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Inorganic Synthesis

# Ionic Liquids: New Perspectives for Inorganic Synthesis?

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halogen-rich compounds · inorganic synthesis · ionic liquids · metal–metal bonds · network compounds

*Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 70th birthday*

*Ionic liquids are credited with a number of unusual properties. These include a low vapor pressure, a wide liquid-phase range, weakly coordinating properties, and a high thermal/chemical stability. These properties are certainly of great interest for inorganic synthesis and the creation of novel inorganic compounds. On the other hand, the synthesis repertoire for preparing inorganic compounds has always been broad, ranging from syntheses in solutions and melts to solid-state reactions, and from crystal growth in the gas phase to high-pressure syntheses. What new aspects can ionic liquids then add to the synthesis of inorganic compounds? This Minireview uses some early examples to show that the use of ionic liquids indeed provides access to unusual inorganic compounds.*

## 1. Introduction

The range of synthetic methods and reaction conditions is traditionally large in inorganic chemistry. It includes syntheses in low-boiling liquids (such as liquid $NH_3$ and $SO_2$), water, inorganic acids or bases, as well as in classical organic solvents (such as alcohols, amines, and carbonic acids). Reactions in molten salts or metals, solid-state reactions, and crystallization from the gas phase are also worth mentioning.[1] The reaction conditions cover a temperature range from about $-50\,°C$ (for example liquid $NH_3$) via room temperature (conventional solvents) and up to some hundreds of degrees (molten salts and solid-state reactions) and a pressure range from almost vacuum (chemical transport) via standard pressure and up to a few GPa (high-pressure molding). In view of this well-established repertoire of synthetic methods, the question arises as to what ionic liquids, as a novel type of solvent, can offer for synthesis of inorganic compounds that is new.

The term ionic liquids (IL) is generally applied to salts with a melting point that lies below 100 °C.[2] Beginning with the ethylammonium nitrate salt $[EtH_3N]^+[NO_3]^-$, which Walden presented as early as 1914 and which has a melting point of 12 °C, ionic liquids have been known for almost a hundred years.[3] Starting from there, there are now up to $10^{18}$ ionic liquids that can in principle be produced, and a few hundreds of these are indeed commercially available (Figure 1).[4] This multitude of ionic liquids, and their physicochemical properties, has been summarized in various current review articles.[2,5] The subject of this Minireview is, however, not compounds that themselves belong to the class of ionic liquids, but on those that have been obtained using ionic liquids as solvents/medium of reaction. Thus, our subject is not ionic liquids for their own sake, but as a means for preparing novel inorganic compounds, the existence and structure of which is typically confirmed by single-crystal structural analysis.

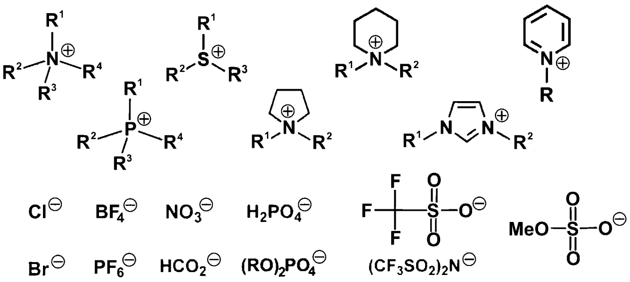

*Figure 1.* Overview of typical cations and anions used as constituents of ionic liquids (ILs).

The unusual properties that are attributed to ionic liquids, and that are not found in this combination in conventional solvents, can certainly be very interesting for the synthesis of new inorganic compounds. These include a wide range for the liquid phase (for some, $-50\,°C$ to $+400\,°C$), a low vapor pressure, weakly coordinating properties, high-temperature stability (for some, up to 400 °C), and a broad electrochemical

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window (for some, −4 V to +4 V).[2,5] Selected ionic liquids can thus make it possible to work with elemental fluorine ($E_0 = +3.1$ V) and with elemental cesium ($E_0 = -2.9$ V) without the solvent decomposing! As many ionic liquids do not contain protic functional groups (such as −OH, $-NH_2$, −COOH), they can combine polar, aprotic, and weakly coordinating properties.[2,5] Finally, the vast number of ionic liquids that can be realized by permutation of cations and anions alone permits a design of properties that is hardly possible in this way with conventional solvents. Besides the modification of typical properties of solvents (such as thermal/chemical stability, polarity, viscosity, miscibility with other solvents, and ability to dissolve solids),[2,5] liquid three-phase systems can even be formed.[6] The introduction of selected functional groups or metal atoms into the constituents of the ionic liquid can also provide specific physicochemical properties, such as chirality,[7] catalytic activity,[2,8] magnetism,[9] or luminescence.[10] Such "task-specific ionic liquids"[11] offer a variety of perspectives; as pure compounds they will however not be discussed herein, in accordance with the subject of this Minireview.

Based on their unusual properties, ionic liquids have already obtained considerable importance in recent years in organic synthesis,[12] in catalysis,[13] as an inert electrolyte,[14] and for the synthesis of nanomaterials.[15] There are current reviews on these fields, which show the potential for basic chemical research and technical application. But what specifically can the role and advantage of ionic liquids in inorganic synthesis chemistry be? On one hand, a certain disillusion has set in, as the thermal/chemical stability of many ionic liquids in specific syntheses is often not as high as hoped. But on the other hand, the preparation of some very remarkable compounds has been achieved using ionic liquids. Therefore, this Minireview will concentrate on the potential of ionic liquids for synthesizing novel inorganic compounds, and make an initial evaluation.

## 2. Constraints on the Use of Ionic Liquids in Synthetic Inorganic Chemistry

If the special properties of ionic liquids are taken as given (see Section 1), their potential for synthetic inorganic chemistry seems obvious. But practical experience in synthesis soon shows that careful selection of the ionic liquid that is suitable for the specific problem is essential. Thus, a suitable ionic liquid must be chemically inert to the initial compounds, while at the same time ensuring sufficient solubility. As novel inorganic compounds are characterized by means of single-crystal structural analysis in the great majority of cases, the growing of suitable single crystals in ionic liquids is also necessary. This typically requires running a reaction for lengthy periods (hours to days) at elevated temperatures (room temperature to 400 °C). Only if the various constraints are met simultaneously, the synthesis of new inorganic compounds in ionic liquids can be successful. To date, there are detailed experimental or theoretical studies of the stability and reactive behavior of ionic liquids in only a few cases, for example for the system $[EMIm][NTf_2]–AlCl_3$ or $[C_4MPyr][NTf_2]–AlCl_3$ (EMIm = 1-ethyl-3-methylimidazolium, $C_4MPyr$ = N-butyl-N-methylpyrrolidinium, $NTf_2$ = bis(trifluoridomethansulfonyl)imide).[16] As corresponding experimental values in particular are seldom recorded in publications, an assessment, even if only qualitative, would be

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*Claus Feldmann studied chemistry (University of Bonn, graduating 1991) and carried out his doctorate in solid-state chemistry in 1994 under Martin Jansen. After post-doctoral studies with Hans-Georg von Schnering (Max Planck Institute of Solid-State Research, Stuttgart), he moved to industry in 1996 (Philips Research Laboratories), where he was engaged in research on luminescent materials. Simultaneously, he completed his habilitation on nanomaterials at the RWTH Aachen. In 2003, he was appointed to the University of Karlsruhe, the present Karlsruhe Institute of Technology (KIT). His research interests include solid-state chemistry and nanomaterials.*

helpful to initiate the broad use of ionic liquids in inorganic synthesis.

The thermal stability of ionic liquids is in principle ideal for synthetic inorganic chemistry. But in fact, far from all ionic liquids are stable at temperatures above 200 °C and/or over longer periods of time. Their thermal/chemical stability can also sometimes collapse if only small quantities of water or residues from the preparation of the ionic liquids are present as impurities. The starting materials, employed in the specific case, can reduce the thermal/chemical stability of the ionic liquids considerably as well (Figure 2). The solubility of initial compounds in ionic liquids must not be overestimated. It is true that these are molten salts, but the low charge density and the low coordinating capacity of the IL constituents usually limit their polarity severely. For example, simple salts (such as metal halides) often do not exist as free ions in solution, but in the form of ion pairs.[2,6] If the crystallization of a novel compound finally succeeds, its extraction from the often highly viscous ionic liquids presents a further challenge. Extraction is particularly difficult if constituents of the ionic liquid have been incorporated into the compound obtained, as the solubilities of the ionic liquid and the compound are then usually very similar.

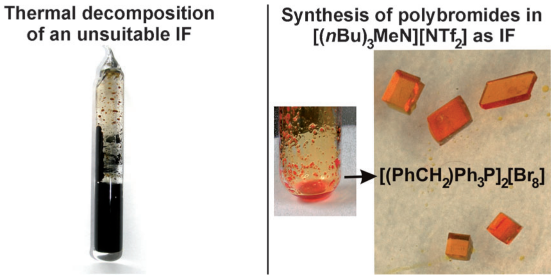

***Figure 2.*** Unsuccessful (left) and successful preparation (right) of new inorganic compounds in ionic liquids, performed in both cases in glass ampoules sealed under argon (see Section 5).

If we consider the various constituents of ionic liquids (Figure 1), then perfluorinated anions, such as $[BF_4]^-$, $[PF_6]^-$, and $[SiF_6]^{2-}$ are often rather thermally and/or chemically unstable, as in the presence of dissolved metal cations, free $BF_3$, $PF_5$, or $SiF_4$ can be generated by Lewis acid–base reactions, resulting in the decomposition of the IL cation. IL cations with an aromatic backbone (such as imidazolium, pyridinium, or pyrimidinium) often display a certain C–H acidity in the α- or β-position to the heteroatom, which also limits the thermal/chemical stability. A similar C–H acidity is also observed with methylammonium groups. IL cations with long alkyl substituents are thermally and chemically more stable. In this case, the polarity of the ionic liquids and the solubility of polar starting compounds naturally drop considerably.

Overall, IL combinations with quaternary ammonium cations that contain ethyl, propyl, or butyl groups, and anions such as $[CF_3SO_3]^-$, $[N(SO_2CF_3)_2]^-$, or $[N(PO_2C_2F_5)_2]^-$, turn out to be especially thermally and chemically stable (see Sections 3–5).[17] Perfluorinated anions are preferred with regard to noncoordinating properties (see Sections 3 and 6).[18] The almost classical Lewis acid ionic liquids with $[AlCl_4]^-$, $[Al_2Cl_7]^-$, or similar anions display excellent solubility of elemental metals (such as Ga, In, Sn, Bi) and chalcogens (see. Sections 4 and 5). Thus, only a relatively limited number of ionic liquids has been used to date for the reactions and compounds presented below.

## *3. Weakly Coordinating Anions*

As a result of their weakly coordinating properties, the constituents of the ionic liquids are frequently not incorporated into the compounds synthesized in these reactions, in contrast to conventional polar (and therefore usually coordinating) solvents and classical molten salts. This "coordinative inertness" is naturally an interesting aspect for synthetic inorganic chemistry. If IL constituents are incorporated despite this inertness, the large space requirements of the cations or anions at least cause a strongly structure-directing effect, which is often accompanied by novel structural building units. What is much more interesting, however, is the fact that the coordinative inertness of the ionic liquids permits weak interactions between bonding partners, which would normally not be expected in the presence of stronger ligands from the thermodynamic point of view. This is the special advantage of perfluorinated anions, beginning with $[BF_4]^-$, $[PF_6]^-$, or $[SiF_6]^{2-}$ as the simplest, and species of the type $[Al(OR^F)_4]^-$ ($R^F$ = fluoroalkyl) as particularly weakly coordinating representatives of the group. The chemistry of weakly coordinating anions (WCAs) derived from this has already developed into a separate field of research, in parallel with that of ionic liquids. As current reviews exist,[18] this Minireview can be limited to a few more recent results and compounds.

Of great interest at present are studies on the stabilization of low-valent metal cations in ionic liquids or in the presence of WCAs. For example, the synthesis of $[C_3MPyr]_2[Yb^{II}(NTf_2)_4]$ ($C_3MPyr$ = *N*-propyl-*N*-methyl pyrrolidinium) from $YbI_2$ in $[C_3MPyr][NTf_2]$ demonstrates an unusually high stability for a bivalent rare-earth-metal ion (Figure 3).[19] $[C_3MPyr]_2[Yb(NTf_2)_4]$ not only represents the first coordination compound of a transition metal with the WCA $[NTf_2]^-$, but also shows that, owing to steric and electrostatic effects,

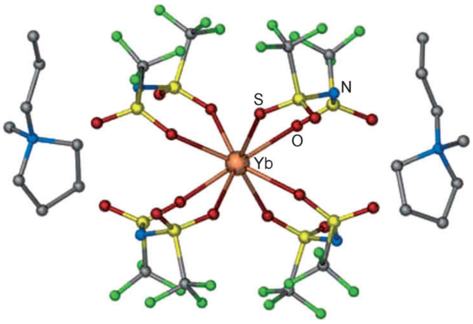

***Figure 3.*** Crystal structure of $[C_3MPyr]_2[Yb^{II}(NTf_2)_4]$ (modified reproduction from Ref. [19]).

an $\eta^2$ coordination of $[NTf_2]^-$ by oxygen can be favored over the typically preferred coordination to the more nucleophilic nitrogen center. The stability of bivalent rare-earth-metal ions in ionic liquids was also demonstrated by Lützenkirchen et al.[20] Besides characterizing the luminescence caused by $Eu^{2+}$, they were able to show that in $[BMIm][PF_6]$ (BMIm = 1-butyl-3-methylimidazolium) as an ionic liquid, neither the incidence of light nor the addition of $O_2$, $Ce(SO_4)_2$, or $K_2Cr_2O_7$ leads to an oxidation of $Eu^{II}$ to $Eu^{III}$.

Studies of compounds with the composition $A_nM_mB_{n+m}$ (A = IL cation, M = metal, B = IL anion) confirm the unusual coordinative behavior of rare-earth-metal cations in ionic liquids. With $[PMIm][Eu^{III}(NTf_2)_4]$ (PMIm = 1-propyl-3-methylimidazolium), $[BMIm][Eu^{III}(NTf_2)_4]$, and $[C_4MPyr]_2[Eu^{III}(NTf_2)_5]$, rare-earth-metal-based ionic liquids without stabilization by neutral co-ligands were presented, and substantiated by means of single-crystal structural analyses.[10] As expected, all of the rare-earth-metal compounds mentioned show intensive luminescence. As an analogue to the bivalent rare-earth metals, Mudring and Babai have demonstrated the coordinative behavior of the $[NTf_2]^-$ anion towards alkaline-earth-metal cations.[21] For $[C_3MPyr]_2[M(NTf_2)_4]$ (M = Ca, Sr), isolated square-antiprismatic $[M(NTf_2)_4]^{2-}$ units with bidentate $(NTf_2)$ ligands exist for each. In contrast, for $[C_3MPyr][Ba(NTf_2)_3]$, a coordination of $Ba^{2+}$ with six oxygen atoms, with the participation of three $\eta^2$-coordinating $(NTf_2)$ ligands, is found. With three additional oxygen atoms with $\eta^1$ coordination, an infinite $^1_\infty[Ba(NTf_2)_3]^-$ chain structure results. Taking a similar approach, Binnemans et al. studied the coordinative behavior of nitrile-functionalized ionic liquids, and obtained the compounds $[Co(M_{CN}MPyr)_2(NTf_2)_4]$ ($M_{CN}MPyr$ = *N*-ethyl-nitrile-*N*-methyl pyrrolidinium) and $[Co(C_{2CN}MPyr)_6][NTf_2]_8$ ($C_{2CN}MPyr$ = *N*-ethyl-nitrile-*N*-methyl pyrrolidinium).[22] When the nitrile-functionalized alkyl chain was extended, a shift from a mixed nitrile/$NTf_2$ coordination to a pure nitrile coordination is observed.

A novel octanuclear europium–oxygen complex was synthesized by Mudring and Babai, namely $[C_4MPyr][Eu^{III}{}_8(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(\mu_2\text{-}OTf)_{14}(\mu_1\text{-}OTf)_2](HOTf)_{1.5}$.[23] The compound was obtained by reacting europium triflate in $[C_4MPyr][OTf]$ (OTf = triflate) as the ionic liquid at 100 °C. This polynuclear europium complex has a doubly capped octahedron in which the Eu–Eu distance (393 pm) exceeds the value to be expected for a Eu–Eu bond (< 250 pm) considerably so that there are no metal–metal bonds. Each of the twelve triangular surfaces of the $[Eu_8(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}]$ complex is capped by a $\mu_3$-bridged hydroxide ion, while a $\mu_4$-bound oxygen atom is localized in the center of the europium complex. Furthermore, the polynuclear metal complex is surrounded by a total of sixteen triflate anions, of which fourteen coordinate as dihapto ligands by the corner-sharing of two oxygen atoms of the europium polyhedron. The two remaining triflate anions coordinate as monohapto ligands.

Apart from low-valent rare-earth metals, Krossing et al. recently succeeded in preparing low-valent gallium compounds (Figure 4).[24] Specifically, with $([Ga^I(C_6H_5Me)_2][Al(OC(CF_3)_3)_4]$, $[Ga^I(C_6H_5F)_{2.5}][Al(OC(CF_3)_3)_4]$, and $[Ga^I(PPh_3)_3][Al(OC(CF_3)_3)_4]\cdot 1.5\,C_6H_5F$, three examples with monovalent gallium were obtained by reaction of elemental gallium with $Ag[Al(OC(CF_3)_3)_4]$ in aromatic solvents. Although the synthesis thus did not take place in ionic liquids, the anion $[Al(OC(CF_3)_3)_4]^-$, which is particularly weakly coordinating owing to its trifluoridomethyl groups, makes the coordinative inertness of the WCAs especially apparent once again, and is responsible in this case for the stabilization of the monovalent metal center. Compounds with monovalent indium can also be synthesized in ionic liquids, as the example of $InGa_2Cl_7$ shows.[25]

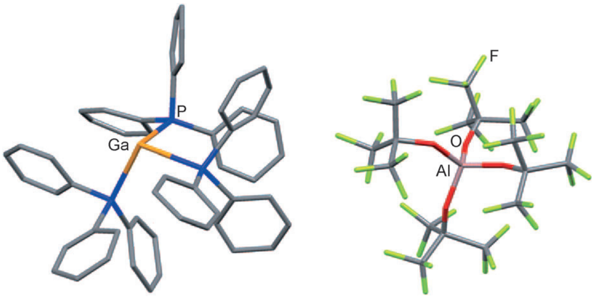

*Figure 4.* $[Ga(PPh_3)_3][Al(OC(CF_3)_3)_4]\cdot 1.5\,C_6H_5F$ with monovalent gallium and $[Al(OC(CF_3)_3)_4]^-$ as WCA (modified reproduction from Ref. [24]).

## 4. Reducing Conditions: Metal–Metal Bonds and Clusters

The interplay of thermal stability and polarity of the ionic liquids, weakly coordinating properties of their constituents, and notably good solubility of elemental metals in the presence of metal halides provide an almost ideal method of access to compounds with metal–metal bonds and clusters. For this purpose, usually ionic liquids with quaternary ammonium, imidazolium, or pyrrolidinium cations and bis(trifluoridomethanesulfonyl)imide and tetrachloridoaluminate anions are used. As the reducing agent, even alkali metals such as potassium can be dissolved in ionic liquids by means of crown ether complexation and used as reactant. For example, by reacting potassium with $WCl_6$ in the presence of [18]crown-6 in $[Bu_3MeN][NTf_2]$ ($Bu_3MeN$ = tributylmethylammonium) as ionic liquid, the synthesis of the compound $[Bu_3MeN]_2[(W^VOCl_4)_2C_4H_8O_2]$ was achieved.[26] Surprisingly, the highly reactive potassium does not cause decomposition of the ionic liquid but rather of the crown ether. The 1,4-dioxane formed in this process functions as a donor molecule bridging the tungsten atoms.

We will first discuss compounds with metals synthesized in ionic liquids, for which metal–metal bonds and clusters have already been well-described, and then go on to some "surprises". For example, element–element bonding is characteristic of the chemistry of boron and its compounds.[27] Vinas et al. show with compounds of the composition $[C_{2n}MIm][Co(C_2B_9H_{11})_2]$ ($n = 1$–$9$) that boron cluster anions can also function as constituents in ionic liquids.[28] The synthesis is carried out by combining $[C_nMIm]Cl$ with $Cs[Co(C_2B_9H_{11})_2]$ in conventional organic solvents. The anion consists of a cobalt ion that is coordinated in a sandwich by two ($B_9C_2H_{11}$) subunits. Hughbanks and Sun use a similar approach with an IL-based extraction and subsequent crystallization of hexanuclear zirconium halide clusters.[29] The compounds $KZr_6CCl_{15}$, $Li_2Zr_6MnCl_{15}$, and $Rb_5Zr_6BCl_{18}$, obtained by classical high-temperature solid-state reactions, are first dissolved in $[EMIm][AlCl_4]$ at 100–120 °C, and then crystallized by cooling down to room temperature. In this way, the compounds $[EMIm]_4[Zr_6CCl_{18}]$, $[EMIm]_5[Zr_6MnCl_{18}]$, and $[EMIm]_4[Zr_6BCl_{18}]$ were obtained. Although these clusters were already known, the synthesis demonstrates impressively the stability and good solution properties of the ionic liquid, especially since, with few exceptions, obtaining zirconium clusters by synthesis has been limited to high temperatures ($>500$ °C) until now.[30] In an early synthesis sequence, Hughbanks and Runyan already reported soluble hexanuclear zirconium clusters in the IL system $[EMIm]Cl–AlCl_3$, and the complete halogen exchange of chlorine for bromine without destruction of the metal cluster, in 1994.[31] An unexpected temperature behavior was also presented by Ruck et al. for the first synthesis of a bismuth cluster in ionic liquids.[32] $BiCl_3$ was combined with elemental Bi in $[BMIm][AlCl_4]$ to form $Bi_5[AlCl_4]_3$, with the already known $[Bi_5]^{3+}$ cation.[33] The formation of the polycation by synproportionation of $Bi^0$ and $Bi^{III}$ at room temperature in an ionic liquid is also remarkable.

Saito et al. described a novel metal cluster from the synthesis of a three-membered rhenium ring in $[EMIm]_3[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_9]Br$.[34] The compound was obtained by reaction of $Re_3S_7Cl_7$ in $[EMIm][AlBr_4]$. A noteworthy aspect of this reaction is that the original Re=Re bonds are split up. Once again, a complete halogen replacement of chlorine by bromine occurred, with three additional bromine atoms being coordinated to the three-membered Re ring. Finally, there is a surprising conversion of $\mu(S_2)$ ligands to $\mu(S)$ ligands. Both the number of remaining electrons (six) in the three-membered Re ring and the observed bond length of 274 pm suggest a three-membered ring with Re−Re single bonds (compare Re=Re: 245 pm). A related subunit, the cluster $[W_3Cl_{13}]^{3-}$, also exists in $Sn^{II}[Sn^{II}Cl][W_3Cl_{13}]$, which has a W−W bond distance of 272 pm.[35] Each tungsten atom of the cluster is coordinated with three terminal chloride ions and also two $\mu_2$-$Cl^-$ and one $\mu_3$-$Cl^-$. The compound was synthesized by reducing $WCl_6$ with elemental tin in $[BMIm]Cl–AlCl_3$ as the ionic liquid. And a triangular chromium cluster with a Cr−Cr distance of 294 pm is also found in $[CrCl_3]_3@[BMIm][OMe]$ and was obtained by reacting $CrCl_3$ with $CrCl_2$ and methanol in $[BMIm]Cl$.[36]

A spectacular result with respect to the realization of metal-metal bonds and clusters in ionic liquids was achieved by Grin et al. through reaction of Zintl phases of germanium, making use of the mild reaction conditions in $[DoMe_3N][AlCl_4]$ ($DoMe_3N$ = dodecyltrimethylammonium) as an ionic liquid. The weak acidity of the β-H atoms of the IL cation, which is undesirable as such, leads to a controlled oxidation of the initial substance, $Na_{12}Ge_{17}$, by Hofmann degradation at 300 °C. In this way, apart from small quantities of α-Ge, the first guest-free germanium clathrate cage with $\square_{24}Ge_{136}$ as crystalline main phase, which is a new modification of germanium composed of $Ge_{28}$ and $Ge_{20}$ cages, was presented (Figure 5).[37]

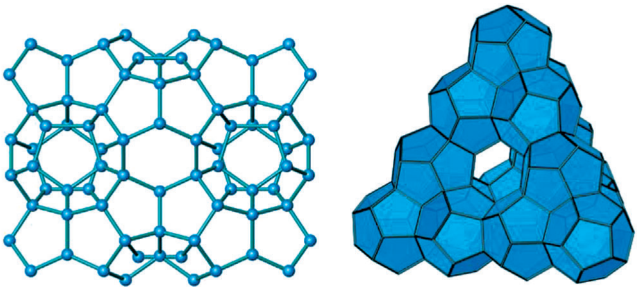

*Figure 5.* Non-filled germanium clathrate $\square_{24}Ge_{136}$, consisting of $Ge_{20}$ and $Ge_{28}$ cages, which together form a supertetrahedron (modified reproduction from Ref. [37]).

An analogous synthesis, starting from $K_4Ge_9$, leads to an amorphous product in the first step, which, after thermal treatment at 370 °C, could be identified as $K_{8.4}Ge_{136}$.[38] The three-dimensional germanium network consists of tetrahedrally coordinated Ge atoms that form $Ge_{20}$ and $Ge_{28}$ cages, which are linked by shared hexagonal surfaces (Figure 6). In contrast to the non-filled $\square_{24}Ge_{136}$, in this case the centers of the cages are partially filled with potassium. The Ge−Ge distances observed, 244–249 pm, are even less than that of completely filled compounds, such as $Cs_8Na_{16}Ge_{136}$.[39] However, in comparison to the unit cell of $\square_{24}Ge_{136}$ ($a$ = 1521.2 pm), that of $K_{8.4}Ge_{136}$ ($a$ = 1530.2 pm) is slightly enlarged, despite additional ionic bonding interactions.

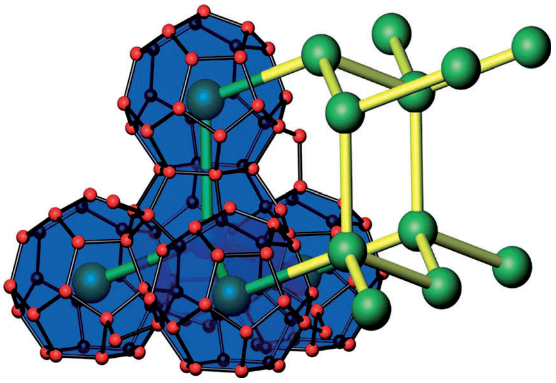

*Figure 6.* $K_{8.6}Ge_{136}$, with $Ge_{20}$ and $Ge_{28}$ cages that are linked by shared hexagonal surfaces (Ge red, K green; modified reproduction from Ref. [38]).

As would be expected, both $\square_{24}Ge_{136}$ and $K_{8.4}Ge_{136}$ are metastable, and transform at 420 °C ($\square_{24}Ge_{136}$) and 471 °C ($K_{8.6}Ge_{136}$) into the thermodynamically stable element modification α-Ge. It is also worth mentioning that semiconducting $\square_{24}Ge_{136}$ shows a band gap (circa 1.4 eV) in the visible spectrum, which may be significant for future optoelectrical applications.

## 5. Oxidizing Conditions: Chalcogen-Rich and Halogen-Rich Compounds

Apart from their great stability against strong reducing agents (see Section 4), selected ionic liquids can also be very stable against strongly oxidizing reaction conditions. Again, ionic liquids with quaternary ammonium, imidazolium, or pyrrolidinium cations and $X^-$, $[AlX_4]^-$ ($X$ = halogen), or $[NTf_2]^-$ as anion are used in particular (see Section 2). In general, the solubility of the chalcogens S, Se, and Te in ionic liquids has turned out to be surprisingly good.[40] This finding, in combination with the thermal stability and oxidation stability, opens unforeseeable possibilities for the use of ionic liquids as solvents in chalcogen chemistry. Furthermore, weakly coordinating anions as a component of the ionic liquids provide a link between reactions in the gas phase and syntheses in condensed matter.

A first milestone was the preparation of new metal complexes with elemental sulfur as neutral ligand. It is remarkable that, to date, only a few compounds have been described in which sulfur rings act as neutral ligands.[41] Typically, coordination compounds of this type do not exist, because of the energetically preferred formation of metal (poly)sulfides in the condensed phase. On the other hand, quantum-mechanical calculations do suggest that sulfur can exist as a neutral ligand in a condensed phase.[42] Following these ideas, Krossing et al. were able to obtain different metal–sulfur complexes, in particular with copper and silver as metal centers, by utilizing the mild reaction conditions and the presence of WCAs (see Section 3). As an approach to the synthesis, sonographic exposure of reaction mixtures of $Ag[Al(OR^F)_4]$ ($R^F = C(CF_3)_3$, for example) and CuI or $[Cu(1,2\text{-}F_2C_6H_4)_2][Al(OR^F)_4]$ in $CS_2$ and $CH_2Cl_2$ with an excess of sulfur were chosen.[43] As the result, the compounds $[(\eta^1\text{-}S_8)Cu(1,5,9\text{-}\eta^3\text{-}S_{12})][Al(OR^F)_4]$ and $[(CH_2Cl_2)Cu(1,5,9\text{-}\eta^3\text{-}S_{12})][Al(OR^F)_4]$ are the first examples of metal complexes with a neutral $S_{12}$ ring as ligand. Furthermore, with $[(\eta^1\text{-}S_8)Cu(1,5,9\text{-}\eta^3\text{-}S_{12})][Al(OR^F)_4]$, the authors succeeded in preparing the first compound containing two modifications of the same element, namely $S_{12}$ and $S_8$, bound to a metal atom (Figure 7). The cause of this unusual coordination is once again the particularly weakly coordinating, perfluorinated $[Al(OR^F)_4]^-$ anions (see Section 3).

Another reaction, involving elemental sulfur and elemental antimony in a mixture of [EMIm]Br and $AlCl_3$, leads to the crystallization of $[Sb_7S_8Br_2][AlCl_4]_3$.[44] This compound, synthesized by Kanatzidis et al., contains an $[Sb_7S_8Br_2]^{3+}$ double heterocubane cation linked at one vertex. The compound is also the first preparation of a heterocubane in ionic liquids, and thus extends the known synthesis strategies to chalcogenide clusters and heterocubanes.[45] A heterocubane is also obtained by the reaction of Bi, $BiCl_3$, $GaCl_3$ and elemental sulfur in [BMIm]Cl. The compound prepared in this way, $[Bi_3GaS_5]_2[Ga_3Cl_{10}]_2[GaCl_4]_2{\cdot}S_8$, contains both a novel $[Bi_3GaS_5]^{2+}$ heterocubane dication and a novel, star-shaped $[Ga_3Cl_{10}]^-$ anion. The latter consists of three $GaCl_4$ tetrahedra that have a common vertex. Besides these two crystal subunits, there are also monomeric $[GaCl_4]^-$ anions and uncharged, crown-shaped $S_8$ molecules in the layered compound (Figure 8).[46]

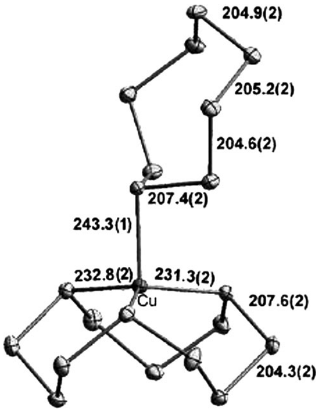

*Figure 7.* $[Cu(S_{12})(S_8)]^+$ cation with an $S_{12}$ and an $S_8$ ring, both coordinating at $Cu^I$ (bond distances in pm; modified reproduction from Ref. [43]).

The heavy chalcogens can also be dissolved in ionic liquids and made to react. For example, tellurium cations, such as $[Te_4]^{2+}$ or $[Te_6]^{2+}$, can be obtained in ionic liquids even at room temperature, which is a very interesting extension of the repertoire of synthesis methods to the known gas-phase transport reactions at 250–350 °C.[47] By reacting the elements tellurium and bismuth at 165 °C in [EMIm]Br–$AlCl_3$, $[Bi_2Te_2Br][AlCl_4]$ can also be obtained.[48] This compound contains infinite cationic $[Bi_2Te_2Br]^+$ layers that are separated by $[AlCl_4]^-$ anions. For structural reasons, an intrinsic two-dimensional semiconductor is formed, which, owing to its band gap (0.8 eV), may be of interest both for thermoelectric applications and for solar cells.

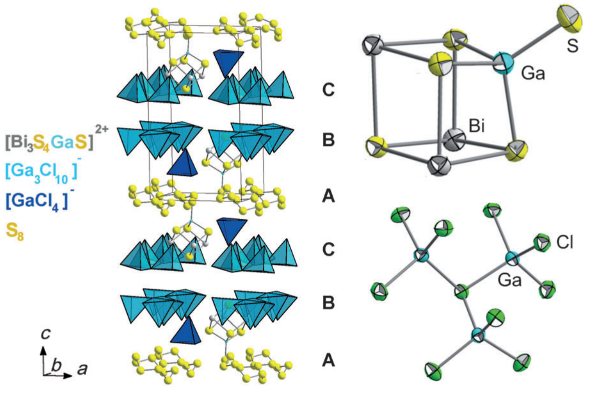

*Figure 8.* $[Bi_3GaS_5]_2[Ga_3Cl_{10}]_2[GaCl_4]_2{\cdot}S_8$ with a $[Bi_3GaS_5]^{2+}$ heterocubane dication, star-shaped $[Ga_3Cl_{10}]^-$ and monomeric $[GaCl_4]^-$ anions, and crown-shaped $S_8$ molecules (modified reproduction from Ref. [46]).

Apart from reactions with elemental chalcogens, the first studies of the use of elemental halogens as reactant in ionic liquids have been presented. For example, fluorination of organic compounds with alkali-metal fluorides can only be achieved in the presence of KF–$CaF_2$[49] by complexing with crown ethers[50] or the addition of suitable polymers, owing to the low nucleophilicity and solubility of these salts in conventional solvents.[51] While alkyl ammonium fluorides, such as $[Bu_4N]F$, are a valuable alternative, they are frequently accompanied by undesirable side reactions, such as elimination reactions.[52] Using a mixture of water, potassium chloride, and a variety of imidazolium-based ionic liquids, Chi et al. succeeded in establishing an efficient synthesis of fluoroalkanes starting from alkyl mesylates and alkyl halides.[53] Along with increased reactivity and yields of over 90%, they were able to reduce the concentration of by-products considerably. Further details on the halogenation of organic compounds in ionic liquids can be found in a review by Stavber et al.[54]

In contrast to the halogenation of organic compounds, little has been reported on the syntheses of novel inorganic halogen compounds in ionic liquids to date (see Section 4). But in principle, the high solubility of many metal halides offers a variety of paths to novel halidometallates. Both isolated subunits and halide-bridged networks can exist.[55] An especially wide variety of structures is to be found in cross-linked building units in the case of the iodidometallates. For example, by reacting bivalent and tetravalent metal iodides in $[Bu_3MeN][NTf_2]$, compounds with crown-ether-complexed metal centers of the type $[\{M^{II}I([18]crown\text{-}6)\}_2I]^+$ can be synthesized (M = Sn, Pb). In $Pb_2SnI_8\cdot 2([18]crown\text{-}6)$[56] and the mixed-valent $Sn_3I_8\cdot 2([18]crown\text{-}6)$,[57] apart from isolated trigonal-bipyramidal $[Sn^{IV}I_5]^-$ anions, there are also dimeric, V-shaped $[\{M^{II}I([18]crown\text{-}6)\}_2I]^+$ cations (M = Pb, Sn), and a non-bridged $[SnI_5]^-$ and the V-shaped cation have been observed for the first time. Furthermore, the mixed valency of an iodidostannate, which was shown conclusively by Mössbauer spectroscopy, is unique to date. Three-dimensional iodidometallate networks can also be realized in ionic liquids with asymmetrically substituted, sterically demanding cations. The cation of the ionic liquids thus exercises a template effect (see Section 6), which leads to new tetrahedral networks in the system $GeI_4$–$I^-$, for example.[58] A template effect of the IL cation used is also credited with the formation of $[Bu_3MeN]_3[\textit{cis}\text{-}Bi_3I_{12}]$.[59] The *cis* linkage of three $(BiI_6)$ octahedra by two shared surfaces each is considerably less favorable with respect to minimization of repulsive $Bi^{3+}$–$Bi^{3+}$ interactions than a *trans* linkage. So it is logical that *trans*-$[Bi_3I_{12}]^{3-}$ has already been described several times, in contrast to the *cis* form.

Our studies of the solubility and reactivity of metal halides in ionic liquids have also shown that ionic liquids can display high solubility and excellent oxidation stability even with elemental halogens. Ionic liquids are thus predestined to be the reaction medium for the synthesis of halogen-rich compounds. Initial experiments with elemental iodine, with a reaction of $CdI_2$ and [18]crown-6 in $[Bu_3MeN][NTf_2]$, resulted in the crystallization of the compound $CdI_2([18]crown\text{-}6)\cdot 2I_2$.[56] This compound consists of $CdI_2([18]crown\text{-}6)$ subunits, which are coordinated terminally by one $I_2$ molecule each. A closer examination of the bond distances and angles shows that, formally, a linear $CdI_2$ exists in which the Cd–I distance corresponds to a $CdI_2$ molecule calculated for the gas phase.[60] Apart from iodine, its more volatile and more reactive homologue bromine can also be made to react in ionic liquids. This is demonstrated, again with $[Bu_3MeN][NTf_2]$ as the ionic liquid, by a reaction of $CuBr_2$ with $P(o\text{-tolyl})_3$ and $Br_2$.[61] The compound obtained, $[\{P(o\text{-tolyl})_3\}Br]_2[Cu_2Br_6](Br_2)$, possesses $[Cu_2Br_6]^{2-}$ anions that are linked by $Br_2$ molecules into $^1_\infty[(Cu_2Br_6)(Br_2)]^{2-}$ chains. It is noteworthy that there is no decomposition of the ionic liquid, even at a reaction temperature of 100 °C, in the presence of elemental bromine.

The oxidation stability of the ionic liquids needed for handling elemental halogens is obvious. But just as important are the high solubility and low vapor pressure of the halogens in the ionic liquid. In this respect, a eutectic mixture of $[C_{10}MPyr][Br]$ ($C_{10}MPyr$ = *N*-decyl-*N*-methyl pyrrolidinium) and $[C_4MPyr][OTf]$ has proven advantageous, as crystallization of target compounds is possible even below room temperature, owing to its low melting point (about −30 °C).[62] Under these conditions, the compound $[C_4MPyr]_2[Br_{20}]$ was obtained recently in the form of deep-red single crystals that are moisture-sensitive and temperature-labile. According to the notation $[C_4MPyr]^+_2[Br^-]_2\cdot 9(Br_2)$, this is a

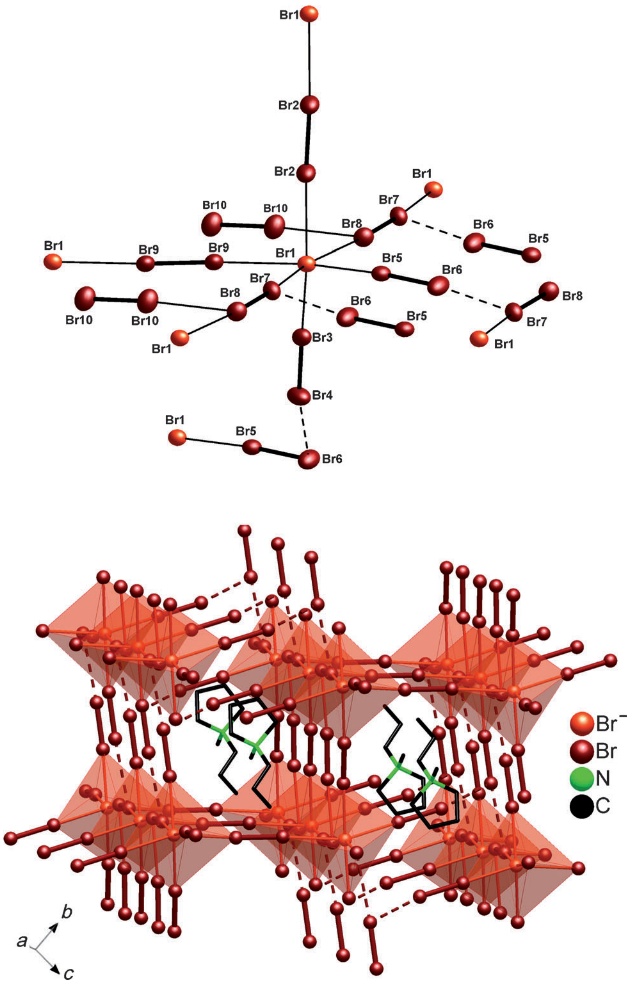

**Figure 9.** $^3_\infty[(Br^-)_2(Br_2)_9]$ network in $[C_4MPyr]_2[Br_{20}]$ with central bromide anions (light red), which are linked by molecular bromine (dark red; above), and three-dimensional arrangement as a distorted CsCl-type of structure with $[C_4MPyr]^+$ cations functioning as a template (below; modified reproduction from Ref. [62]).

polybromide with an unusually high bromine content. Structurally speaking, the compound can be considered as a strongly distorted CsCl-type structure, with $[C_4MPyr]^+$ and $Br^-$ formally occupying the regular lattice sites. The bromide anions, as formal network nodes, are furthermore linked in a distorted octahedron by molecular bromine into a $^{3}_{\infty}[(Br^-)_2(Br_2)_9]$ network (Figure 9). Not only is $[C_4MPyr]_2[Br_{20}]$ the first three-dimensional polybromide network; with a ratio $X^0/X^{-I} = 18:2 = 9$, the compound also possesses a higher content of elemental halogen than the halogen-richest polyhalide to date, $Fc_3I_{29}$ (Fc = ferrocenium; $X^0/X^{-I} = 26:3 = 8.67$).[63] What is also surprising is that according to thermogravimetry, $[C_4MPyr]_2[Br_{20}]$ only releases bromine at above 60 °C.

## 6. Zeolite-like and Metal–Organic Network Compounds

Along with the fields presented above, ionic liquids have found increasing use in recent years as the reaction medium for the synthesis of zeolite-analogous framework compounds or organometallic networks (MOF).[2c,64] Conventionally, the synthesis of zeolite-analogous framework compounds utilizes hydrothermal and solvothermal reaction conditions with the aid of suitable templates.[65] In contrast, in 2004, Morris et al. presented what is called "ionothermal synthesis" in ionic liquids as a new method.[64b,66] Ionic liquids are quite advantageous for this method in several ways. Intrinsically, the voluminous organic cations that are contained can directly act as a template; ionic liquids with quaternary ammonium cations and imidazolium-based cations in particular have acquired some importance. Further to this template effect, a structure-directing influence is observed as well in some cases.[67] Furthermore, the negligible vapor pressure of the ionic liquids makes the use of autoclaves, the associated safety requirements, and costs of equipment unnecessary.[2c] Taking these properties in combination with the thermal/chemical stability, it becomes immediately clear why ionic liquids or mixtures of various ionic liquids are extremely interesting solvent systems for the preparation of zeolite-analogous framework compounds and MOFs.[68] Traces of water, which can still be present even after intensive drying, especially in strongly hygroscopic ionic liquids and which typically diminish the thermal/chemical stability of the ionic liquids significantly (see Section 2), can even be useful as a mineralizer and have a similarly positive effect on the course of the reaction as water, hydroxide, or fluoride ions in classical hydrothermal or solvothermal syntheses.[69] Of course, the deliberate addition of small quantities of water or fluoride in syntheses in ionic liquids often has a corresponding effect.[70]

Based on the advantages named, ionic liquids have come into use, especially for preparing complex aluminophosphates. For example, using [EMIm]Br or mixtures of choline chloride and urea, aluminophosphates designated SIZ-1, SIZ-2, SIZ-3, SIZ-4, SIZ-5, SIZ-6, and ALPO-CJ2 have been synthesized (Figure 10).[69b] Kirschhock et al. were able to prepare other aluminophosphates using [BenzMIm]Cl (BenzMIm = 1-benzyl-3-methylimidazolium) as the ionic liquid.[71]

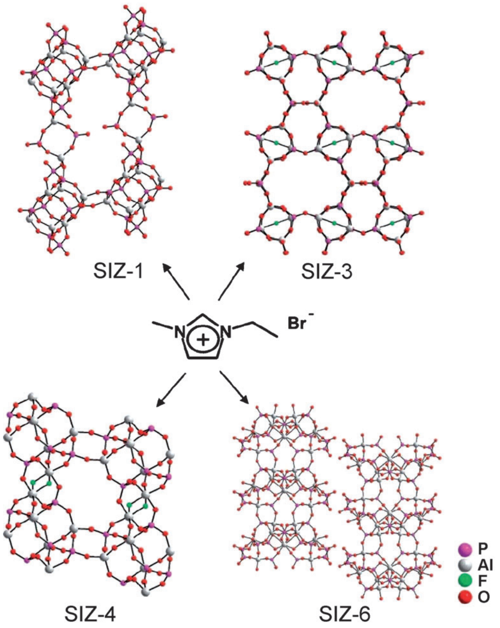

**Figure 10.** Overview of some aluminophosphates synthesized in ionic liquids (modified reproduction from Ref. [69b]).

By means of ionothermal synthesis, numerous MOFs can also be obtained.[72] Kim et al. reported in 2004 the synthesis of the first three-dimensional MOF, $[Cu_3(tpt)_4](BF_4)_3 \cdot (TPT)_{2/3} \cdot 5\,H_2O$ (TPT = 2,4,6-tris(4-pyridyl)-1,3,5-triazine) in an ionic liquid as solvent.[73] The highly symmetrical (3,4)-linked network obtained shows a cubic topology similar to $C_3N_4$. The compound is obtained in the form of deep violet crystals by reacting a mixture of $Cu(NO_3)_2 \cdot 3\,H_2O$ and TPT in $[BMIm][BF_4]$ at 170 °C (Figure 11). The presence of hydrous copper nitrate accelerates the crystallization of the product. The nickel phosphite $[H_3O]_5[Ni_8(HPO_3)_9Cl_3] \cdot 1.5\,H_2O$ is obtained in a similar fashion; with its 18-membered rings, it has unusually wide pores, and for structural reasons, high magnetic anisotropy.[74]

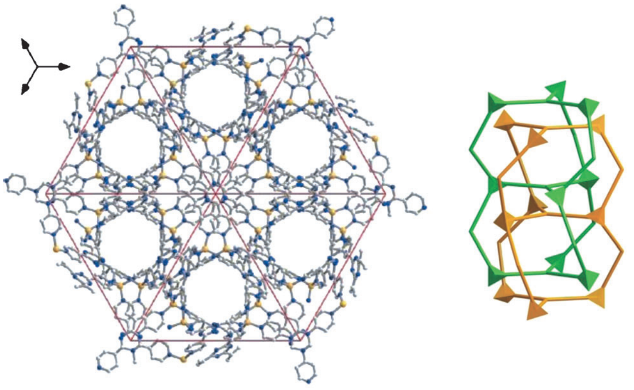

**Figure 11.** Three-dimensional network in $[Cu_3(tpt)_4](BF_4)_3 \cdot (TPT)_{2/3} \cdot 5\,H_2O$ (left) and diagram of the interpenetrating networks (right). Copper atoms are shown with tetrahedral coordination, TPT ligands as rods; for the sake of clarity, interstitial water in the cavities and $[BF_4]^-$ are not shown (modified reproduction from Ref. [73]).

Li et al. succeeded in synthesizing the unusual two-dimensional MOF [Cu(bpp)][$BF_4$] (BPP: 1,3-bis(4-pyridyl)-propane) by using [BMIm][$BF_4$].[75] On the basis of hydrous copper nitrate and BPP, the compound crystallizes in the form of orange crystals. In accordance with the crystal structure, $Cu^I$ cations are each coordinated by a nitrogen atom of the BPP ligand, resulting in undulated $^1_\infty$[Cu(bpp)] chains. The copper atoms also have $d^{10}$–$d^{10}$ interactions with adjacent copper atoms, so that a two-dimensional network structure results overall. In contrast to this cationic network, in [EMIm][Cd(btc)] (BTC = 1,3,5-benzenetricarboxylate) there is an anionic network, which was also obtained in ionic liquids.[76] The anionic $[Cd(btc)]^-$ unit consists of cadmium atoms that are surrounded octahedrally by oxygen atoms of the BTC ligands. Thermogravimetrical analyses confirm that the compound remains thermally stable up to a temperature of 300 °C. Other studies have reported the synthesis of a three-dimensional zinc-based MOF[77] and of a heterometallic $La^{III}$–$Co^{II}$ network.[78] Further developments with respect to the reaction process concern microwave heating in ionothermal syntheses[64a] and the synthesis of homochiral MOFs, such as $[BMIm]_2[Ni(tma)_2(H_2O)_2]$ (TMA = trimesate), which was obtained starting from the chiral ionic liquid 1-butyl-3-methylimidazolium-L-aspartate.[2c,79]

The influence of the ionic liquid on the composition of the MOF framework was demonstrated by Kwon et al. in the system $Ni(OAc)_2$–$H_3BTC$ (OAc = acetate; $H_3BTC$ = 1,3,5-benzenetricarbonic acid or trimesic acid).[80] Depending on the type of alkyl chains of the cation and the type of anion in $[C_nMIm]X$ as ionic liquid ($C_n$ = ethyl, $n$-propyl, $n$-butyl; X = Cl, Br, I), five different organometallic networks of the general composition $[C_nMIm]_2[Ni_3(btc)_2(Ac)_2]$ ($C_n$ = ethyl (A1), $n$-propyl (A2), $n$-butyl (A3)) and $[C_nMIm]_2[Ni_3(Hbtc)_4(H_2O)_2]$ ($C_n$ = $n$-propyl (B1), $n$-butyl (B2)) are available (Figure 12). Of interest with regard to the choice of anion of the ionic liquid is that the halide controls the kinetics of the reaction, and thus the resulting structure. The two possible structure types A and B have linear trinuclear $Ni_3$ units, which are formed by vertex-linked ($NiO_6$) octahedra and bridged by (H)BTC units.

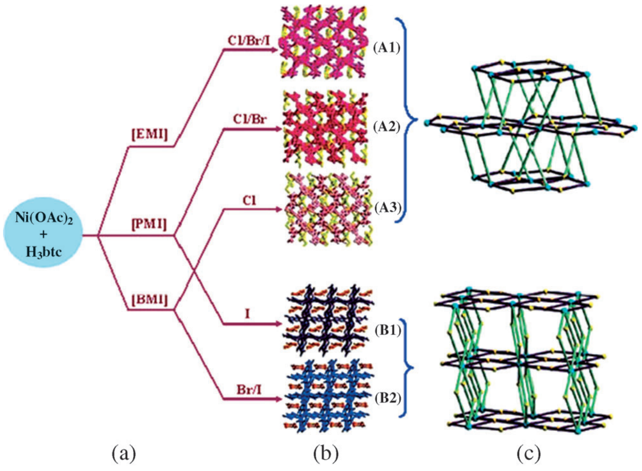

***Figure 12.*** Control of MOF formation by variation of the ionic liquid in the system $Ni(OAc)_2$–$H_3BTC$: influence of cation (a) and anion (b) on the structure and composition of the resulting network (c). IL (A1–A3) yellow, IL (B1–B2) orange, Ni turquoise, BTC yellow, two-dimensional layers green/violet (modified reproduction from Ref. [80b]).

Organophosphates, as a further group of organic–inorganic network compounds, are being discussed with respect to various fields of applications ranging from gas storage[83] to pharmacotherapy.[82] Morris et al. reported the synthesis and characterization of two new organophosphates, $Al_5F(C_4H_9PO_3)_6(OH)_2(C_4N_2H_6)_2$ and $Ga_4F_2(C_4H_9PO_3)H_5\cdot(C_7N_2H_{11})$, using [EMIm]Br as ionic liquid and HF as mineralizer.[83] In both compounds, the metal centers are surrounded octahedrally by oxygen and fluorine, with the nitrogen atom of the $[EMIm]^+$ cation contributing to the coordinative saturation of the metal. A molecular sieve based on aluminum phosphate, with interesting structural and material properties, was reported by Tian et al.[84] Structurally speaking, there are two three-dimensional channel systems that are independent of one another, consisting of 8-membered and 20-membered rings as pores. Furthermore, free Al–OH and P–OH groups protrude into the channel system, permitting a functionalization of the channel wall. The compound, named DNL-1, with the composition $[(C_6N_2H_{18})_{104}(C_6N_2H_{11})_{80}(H_2O)_{910}][Al_{768}P_{768}O_{2976}(OH)_{192}F_{288}]$, was synthesized in [EMIm]Br as the ionic liquid, and shows a high potential as catalyst and gas storage medium, or membrane for gas separation, in initial studies.

## *7. Summary*

Although the number of examples is still fairly limited, the utility of ionic liquids for inorganic synthesis and the preparation of new inorganic compounds is apparent. The combination of thermal/chemical stability, space-filling cations or anions, coordinative inertness, polar aprotic properties, and low vapor pressure make ionic liquids unique solvents. These advantages are already being made use of in syntheses of low-valent cations, novel compounds with metal–metal bonds and clusters, the preparation of chalcogen-rich and halogen-rich compounds, and the creation of unusual coordinative bonding situations and new network compounds. However, a prerequisite for the successful synthesis of novel compounds is the careful selection of a suitable ionic liquid for the specific problem. The crystallization and separation of new compounds from the mostly highly viscous solvents are further challenges. The relatively high manufacturing costs and the massive loss of quality of the ionic liquids if they are contaminated with traces of water or decomposition products can lead to considerable limitations in inorganic synthesis chemistry as well.

But overall, the potential of ionic liquids for synthetic inorganic chemistry is far from fully exploited, and offers scope for many more spectacular compounds. This Minireview should also be understood as encouragement to incorporate reactions in ionic liquids for preparing inorganic compounds into the repertoire of synthesis methods.

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