

Crystal Engineering in Ionic Liquids. The Crystal Structures of [Mppyr]₃[Ndl₆] and [Bmpyr]₄[Ndl₆][Tf₂N]

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Single crystals of [mppy]₃[Ndl₆] and [bmpyr]₄[Ndl₆][Tf₂N] are the first surprising examples of how the cation of an ionic liquid determines the compound formation from an ionic liquid. Depending upon the variation of the length of the alkyl chain of the quaternary pyrrolidinium cation (C3 and C4, respectively), incorporation of the anion of the ionic liquid, [Tf₂N]⁻, can either be evoked or suppressed.

Introduction

ILs (ionic liquids) are, by a common definition, salts that melt below 100 °C. RTILs (room temperature ionic liquids) are even liquid at room temperature. This new and rapidly expanding class of compounds of (mostly organic) salts is currently gaining tremendous interest and importance as “green” solvents for organic catalysis and synthesis,¹ for electrochemical applications,² and for f-element separation.³ One of the important features of this class of solvents is their negligible vapor pressure which, on one hand, makes them environmentally benign solvents; on the other hand, due to their uncommon physical properties, it is difficult to isolate any solvated compounds. In particular, any growth of single crystals is unusually demanding as most common techniques

for single-crystal growth from solution, such as any form of (isothermal) evaporation of the solvent, freezing-out the solvent, dry-freezing, and hydrothermal crystallization⁴ cannot be applied. One further severe problem that is inherent to most ionic liquid systems is the problem of glass formation. This turns out to be a special problem when either the anion and/or the cation of the ionic liquid become part of the product to be crystallized. Then, the same technical problems occur which are generally observed when crystallizing an ionic liquid itself. On one hand, disperse interatomic forces with a low degree of orientation, low symmetry of the ions, and packing frustration are desirable when designing ILs, as they lead to a low melting point.⁵ On the other hand, the same features easily lead to the formation of supercooled liquids. It is, therefore, not surprising that only a few reports on crystal structures of ILs compared to the vast amount synthesized so far have appeared and mostly of compounds that are solid at room temperature.⁶ Furthermore, just a few account for crystal growth of metal–organic or inorganic compounds from RTILs.⁷ However, the large set of ILs available should offer a great toolbox for crystal engineering⁸ as it is already known that they are highly structured in the liquid state⁹ and can crucially influence the result of

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reactions.¹⁰ Whereas much work has been done on how conventional solvents influence reactions,¹¹ compound formation¹² and crystal growth¹³ little to no work has appeared when it comes to ILs as solvents. In this Communication, we report not only on the crystal growth of quasi-ternary neodymium iodides from quaternary pyrrolidinium-bis-(trifluoromethylsulfonyl)imide (Tf₂N) ILs but also on the influence of slight variations of the cation on the resulting crystal structure.

Results and Discussion

The Tf₂N⁻ anion is today one of the most popular anions used for ILs since it has been found to frequently produce low melting salts due to strong charge delocalization and large conformational flexibility, together with a low tendency to form hydrogen bonds.²⁰ Recently, we were able to present the first crystal structure determination of a divalent lanthanide complex, [mppyr]₂[Yb(Tf₂N)₄], obtained from a solution of YbI₂ in [mppyr][Tf₂N] (mppyr = 1-methyl-1-propylpyrrolidinium).²¹ In this complex, four Tf₂N⁻ anions coordinate η²-bidentately to the metal center. In contrast, under similar reaction conditions, with a trivalent lanthanide iodide, NdI₃, and the same ionic liquid, [mppyr][Tf₂N], single crystals of the quasi-ternary neodymium iodide, [mppyr]₃[NdI₆] were obtained. The general route to obtain crystalline samples of sufficient quality for single-crystal X-ray analysis in this systems is to completely dissolve the educts in the heat (~120 °C) and to subsequently cool the solution slowly to room temperature (1–2 °C/h).

The compound [mppyr]₃[NdI₆] crystallizes in the tetragonal noncentrosymmetric space group *P*4₁2₁2 (no. 92) with eight formula units in the unit cell (Figure 1a). The asymmetric unit contains two symmetry-independent neodymium cations which are each surrounded by an only slightly distorted octahedron of iodine anions with a mean neodymium–iodide interatomic distance of about 311.4 pm (Figure

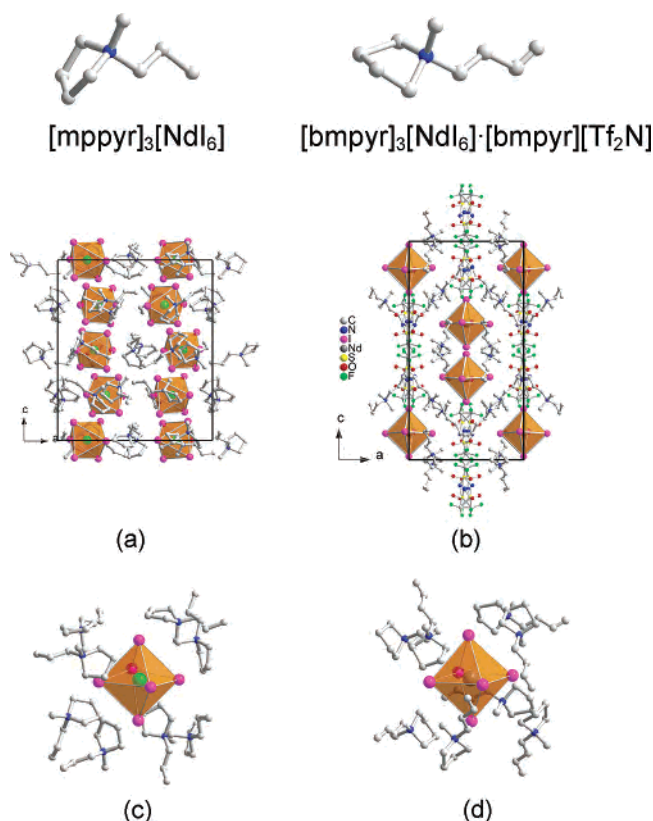


Figure 1. Details of the crystal structures of [mppyr]₃[NdI₆] (left) and [bmpyr]₄[NdI₆][Tf₂N] (right). Projection of the crystal structures of [mppyr]₃[NdI₆] (a) and [bmpyr]₄[NdI₆][Tf₂N] (b) along the crystallographic *b* axis. Local surrounding of the [NdI₆] octahedral by [mppyr] in [mppyr]₃[NdI₆] (c) and by [bmpyr] in [bmpyr]₄[NdI₆][Tf₂N] (d).

1a and c). It is noteworthy that the acentricity of the whole crystal structure is introduced by these (highly symmetric) octahedra which are tilted with respect to the *c* crystallographic axis and wind themselves along the parallel 4₁ screw axis. Above each of the triangular faces of the [NdI₆]³⁻ octahedron a mppyr cation is located tangentially (Figure 1c) like it was already predicted from molecular dynamic studies for tetrachlorocomplexes of trivalent lanthanide cations.²²

A small change of the ionic liquid, from [mppyr][Tf₂N] to [bmpyr][Tf₂N] (bmpyr = 1-butyl-1-methyl-pyrrolidinium), results surprisingly in single crystals of a (at first sight) rather different compound, [bmpyr]₄[NdI₆][Tf₂N] (Figure 1b). That exclusively either [mppyr]₃[NdI₆] or [bmpyr]₄[NdI₆][Tf₂N] are formed depending on the choice of the ionic liquid, hence the cation of the ionic liquid, is reliable, as confirmed by X-ray powder diffraction. The powder diffractograms of the respective bulk samples are well matched with the from single-crystal data expected one (Supporting Information).

[bmpyr]₄[NdI₆][Tf₂N] crystallizes in the (centrosymmetric) space group *I*4₁/*a* (no. 88) with four formula units in the unit cell. Again, the main structural feature is neodymium cations surrounded by a nearly ideal octahedron of iodine anions (mean neodymium–iodine interatomic distance *d*(Nd–I) = 310.6 pm). Not only is the first coordination sphere around the neodymium cation in [bmpyr]₄[NdI₆][Tf₂N] the

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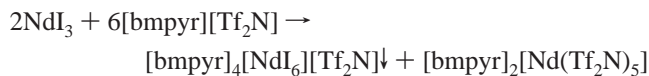
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same as in [mppyr]₃[NdI₆] but also the second. Again, eight cations of the ionic liquid (here: bmpyr) are residing tangentially above the faces of the [NdI₆] octahedron (Figure 1d).

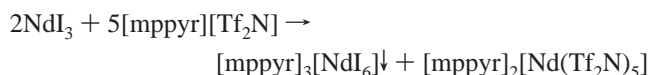
The most important difference between both crystal structures is that in case of [bmpyr]₄[NdI₆][Tf₂N] not only the cation of the ionic liquid participates in the structure but also the anion, Tf₂N⁻, is incorporated in the crystal structure. By extending the alkyl side chain of the quaternary 1-methylpyrrolidinium cation by one carbon atom, optimal space filling for a structure containing only pyrrolidinium cations and [NdI₆] octahedra seems not to be possible. The cation has become too large. To get optimal packing in the solid, one formula unit of the ionic liquid itself has to get included into the structure. This is, thereby, an example of chemospecific crystal engineering.²³ By rewriting the formula [bmpyr]₄[NdI₆][Tf₂N] as [bmpyr]₃[NdI₆]·[bmpyr][Tf₂N] not only the relationship to [mppyr]₃[NdI₆] becomes obvious but this formulation also shows that the compound may be viewed as [bmpyr]₃[NdI₆] with one formula of the “solvent”, [bmpyr][Tf₂N], added. This view is backed by the fact that the bis(trifluoromethylsulfonyl)imide anion gets incorporated in a noncoordinating mode. It has been well established that the bis(trifluoromethylsulfonyl)imide anion shows the essential feature that is necessary for a low tendency to coordinate: delocalization of negative charge over an extended area of functional groups.²⁴ After many unsuccessful attempts²⁵ to crystallize rare earth complexes with the Tf₂N⁻ ligand bonded to the metal center only recently the first structure determinations appeared, featuring La³⁺ in La(Tf₂N)₃·3H₂O,²⁶ Pr³⁺, Nd³⁺, Tm³⁺ in [bmpyr]₃[Ln(Tf₂N)₅], Tm³⁺, Lu³⁺ in [bmpyr][Ln(Tf₂N)₄], and Yb²⁺ in [mppyr]₂[Yb(Tf₂N)₄].²⁷

In [bmpyr]₄[NdI₆][Tf₂N], the bis(trifluoromethylsulfonyl)imide anion adopts a transoid conformation with respect to the -CF₃ groups (Figure 1b), which is generally preferred in the absence of suitable coordination centers as structure determinations of ILs show.²⁸ The transoid conformation of the -CF₃ groups is also found in the free acid [Tf₂N]H (i.e., (CF₃SO₂)₂NH).²⁹ Recent theoretical calculations revealed that transoid [Tf₂N]H is about 8 kJ/mol more stable than cisoid [Tf₂N]H and that transoid [Tf₂N⁻] compared to cisoid [Tf₂N⁻] about 4 kJ/mol.²¹

During the formation of both [bmpyr]₃[NdI₆] and [bmpyr]₄[NdI₆][Tf₂N], the ionic liquid solution depletes of iodide. According to (hypothetical) stoichiometrical reaction equations³⁰



and



aside from the two insoluble reactions products which both have the [NdI₆] octahedron in common, a second neodymium complex which features the lanthanide cation in a coordination of bis(trifluoromethylsulfonyl)imide must form. We have recently characterized this species in case of the [bmpyr] ionic liquid.³¹ The compound [bmpyr]₂[Nd(Tf₂N)₅] is formed. Here neodymium is surrounded by five Tf₂N ligands. Four ligands coordinate bidentately, whereas the fifth coordinates just with one ligand oxygen atom. The Tf₂N ligands adopt both a cisoid and a transoid conformation.

Conclusion

The examples of [mppyr]₃[NdI₆] and [bmpyr]₄[NdI₆][Tf₂N] show how crucially the structure of the self-organization of matter in ILs can be influenced by only such small changes such as replacing a butyl for a propyl side chain in the cation of the ionic liquid. At the same time, the high potential of ILs for the synthesis of specially designed solid compounds becomes obvious.

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Supporting Information Available: X-ray crystallographic files in CIF format; X-ray powder patterns of [bmpyr]₃[NdI₆] and [bmpyr]₄[NdI₆][Tf₂N]; and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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