the spent fuel elements have been dissolved in the nitric acid solution, the acidic solution is contacted with a water-immiscible organic solution, which can selectively extract the desired elements. The PUREX process uses tri-*n*-butyl phosphate (TBP) as a 30% solution in kerosene as the extractant in the solvent extraction step.[144] There are some technical and safety problems related to the PUREX process. First of all, tri-*n*-butyl phosphate is not very stable against radiolysis. In the presence of highly active fission products and higher actinides, it decomposes to *n*-butanol and lower phosphates (mainly dibutyl phosphate and monobutyl phosphate). The phosphate decomposition products are complex forming agents for many fission products, and they interfere with the separation process. Second, the organic solvents used in the PUREX process are volatile and flammable. Last, but not least, one has to take precautions that the concentration of the fissile products in the aqueous phase does not become too high, because otherwise the critical mass will be exceeded and the system becomes supercritical. This will result in an uncontrolled nuclear chain reaction. For instance, a criticality accident happened in the nuclear fuel factory in Tokai-Mura, Japan, in 1999.[157]

Preliminary investigations show that 1,3-dialkylimidazolium ionic liquids with chloride and nitrate anions are relatively radiation resistant and do not undergo significant decomposition by radiolysis upon exposure to high radiation doses. When these ionic liquids were subjected to a radiation dose of 400 kGy by γ-irradiation, β-particle irradiation, or α-particle irradiation, less than 1% of the ionic liquid underwent radiolysis.[139] The stability of the ionic liquids against high radiation doses is comparable to that of benzene but is much higher than that of the TBP/kerosene mixtures used in the PUREX process. The relatively high radiation resistance of imidazolium ionic liquids can be attributed to the presence of the aromatic imidazolium ring. Aromatic compounds have a higher stability against irradiation than nonaromatic compounds, because the aromatic ring can absorb radiation energy and can relax nondissociatively. Moreover, mixtures of aromatic and nonaromatic compounds undergo less radiolytic decomposition than what is expected on the basis of the concentration of the nonaromatic compound, because of energy transfer to the aromatic compound. Analysis of the radiolysis products of 1,3-dialkylimidazolium chloride and nitrate ionic liquids show that the ionic liquids behave like a combination of an aromatic compound, an alkane, and a salt.[158]

Another advantageous property of ionic liquids that makes them useful for applications in the processing of spent nuclear fuel rods is their very low vapor pressure, so that they are nonvolatile. Moreover, many ionic liquids are nonflammable and combustion resistant. Ionic liquids are safer solvents for processing of spent nuclear fuel rods, because the probability for criticality accidents in ionic liquids is smaller than that in aqueous solutions. Part of the problems associated with the criticality of aqueous systems is due to the neutron-moderating properties of the hydrogen atoms in water. Neutrons are slowed down in the moderation process by collisions with the nuclei in the moderator until their energy is of the same order as the thermal energy (∼0.025 eV). At this thermal energy, the fission cross section of ^{235}U (and also of ^{239}Pu and ^{241}Pu) becomes so high that fission is more probable than absorption or scattering. Water is an excellent moderator of neutrons, because of its high hydrogen atom density. Ionic liquids are less efficient moderators than water, because they contain lower hydrogen to non-hydrogen ratios than water. A fast neutron retains its speed over a larger distance in an ionic liquid than in water and has therefore a large probability to escape from the system. This increases the system's critical mass. Of special interest are ionic liquids that contain chlorine and boron atoms, because ^{35}Cl, ^{10}B, and ^{11}B have a large capture cross section for thermal neutrons and are thus strong neutron absorbers. This increases the critical mass. Calculations have shown that plutonium in 1-ethyl-3-methylimidazolium tetrafluoroborate has an infinite critical mass at concentrations below 1000 g L^{-1}, whereas in aqueous solutions an infinite critical mass can be obtained only at concentrations below 8 g L^{-1}.[159] Systems with infinite critical mass are absolutely criticality safe, because no criticality accident can occur when the solution volume is enlarged. The critical mass of the aqueous solution can be increased by partially replacing water by a hydrophilic ionic liquid.

Molten salt extraction has been explored for a long time in nuclear technology, so that the step to extraction processes based on room-temperature ionic liquids is small. Ionic liquids have the major advantage over high-temperature molten salts that the extraction process can take place at a much lower temperature. This is not only safer but also cheaper. Moreover, fewer problems with corrosion are expected.

The possibility to dissolve UO_2 oxidatively in nitrate ionic liquid/nitric acid mixtures has been reported.[139,160] For instance UO_2 could be dissolved in a mixture of 1-butyl-3-methylimidazolium nitrate and concentrated nitric acid (90:10 vol % ratio) at 70 °C. However, it can be expected that under such reaction conditions also nitration of the imidazolium ring occurs. It is also often observed that upon cooling of reaction mixtures in which UO_2 was oxidatively dissolved, crystalline solids are precipitated. One of these compounds is a dimeric uranyl bisnitrate complex with bridging oxalate groups (Figure 12).[161] It was suspected that the source of the bridging oxalate moiety is the acetone that was used to rinse the glassware and that can be oxidized by nitric acid.[162] Another source can be impurities in the ionic liquid, like glyoxal, which is a starting material for the synthesis of the ionic liquid precursor imidazole.[163] Even impurities in the nitric acid were considered as the source of the oxalate ions. The insolubility of uranyl oxalate species in ionic liquids can be explored for the separation of uranium from ionic liquids by precipitation as oxalate complexes.[139]

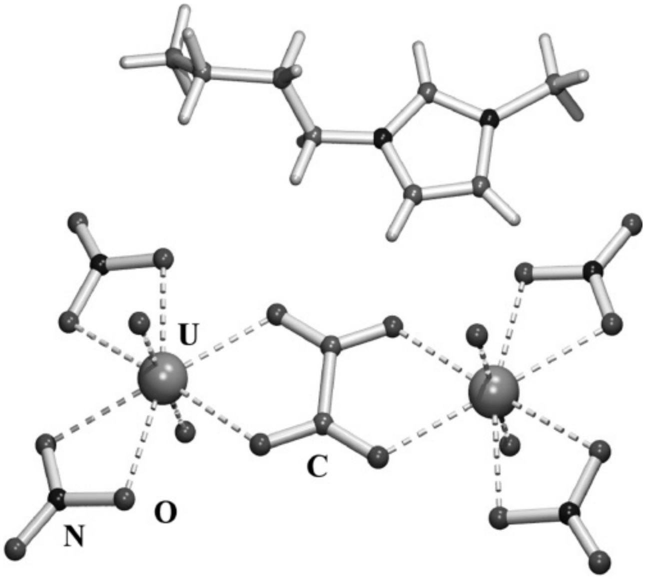


Figure 12. Molecular structure of $[BMIM]_2[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$. The atomic coordinates were taken from ref 161.

Another topic related to the use of ionic liquids in the nuclear industry is the electrorefining process. This process has been discussed above in section 4.

7. Lanthanide-Mediated Organic Reactions

Ionic liquids are popular neoteric solvents for organic synthesis.[4] The main drive for research in the field of organic reactions in ionic liquid solvents is that ionic liquids are potentially environmentally friendly solvents: they have a very low vapor pressure, and they are not flammable. These studies illustrate that in many cases, the yields of the reactions in ionic liquids are comparable to those in classic organic solvents. In other cases, the yields are lower in ionic liquids. When a reaction works well in a given organic solvent, there is not much need to replace that solvent by an ionic liquid. Of more importance are the reactions that work better in ionic liquids than in other solvents.[164,165] In principle, also the chemoselectivity and regioselectivity of a reaction can be changed by a proper choice of the ionic liquid.

On the other hand, lanthanide compounds are often used a reagents in organic synthesis. Several reviews on lanthanide-mediated organic reactions are available.[166−172] Rare-earth triflates and especially scandium(III) triflate have been widely explored as Lewis acids to mediate different types of organic reactions, mainly thanks to the pioneering work by Kobayashi.[172−177] Major advantages of these rare-earth salts are that they are water-tolerant Lewis acids (in contrast to strong Lewis acids like $AlCl_3$) and that catalytic amounts rather than stoichiometric amounts can be used in many cases. Although the rare-earth salts have to compete in Lewis acid chemistry with other metal salts like indium(III),[178−180] gallium(III),[181,182] and bismuth(III) salts,[183−186] they still remain popular reagents for organic synthesis. It is therefore not surprising that ionic liquids have been explored as solvents for lanthanide-mediated organic reactions.[187] The main rationale for choosing ionic liquids in these reactions is the recyclability of the solvent/catalyst systems and the easy product separation. However, in most of these studies, no higher reactivities or different selectivities could be observed in comparison with the conventional organic solvents. But there are some remarkable exceptions. The immobilizing of lanthanide reagents in ionic liquids is an alternative approach to the use of solid-phase supports[188] or fluorous solvents[189] in lanthanide-mediated organic synthesis.

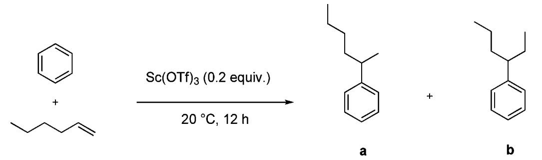
7.1. C–C Bond Formation

7.1.1. Friedel–Crafts Reactions

Friedel−Crafts reactions are an archetype of reactions on which rare-earth Lewis acids catalysts have been tested. A seminal paper on the use of lanthanide salts as catalysts in ionic liquids is the work of Song et al. on the Friedel−Crafts alkylation of aromatic compounds with alkenes, which is catalyzed by scandium(III) triflate, $Sc(OTf)_3$.[190] No reaction occurred between benzene and 1-hexene in the presence of 20 mol % $Sc(OTf)_3$ in water, in organic solvents (dichloromethane, acetonitrile, nitromethane, nitrobenzene), or in the absence of an solvent. The reaction did not proceed in hydrophilic imidazolium ionic liquids with $[OTf]^-$ or $[BF_4]^-$ anions, although $Sc(OTf)_3$ is well soluble in these ionic liquids. However, in hydrophobic imidazolium ionic liquids with $[PF_6]^-$ and $[SbF_6]^-$ counterions, alkylation proceeded smoothly at room temperature, and quantitative conversion was obtained after 12 h (Table 1). This behavior was unexpected, because $Sc(OTf)_3$ is not soluble in these hydrophobic ionic liquids. The observation that isomerization of the alkene took place prior to ring substitution shows that first a carbocation is formed. The ionic liquid stabilizes the cationic intermediate. Very little dialkylated product was obtained. Aromatic compounds other than benzene that have been tested for this reaction were phenol and anisole. Alkenes other than 1-hexene are cyclopentene, cyclohexene, and norbornene. When $Sc(OTf)_3$ was replaced by another rare-earth triflate, the yields were much lower. In fact, besides $Sc(OTf)_3$, only $Y(OTf)_3$, $Ho(OTf)_3$, $Tm(OTf)_3$, and $Lu(OTf)_3$ showed reactivity in the reaction of benzene with cyclohexene.

The use of ionic liquids for the Friedel−Crafts alkenylation of aromatic compounds with alkynes and with rare-earth triflates as catalysts resulted not only in an increased reaction

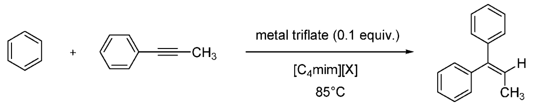
Table 1. Friedel−Crafts Alkylation of Benzene with 1-Hexene in the Presence of 20 mol % $Sc(OTf)_3$ in Various Solvents[190]



solvent	conversion of 1-hexene [%]	yield [%] of monoalkylated product (ratio **a**/**b**)
none	0	0
CH_2Cl_2	0	0
CH_3CN	0	0
CH_3NO_2	0	0
$PhNO_2$	0	0
H_2O	0	0
$[C_2mim][SbF_6]$	>99	96 (1.5:1)
$[C_2mim][BF_4]$	0	0
$[C_2mim][OTf]$	0	0
$[C_4mim][PF_6]$	>99	96 (2:1)
$[C_4mim][SbF_6]$	~99	93 (1.5:1)
$[C_4mim][BF_4]$	0	0
$[C_4mim][OTf]$	0	0
$[C_5mim][PF_6]$	>99	95 (1.6:1)
$[C_6mim][PF_6]$	>99	95 (2:1)

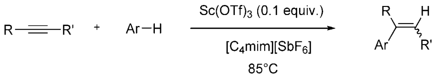
rate but also in the formation of less byproducts.[191] The reaction between benzene and 1-phenyl-1-propyne proceeded in good yields in the hydrophobic ionic liquids [C_4mim][PF_6] and [C_4mim][SbF_6] with scandium(III) triflate as the catalyst (0.1 equiv of the catalyst) (Table 2). A much lower yield was obtained in the absence of the ionic liquid, and after long reaction times, large quantities of side products were obtained. Also the use of the hydrophilic ionic liquids [C_4mim][BF_4] and [C_4mim][OTf] resulted in very low yields. Different rare-earth triflates were tested, and besides scandium(III) triflate, good catalytic activity was found for yttrium(III), ytterbium(III), and lutetium(III) triflates. It is remarkable that a higher catalytic activity was observed for yttrium(III) triflate than for scandium(III) triflate, although holmium(III) and erbium(III) triflate are much less active. This is remarkable because yttrium(III), holmium(III), and erbium(III) are expected to have a similar Lewis acidity due to their similar ionic radii. After reaction, the ionic liquid phase containing the rare-earth catalysts could simply be separated from the organic products by decantation. Although the ionic liquid with catalyst could be reused, a decrease in reactivity was observed. To rule out the possibility that the reactivity was due to hydrogen fluoride impurities from the hydrolysis of the hexafluorophosphate ions, the reaction was tested in the absence of metal triflates; in this case, the reaction did not occur. Different types of arenes and alkynes have been tested to study the scope of the reaction (Table 3).

Table 2. Friedel−Crafts Alkenylation of Benzene with 1-Phenyl-propyne[191]



catalyst	ionic liquid	time [h]	yield [%]
Sc(OTf)$_3$	none	96	27
Sc(OTf)$_3$	[C_4mim][SbF_6]	4	91
Sc(OTf)$_3$	[C_4mim][PF_6]	4	90
Y(OTf)$_3$	[C_4mim][SbF_6]	2	80
Yb(OTf)$_3$	[C_4mim][SbF_6]	4	81
Lu(OTf)$_3$	[C_4mim][SbF_6]	4	94

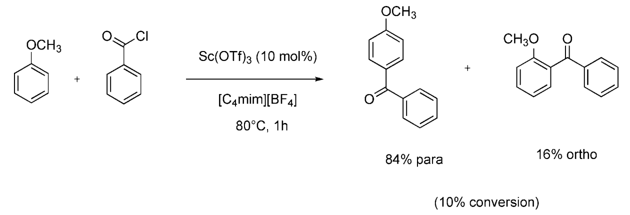
Table 3. Friedel−Crafts Alkenylation of Various Arenes with Various Alkynes[191]



R	R′	arene	time [h]	yield [%]
Ph	Me	*p*-xylene	4	96
Ph	H	benzene	4	68
Ph	H	*p*-xylene	4	60
Ph	Ph	benzene	2	59
Ph	Ph	benzene	4	62
Ph	Ph	*p*-xylene	4	80
Ph	Ph	toluene	2	83
Ph	Ph	chlorobenzene	6	44
Ph	Ph	anisole	2	73
p-CF_3Ph	H	*p*-xylene	22	73
p-ClPh	H	*p*-xylene	12	63

Ross and Xiao have investigated benzoylation of anisole catalyzed by metal triflates in the ionic liquid [C_4mim][BF_4] (Scheme 1).[192] The triflates Cu(OTf)$_2$, Zn(OTf)$_2$, Sn(OTf)$_2$, and Sc(OTf)$_3$ have been tested. The highest activity was found for Cu(OTf)$_2$, while Sc(OTf)$_3$ was least active: under the conditions where Cu(OTf)$_2$ gave quantitative conversion of benzoyl chloride, a conversion of only 10% was observed for Sc(OTf)$_3$. Addition of trifluoroacetic acid increased the activity of Sc(OTf)$_3$, although the reaction did not proceed when trifluoroacetic acid was used in the absence of Sc(OTf)$_3$. The kinetics of the Friedel−Crafts benzoylation of anisole with benzoic anhydride to yield 4-methoxy benzophenone have been studied in different types of ionic liquids and metal triflate catalysts, including rare-earth triflates (Scheme 2).[193] The ionic liquids [C_4mim][BF_4], [C_4mim][OTf], and [C_4mim][Tf_2N] have been tested, and initial screening showed that little reactivity could be observed in the hydrophilic ionic liquids [C_4mim][BF_4] and [C_4mim][OTf] but good reactivity in the hydrophobic ionic liquid [C_4mim][Tf_2N]. The activity of Sm(OTf)$_3$, Yb(OTf)$_3$, and Y(TfO)$_3$ is much lower than that of Sc(OTf)$_3$. The activity of Sc(OTf)$_3$ is slightly lower than those of Al(OTf)$_3$ and In(OTf)$_3$. The authors propose a model in which the catalyst undergoes ligand exchange with benzoic anhydride, so that the free acid is formed in situ. This free acid (HOTf or HTf_2N) is the active catalyst. Friedel−Crafts acylations of ferrocene with acyl chlorides and anhydrides and with ytterbium(III) triflate as the catalyst were carried out in the ionic liquid *N*-butylpyridinium tetrafluoroborate, [C_4py][BF_4].[194] Monoacylated products were obtained under mild conditions (Table 4). No diacylated products were observed.

Scheme 1. Benzoylation of Anisole



Scheme 2. Friedel−Crafts Benzoylation of Anisole with Benzoic Anhydride To Yield 4-Methoxybenzophenone

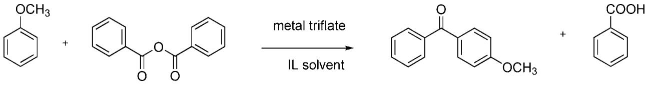
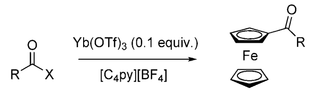


Table 4. Friedel−Crafts Acylation of Ferrocene[194]

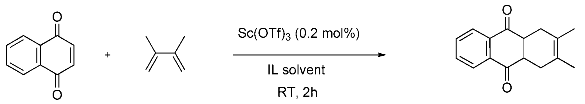


R	X	time [h]	temp [°C]	yield [%]
CH_3	OAc	6	RT	97
CH_3	Cl	6	RT	94
CH_2CH_3	OAc	6	RT	92
CH_2CH_3	Cl	6	RT	90
$C_{17}H_{35}$	Cl	8	50	89
Ph	Cl	8	50	72
p-CH_3Ph	Cl	8	50	83
p-CH_3Oph	Cl	8	50	89
p-ClPh	Cl	24	50	46
PhCH_2	Cl	8	50	88
PhCH═CH	Cl	12	50	90

7.1.2. Diels–Alder Reactions

Scandium(III) triflate was used as a catalyst for Diels−Alder reaction in ionic liquids.[195] In contrast to the Friedel−Crafts alkylation reaction, the Diels−Alder reaction of 1,4-

Table 5. $Sc(OTf)_3$-Catalyzed Diels−Alder Reaction between 1,4-Naphthoquinone and 1,3-Dimethylbutadiene[195]

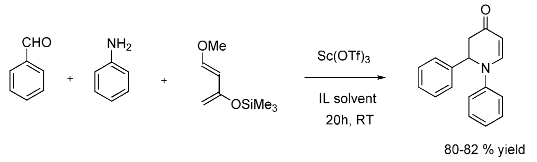


solvent	yield [%]
CD_2Cl_2	22
$[C_4mim][PF_6]$ (0.1 equiv) + CD_2Cl_2	46
$[C_4mim][PF_6]$ (0.5 equiv) + CD_2Cl_2	85
$[C_4mim][PF_6]$ (1 equiv) + CD_2Cl_2	>99
$[C_4mim][PF_6]$	>99
$[C_4mim][SbF_6]$	>99
$[C_4mim][OTf]$	>99

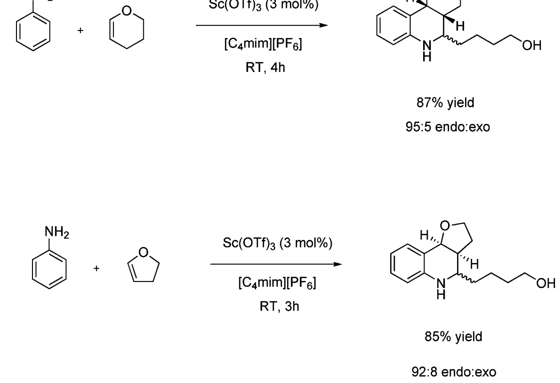
naphthoquinone with 1,3-dimethylbutadiene also proceeds in a hydrophilic triflate ionic liquid (Table 5). An amount as low as 0.2 mol % of $Sc(OTf)_3$ was enough for quantitative conversion of the reagents in 2 h at room temperature. With 10 mol % of $Sc(OTf)_3$, the reaction was complete in seconds. Different dienophiles and dienes have been tested. An interesting observation was the improvement of the *endo*/*exo* selectivity (*endo*/*exo* ≥ 99:1). The reactions could also be carried out in dichloromethane with the ionic liquid as an additive. The ionic liquid with the $Sc(OTf)_3$ catalyst dissolved in it could be recycled and reused many times without loss in activity.

Microencapsulated scandium(III) triflate was found to be active as a catalyst for an aza-Diels−Alder reaction between an aldehyde, an amine, and 1-methoxy-3-(trimethylsilyl)-oxybuta-1,3-diene to produce 5,6-dihydro-4-pyridone (Scheme 3).[196] The ionic liquids were 8-ethyl-diazabicyclo[4,5,0]-7-undecenium triflate and 1-ethyl-3-methyl-1*H*-imidazolium triflate. Scandium(III) triflate in $[C_4mim][PF_6]$ catalyzes the [4 + 2] cycloaddition reaction of imines (formed in situ from enol ethers and amines) with cyclic enol ethers to afford pyrano[3,2-*c*]quinoline or furo[3,2-*c*]quinoline derivatives (Scheme 4).[85] In the hydrophilic ionic liquids $[C_4mim][BF_4]$ and $[C_4mim][OTf]$, only moderate yields were obtained. The ionic liquid phase containing $Sc(OTf)_3$ could be recovered after reaction by extraction with diethyl ether.

Scheme 3. One-Pot Synthesis of *N*-Phenyl-6-phenyl-5,6-dihydro-4-pyridone



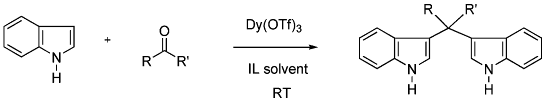
Scheme 4. $Sc(OTf)_3$-Catalyzed Synthesis of Pyrano- and Furo[3,2-*c*]quinolines



7.1.3. Other C–C Bond-Forming Reactions

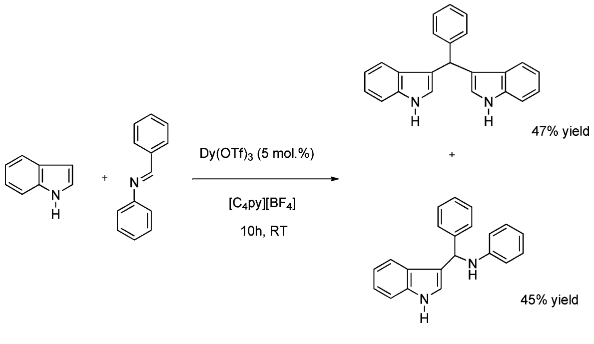
An enhanced activity was observed for the electrophilic reactions of indoles with aldehydes and ketones that were catalyzed by $Dy(OTf)_3$ in imidazolium and pyridinium ionic liquids with tetrafluoroborate or hexafluorophosphate anions (Table 6).[197] The reaction of hexanal with indole was tested as a model reaction in the ionic liquids $[C_4mim][BF_4]$, $[C_4mim][PF_6]$, and $[C_4py][BF_4]$, and the highest yield was observed in $[C_4mim][BF_4]$. No rare-earth triflates other than $Dy(OTf)_3$ have been tested. Imines undergo electrophilic reactions in a way similar to the carbonyl compounds. Two major products are formed, a secondary indolyl amine and a bisindolyl methane (Scheme 5). The highest yield for the secondary indolyl amine was observed in the ionic liquid $[C_4py][BF_4]$. In a comparative study of different Lewis acids as catalyst for the synthesis of bis(indolyl)methanes by reaction between aldehydes and indoles in ionic liquids, a reasonable reactivity was found for $YbCl_3$, but this salt was much less reactive than the best catalyst, $In(OTf)_3$ (Scheme 6).[198]

Table 6. $Dy(OTf)_3$-Catalyzed Reaction of Indoles with Aldehydes or Ketones[197]



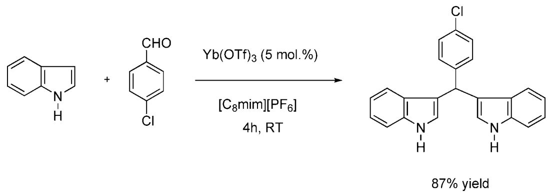
R	R′	mol % $Dy(OTf)_3$	ionic liquid	time [h]	yield [%]
C_6H_{13}	H	2	$[C_4mim][BF_4]$	1	95
C_6H_{13}	H	0	$[C_4mim][BF_4]$	1	0
C_6H_{13}	H	2	$[C_4mim][PF_6]$	1	88
C_6H_{13}	H	2	$[C_4py][BF_4]$	1	89
Ph	H	2	$[C_4mim][BF_4]$	1	98
p-ClPh	H	2	$[C_4mim][BF_4]$	1	96
p-CH_3OPh	H	2	$[C_4mim][BF_4]$	1	99
CH_3	CH_3	5	$[C_4mim][BF_4]$	24	96
CH_3	CH_3	5	$[C_4mim][PF_6]$	24	94
CH_3	CH_3	5	$[C_4py][BF_4]$	24	98
Ph	CH_3	10	$[C_4mim][BF_4]$	24	88

Scheme 5. $Dy(OTf)_3$-Catalyzed Reaction of Indole with *N*-Benzylidene Aniline in $[C_4py][BF_4]$

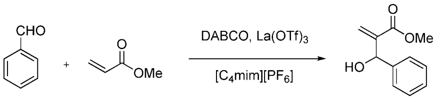


The Baylis−Hillman reaction, that is, the coupling of activated alkenes with aldehydes promoted by tertiary amines, proceeds faster in ionic liquids than in acetonitrile.[199] The authors tested the reaction of methyl acrylate, benzaldehyde, and 1,4-diazabicyclo[2,2,2]octane (DABCO) (1:1:1 molar ratio) in different ionic liquids of the type $[C_4mim]X$

Scheme 6. Yb(OTf)$_3$-Catalyzed Synthesis of 3,3′-Bis(indolyl)-4-chlorophenylmethane in [C$_8$mim][PF$_6$]



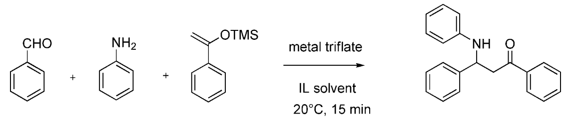
Scheme 7. Baylis−Hillman Reaction of Benzaldehyde with Methylacrylate



(X = OAc, OTf, Tf$_2$N, BF$_4$, SbF$_6$, and PF$_6$) with La(OTf)$_3$ or Sc(OTf)$_3$ as the catalyst (Scheme 7). The best results were obtained with [C$_4$mim][PF$_6$] and [C$_4$mim][OTf]. Lanthanum(III) triflate was found to be a more efficient catalyst than scandium(III) triflate for this reaction.

Lee and Park described a one-pot three-component Mannich reaction between an aldehyde, an amine, and a silyl enol ether catalyzed by ytterbium(III) triflate in imidazolium ionic liquids with benzene as a cosolvent.[200] Benzaldehyde, aniline, and acetophenone trimethylsilylenolate react to give a β-amino ketone (Table 7). Yb(OTf)$_3$ is a very active catalyst; a fast reaction was observed with an amount as low as 0.1 mol %. This is also one of the few examples where Sc(OTf)$_3$ is a poorer catalyst than Yb(OTf)$_3$. The use of an ionic liquid is essential, because in benzene as solvent the yields were much lower. [C$_4$mim][PF$_6$] gave higher yields than [C$_4$mim][SbF$_6$] or [C$_4$mim][BF$_4$].

Table 7. One-Pot Mannich-Type Reaction of Benzaldehyde, Aniline, and Acetophenone Trimethylsilylenolate[200]



catalyst	catalyst loading [mol %]	ionic liquid	yield [%]
Yb(OTf)$_3$	1	[C$_4$mim][PF$_6$]	85
Yb(OTf)$_3$	1	[C$_4$mim][PF$_6$]	91
Yb(OTf)$_3$	0.1	[C$_4$mim][PF$_6$]	80
Yb(OTf)$_3$	1	none	50
Yb(OTf)$_3$	1	[C$_4$mim][SbF$_6$]	72
Yb(OTf)$_3$	1	[C$_4$mim][BF$_4$]	40
Sc(OTf)$_3$	1	[C$_4$mim][PF$_6$]	76

Cyclic aliphatic ketones can condense with aldehydes to α,α′-bis-(substituted benzylidene) cycloalkanones by the action of SmI$_3$ as the catalyst (20 mol %) (Scheme 8).[201] The reactions were carried out in [C$_4$mim][BF$_4$]. As cyclic aliphatic ketones, cyclopentanone and cyclohexanone have been used. Cycloheptanone did not react. Benzaldehyde, aniline, and diethyl phosphonate react in a three-component reaction with rare-earth triflates to afford α-amino phosphonates (Table 8).[202] Anhydrous Sm(OTf)$_3$ is the most effective rare-earth catalyst in the ionic liquid [C$_4$mim][PF$_6$], whereas anhydrous Yb(OTf)$_3$ is more effective in organic solvents. Sc(OTf)$_3$ was only moderately active with diethyl phosphonate but was very active when triethyl phosphite, P(OEt)$_3$, was used as the phosphorus-containing nucleophile. The hydrated rare-earth triflates have a much lower activity than the corresponding anhydrous salts. For a given rare-earth triflate, the reaction yields depend on the ionic liquid: [C$_4$mim][PF$_6$] > [C$_4$mim][OTf] > [C$_4$mim][SbF$_6$] > [C$_4$mim][BF$_4$]. Aldehydes react with a homoallyl alcohol to afford tetrahydropyranol derivatives. This reaction is catalyzed by hydrated cerium(III) triflate (Scheme 9).[203] Yields were only moderate. It was found that the use of the ionic liquid [C$_4$mim][PF$_6$] as solvent resulted in the formation of less side products than when chloroform was used as solvent.

Scheme 8. SmI$_3$-Catalyzed Condensation of Cyclopentanone and Cyclohexanone

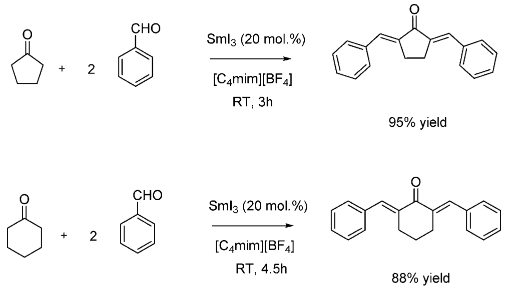
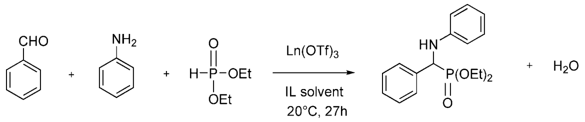
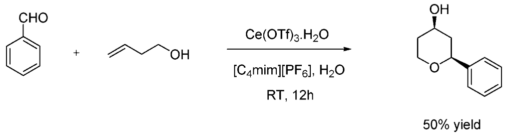


Table 8. Three-Component Reaction of Benzaldehyde, Aniline, and Diethyl Phosphonate Affording an α-Amino Phosphonate in Ionic Liquids[202]



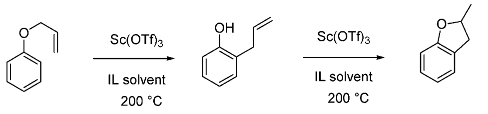
catalyst	catalyst loading [mol %]	ionic liquid	yield [%]
Yb(OTf)$_3$	10	[C$_4$mim][PF$_6$]	95
Sc(OTf)$_3$	10	[C$_4$mim][PF$_6$]	80
Dy(OTf)$_3$	10	[C$_4$mim][PF$_6$]	94
Sm(OTf)$_3$	10	[C$_4$mim][PF$_6$]	99
Yb(OTf)$_3$·H$_2$O	10	[C$_4$mim][PF$_6$]	63
La(OTf)$_3$·H$_2$O	10	[C$_4$mim][PF$_6$]	39
Sm(OTf)$_3$	1	[C$_4$mim][PF$_6$]	95
Sm(OTf)$_3$	10	[C$_4$mim][SbF$_6$]	71
Sm(OTf)$_3$	10	[C$_4$mim][BF$_4$]	18
Sm(OTf)$_3$	10	[C$_4$mim][OTf]	89

Scheme 9. Formation of Tetrahydropyranols by Reaction between Homoallyl Alcohol and Benzaldehyde



Zulfiqar and Kitazume illustrated the usefulness of ionic liquids as a solvent for high-temperature reactions by carrying out sequential Claisen rearrangements and cyclization reactions at 200 °C in the presence of anhydrous scandium(III) triflate as catalyst (Scheme 10).[204] The ionic liquids tried out are [C$_4$mim][BF$_4$], [C$_4$mim][PF$_6$], 8-ethyl-1,8-diazabicyclo[5,4,0]-7-undecenium triflate and 8-methyl-1,8-diazabicyclo[5,4,0]-7-undecenium triflate. Grée and co-workers

Scheme 10. Sc(OTf)$_3$-Catalyzed Sequential Reaction Involving a Claisen Rearrangement and a Cyclization



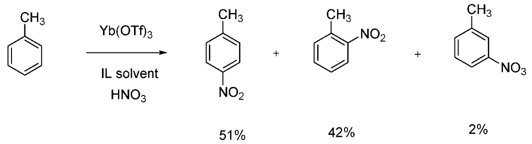
showed that ytterbium(III) triflate catalyzes the carbon-Ferrier rearrangement of tri-*O*-acetyl derivatives of *d*-glucal with allyl silanes, propargyl silane, and silyl enol ethers in ionic liquid solvents ([C_4mim][BF_4] and [C_4mim][Tf_2N]).[205]

Kobayashi and co-workers showed that the combination of silica gel supported scandium(III) triflate with a hydrophobic ionic liquid creates a hydrophobic environment in water.[206] In this way, reactions with water-labile substrates could be performed in water. The catalyst was prepared by adding silica gel supported Sc(OTf)$_3$ to a solution of an ionic liquid in ethyl acetate, and the solvent was removed under reduced pressure. The final catalyst is a free-flowing powder and forms a colloidal suspension in water. Different types of C−C bond formation reactions were tested, including Mukaiyama aldol condensations, Mannich reactions, allylations, and hydromethylations. For most reactions, 1-butyl-3-decylimidazolium hexafluorophosphate has been selected as the ionic liquid.

7.2. C–X Bond Formation

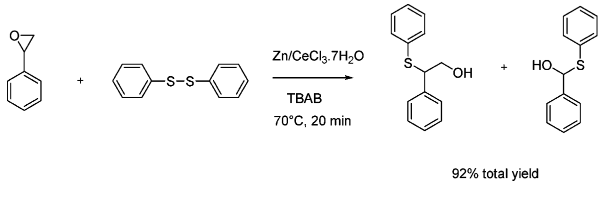
Handy and Egrie reported the use of ytterbium(III) triflate, Yb(OTf)$_3$, as a catalyst for the nitration of aromatic compounds with HNO_3 in the ionic liquid *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Scheme 11).[207] A pyrrolidinium ionic liquid rather than an imidazolium ionic liquid was chosen as the solvent, in order to avoid problems with the nitration of the imidazolium ring under the given reaction conditions. The yields and regioselectivities (*ortho*/*meta*/*para* isomer distributions) were comparable with those in other solvents. However, only electron-rich aromatics could be nitrated; no reaction was observed for bromobenzene. The catalyst loading was 10 mol %.

Scheme 11. Yb(OTf)$_3$-Catalyzed Nitration of Toluene

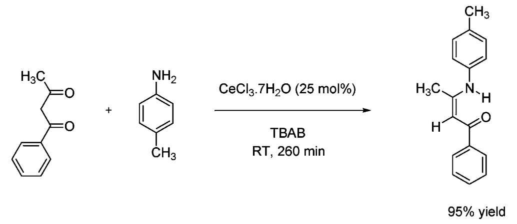


Tetrabutylammonium and tetrabutylphosphonium halides have been applied as ionic liquid solvents. For instance, a mixture of zinc powder and $CeCl_3 \cdot 7H_2O$ was used as reagent for the thiolization of 1,2-epoxides with aryl disulfides in tetrabutylammonium and tetrabutylphosphonium halides (Scheme 12).[208] The highest yields were observed when tetrabutylphosphonium bromide was chosen as the solvent. $CeCl_3 \cdot 7H_2O$ is a good catalyst for the enamination of benzoylacetone and *p*-toluidine, and better yields were obtained in the tetrabutylammonium bromide (TBAB) ionic liquid than under solvent-free conditions (Scheme 13).[209] Although reactions in ionic liquids are generally carried out at room temperature or at moderate temperatures, some reactions require higher reaction temperatures. Here the low volatility and the thermal stability of ionic liquids offer an advantage.

Scheme 12. Thiolysis of Styrene Oxide with Phenyldisulfide in the Ionic Liquid Tetrabutylammonium Bromide (TBAB) in the Presence of Zinc Powder and Cerium(III) Chloride Heptahydrate

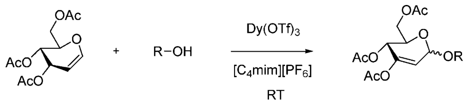


Scheme 13. Enamination of Benzoylacetone and *p*-Toluidine, Catalyzed by Cerium(III) Chloride Heptahydrate



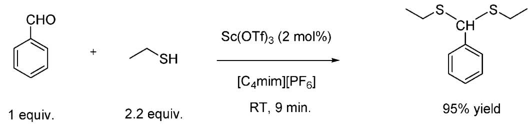
O-Glycopyranosides were prepared in good yields from tri-*O*-acetyl derivatives of *d*-glucal and alcohols, phenols, and hydroxy α-amino acids in [C_4mim][PF_6] with dysprosium(III) triflate as the catalyst (Scheme 14).[86] Dysprosium(III) triflate is not soluble in [C_4mim][PF_6], but nevertheless the yields were much better in this ionic liquid than in the ionic liquid [C_4mim][BF_4], in which the rare-earth salt could be solubilized.

Scheme 14. Synthesis of 2,3-Unsaturated Glycopyranosides

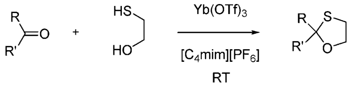


Scandium(III) triflate in the imidazolium ionic liquids [C_4mim][PF_6] and [C_4mim][BF_4] is an efficient reaction medium for the thioacetalization and transthioacetalization of aldehydes (Scheme 15).[210] Thioacetals are important protecting groups for aldehydes. A transthioacetalization reaction converts an *O*,*O*-acetal into an *S*,*S*-acetal. The reaction of a carbonyl compound with 2-mercaptoethanol affords a 1,3-oxathiolane (Scheme 16). Ytterbium(III) triflate has been chosen as a catalyst for the reaction in imidazolium ionic liquid solvents.[211] The highest yields were obtained in [C_4mim][PF_6]. [C_4mim][BF_4] and [C_4mim][Br] gave lower yields.

Scheme 15. Thioacetalization of Benzaldehyde, Catalyzed by Sc(OTf)$_3$



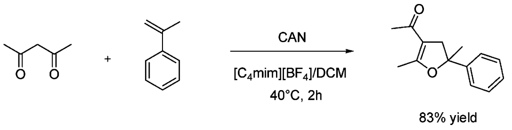
Scheme 16. Yb(OTf)$_3$-Catalyzed Conversion of Carbonyl Compounds into 1,3-Oxathiolanes



7.3. Oxidation and Reduction Reactions

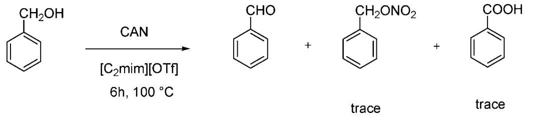
Salts of tetravalent cerium and especially $(NH_4)_2$-[$Ce(NO_3)_6$] (cerium(IV) ammonium nitrate or CAN) and Ce(OTf)$_4$ have often been used as selective oxidants in organic synthesis.[166,169,212−214] However, only a few studies have been reported on the cerium(IV)-mediated oxidation reactions in ionic liquids.[87] This is partially due to the poor solubility of cerium(IV) salts in different classes of ionic liquids. A mixture of [C_4mim][BF_4] and dichloromethane was the solvent for oxidative free radical reactions mediated by cerium(IV) ammonium nitrate (CAN).[215] [C_4mim][BF_4] has also been replaced by 1-butyl-2,3-dimethylimidazolium tetrafluoroborate. A typical reaction is the reaction of 2,4-pentanedione (1 equiv) and α-methylstyrene (5 equiv) with CAN (2.1 equiv) in [C_4mim][BF_4]/dichloromethane (1:5) (Scheme 17). The yield was similar to that observed in acetonitrile, but much higher than that in dichloromethane without ionic liquid additive. The ionic liquid facilitates the oxidative cyclization reaction. The authors report that the reactions can also be carried out solely in the ionic liquid but that the yields are lower than those in ionic liquid/dichloromethane mixtures. For instance, the reaction shown in Scheme 17 gave 83% yield after 2 h in [C_4mim][BF_4]/dichloromethane (1:5) solvent, compared with 56% yield in [C_4mim][BF_4] solvent. The cerium byproducts precipitated at the end of the reaction.

Scheme 17. CAN-Mediated Oxidative Cyclization Reaction between 2,4-Pentadione and α-Methylstyrene



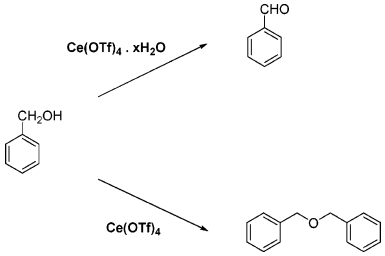
Mehdi et al. evaluated the use of imidazolium ionic liquids as solvents for organic transformations with tetravalent cerium salts as oxidizing agents.[87] Good solubility was found for ammonium hexanitratocerate(IV) (ceric ammonium nitrate, CAN) and cerium(IV) triflate in 1-alkyl-3-methylimidazolium triflate ionic liquids. The authors studied the oxidation of benzyl alcohol to benzaldehyde in 1-ethyl-3-methylimidazolium triflate by in situ FTIR spectroscopy and by ^{13}C NMR spectroscopy of carbon-13 labeled benzyl alcohol. It was found that careful control of the reaction conditions was necessary, because ammonium hexanitratocerate(IV) dissolved in an ionic liquid can transform benzyl alcohol not only into benzaldehyde but also into benzyl nitrate or benzoic acid (Scheme 18). The selectivity of the reaction of cerium(IV) triflate with benzyl alcohol in dry ionic liquids depends on the degree of hydration of cerium(IV) triflate: anhydrous cerium(IV) triflate transforms benzyl alcohol into dibenzyl ether, whereas hydrated cerium(IV) triflate affords benzaldehyde as the main reaction product (Scheme 19). 1,4-Hydroquinone is quantitatively transformed into 1,4-quinone. Anisole and naphthalene are nitrated. The authors reported that for the cerium-mediated oxidation reactions in ionic liquids, high reaction temperatures are an advantage because under these conditions smaller amounts of byproducts are formed.

Scheme 18. Reaction Products Observed upon Oxidation of Benzyl Alcohol by Cerium(IV) Ammonium Nitrate (CAN) in the Ionic Liquid [C_2mim][OTf]



Although samarium(II) iodide (SmI_2, Kagan's reagent) is widely used as a selective reductant in organic synthesis,[166,168] so far no studies on lanthanide(II)-mediated reactions have been reported. It can be anticipated that it is just a matter of time before the first papers on organic reactions with low-valent lanthanide compounds in ionic liquid solvents will be published.

Scheme 19. Different Reaction Products for the Reaction of Benzyl Alcohol with Hydrated or Anhydrous Cerium(IV) Triflate in the Ionic Liquid [C_2mim][OTf]



7.4. Polymerization Reactions

A ring-opening polymerization of ϵ-caprolactone has been carried out in [C_4mim][BF_4] with a mixtures $LnCl_3$ and an epoxide as the catalyst. The highest catalytic activities were observed for $GdCl_3$ and $ErCl_3$.[216] Shen and co-workers investigated the polymerization of methyl methacrylate by a binary catalyst consisting of neodymium(III) versatate and isobutylaluminum in ionic liquids.[217] The ionic liquids [C_2mim][BF_4], [C_2mim][PF_6], [C_4mim][BF_4], and [C_4mim][PF_6] have been tested. The authors found a higher polymerization rate of methyl methacrylate and a higher molecular weight of poly(methyl methacrylate) in the ionic liquids than in toluene or under solventless conditions. The best results were obtained for [C_2mim][BF_4]. The ionic liquid could be recycled and reused. It was also possible to prepare random and block copolymers of methyl methacrylate and styrene in these ionic liquids.

8. Applications in Materials Sciences

Although applications of lanthanide-containing ionic liquids are not strictly within the scope of this review and this field is still in its infancy, some examples will be given. An interesting paper by Gedanken and co-workers illustrates how lanthanide fluoride nanoparticles can be synthesized by decomposition of fluorine-containing ionic liquids.[218] When a solution of $La(NO_3)_3{\cdot}6H_2O$ or $Y(NO_3)_3{\cdot}xH_2O$ in the ionic liquid [C_4mim][BF_4] was subjected to microwave irradiation in a domestic microwave oven, formation of LaF_3 and YF_3 was observed after a short time interval (5 min). The nanosized fluoride particles had an oval shape in the case of LaF_3 and a needlelike shape in case of YF_3. The source of fluoride ions is the tetrafluoroborate ion, which undergoes hydrolysis in the presence of the hydration water molecules of the metal salts.

Ionogels are new materials in which an ionic liquid is confined within a silica network that can be synthesized by sol−gel processing.[219] The ionogels can be prepared as perfectly transparent monoliths that retain the ionic conductivity of the ionic liquid. Although an ionogel contains up to 80 wt % ionic liquid, it is a solid compound. Luminescent ionogels were prepared by doping them with a europium(III) β-diketonate complex.[220] A very intense red photoluminescence could be observed upon irradiation with ultraviolet light. These materials are at the same time luminescent and ion-conductive.

Lanthanide-containing ionic liquids crystals (*ionic lanthanidomesogens*) will not be discussed here; the reader is referred to other recent reviews on this topic.[221−225] The main rationale to incorporate lanthanides into liquid crystals is the possibility to design materials that combine the properties of lanthanides (luminescence, paramagnetism) with the properties of liquid crystals (switching behavior in external magnetic and electric fields). There exists only one example of an actinide-containing ionic liquid crystal, being a uranyl complex of a substituted imidazo[4,5-*f*]-1,10-phenanthroline ligand with triflate counterions (Figure 13).[226] The compound exhibits a hexagonal columnar mesophase between 95 and 181 °C. Related to ionic liquids are the inorganic−organic hybrid materials that are prepared by ionic self-assembly.[227−230]

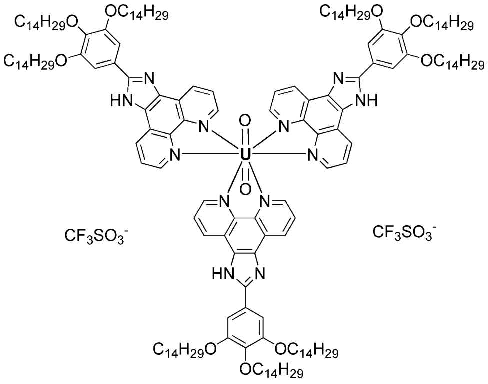


Figure 13. Uranium-containing ionic liquid crystal.

9. Conclusions and Outlook

This review gives an overview of the research possibilities that are offered by combining ionic liquids with f-elements. Many ionic liquids are solvents with weakly coordinating anions, and solvation of lanthanide and actinide ions in these solvents is different from what is observed in conventional organic solvents and water. The poorly solvating behavior can also lead to the formation of coordination compounds with low coordination numbers. The solvation of f-elements can be simulated by molecular dynamics simulations with explicit representation of the solvent or can be directly probed by spectroscopic methods. Ionic liquids turned out to be a promising solvent for near-infrared emitting lanthanide complexes. It is often mentioned that one of the main advantages of ionic liquids is their resistance to strongly oxidizing or reducing agents; that is, ionic liquids have a large electrochemical window. However, not all ionic liquids are suitable for study of the electrochemical properties and electrodeposition of f-elements. The metals of the lanthanides and actinides are very electropositive elements, and they will reduce imidazolium cations. More resistant against reduction are quaternary ammonium and phosphonium cations. Ionic liquids offer a large potential in the field of processing of spent nuclear fuel elements. The advantage is that the processing can be carried out at much lower temperature in ionic liquids than in inorganic molten salts. This not only reduces the energy cost but also increases the safety. The fact that several ionic liquids strongly absorb neutrons (especially boron- and chlorine-containing ionic liquids) reduces the risk of criticality accidents. The study of metal-catalyzed organic reactions in ionic liquid media is a very popular research theme. It is therefore not surprising that lanthanide-mediated organic reactions are being performed in ionic liquids as well. The possibility to recycle the lanthanide catalyst that is immobilized in the ionic liquid and the possibility of easy product separation have stimulated researchers to work in this field. However, in only a few cases the use of (expensive) ionic liquids can be justified by the higher reactivity or selectivity. Research should be directed to find lanthanide-mediated organic reactions that do not work in conventional organic solvents but that cleanly react in ionic liquids. Finally, the combination of lanthanides and ionic liquids can lead to new types of advanced materials (luminescent or magnetic liquid crystals, ionogels, nanoparticles, etc.).

10. Abbreviations

bmpyr	1-butyl-1-methylpyrrolidinium
bppyr	1-butyl-1-propylpyrrolidinium
C_2mim	1-ethyl-3-methylimidazolium
C_4mim	1-butyl-3-methylimidazolium
C_6mim	1-hexyl-3-methylimidazolium
C_{10}mim	1-decyl-3-methylimidazolium
C_4py	*N*-butylpyridinium
CPMO	octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide
DTPA	diethylenetriamine pentaacetic acid
EDTA	ethylenediaminetetraacetic acid
EXAFS	extended X-ray absorption fine structure
Htta	2-thenoyltrifluoroacetone
IL	ionic liquid
Ln	lanthanide
mppyr	1-methyl-1-propylpyrrolidinium
OTf	trifluoromethanesulfonate or triflate
phen	1,10-phenanthroline
RTIL	room-temperature ionic liquid
SEt_3	triethylsulfonium
SHE	standard hydrogen electrode
Tf_2N	bis(trifluoromethylsulfonyl)imide
tta	2-thenoyltrifluoroacetonate

11. Acknowledgment

The author wishes to thank Dr. Peter Nockemann for his help in preparing the figures of the crystal structures and to acknowledge the K.U.Leuven for financial support (Project IDO/05/005).

12. Note Added in Proof

After the submission of the final version of the manuscript, some additional papers were brought to my attention and new papers relevant to the subject of this review have been published. Khosropour and coworkers tested the cerium salts $Ce(NO_3)_3{\cdot}xH_2O$, $CeCl_3{\cdot}7H_2O$ and $(NH_4)_2[Ce(NO_3)_6]$ as catalysts for the dehydropyranylation of benzyl alcohol in the ionic liquid $[C_4py][FeCl_4]$.[231] Excellent results were obtained for $(NH_4)_2[Ce(NO_3)_6]$ (CAN). This salt was found to be a useful reagent for the protection of hydroxyl group by conversion to the corresponding tetrahydropyranyl, tetrahydrofuranyl and trimethylsilyl ethers. Gadolinium(III) triflate was used as a catalyst for the acylation of alcohols, phenols and amines in the ionic liquids $[C_4mim][BF_4]$ and $[C_4mim][PF_6]$.[232] β-Lactams were obtained from imines and acetyl chlorides in $[C_4py][BF_4]$, with the aid of catalytic amounts of ytterbium(III) triflate.[233] The same rare-earth salt was used for the synthesis of 1,2-dihydroquinolines from anilines and acetone in the ionic liquid $[C_4mim][BF_4]$.[234] Sun and coworkers separated scandium(III) from yttrium(III), lanthanum(III) and ytterbium(III) by solvent extraction using the $[C_8mim][PF_6]$/Cyanex 925 system as the organic phase.[235] Bünzli and coworkers investigated the phase transitions in the europium(III)-doped ionic liquid crystal [C_{12}mim]Cl by monitoring the luminescence intensity and the luminescence decay time as a function of the temperature.[236] Giridhar et al. reported a study on the electrochemical properties of uranyl nitrate in [C_4mim]Cl.[237]

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