ELSEVIER

Journal of Alloys and Compounds 418 (2006) 122–127

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Rare-earth iodides in ionic liquids: Crystal structures of $[bmpyr]_4[LnI_6][Tf_2N]$ (Ln = La, Er)

Arash Babai, Anja-Verena Mudring *

Universität zu Köln, Institut für Anorganische Chemie, Greinstrasse 6, D-50939 Köln, Germany

Received 30 May 2005; received in revised form 8 July 2005; accepted 25 August 2005

Abstract

Deliberately designed ionic liquids can be excellent solvents for organic reactions with lanthanide compounds, e.g. Lewis catalysis with trivalent lanthanides. Little is known about the solvation and complexation of these Lewis-acid catalysts in these—still uncommon—solvents, although the knowledge of these processes is a prerequisite for a basic understanding of reaction mechanisms and catalytic cycles. Therefore, we have investigated the chemical behaviour of rare-earth metal iodides in the ionic liquid $[bmpyr][Tf_2N]$ (bmpyr = 1,1-*n*-butyl-methylpyrrolidinium; Tf_2N = bis(trifluoromethanesulfonyl)-amide). Compounds of the general composition $[bmpyr]_4[LnI_6][Tf_2N]$ could be crystallized from solutions of LnI_3 (Ln = La, Er), in $[bmpyr][Tf_2N]$. Single-crystal X-ray diffraction data show that the trivalent rare-earth cations are octahedrally coordinated by six iodide anions. Eight cations of the ionic liquid are located tangentially above each of the triangular faces of the $[LnI_6]$ octahedron. According to the size of the trivalent cation, the crystal structure adjusts itself by tilting of the $[LnI_6]$ octahedra to accommodate one anion of the ionic liquid, bis(trifluoromethanesulfonyl)-amide, which completes the crystal structure of the composition $[bmpyr]_4[LnI_6][Tf_2N]$.

Keywords: Crystal structure; Erbium; Iodides; Ionic liquids; Lanthanides; Lanthanum; Rare-earth metals

1. Introduction

Ionic liquids are salts that are—according to a common definition—liquid below 100 °C, often even below room temperature (so-called room temperature ionic liquids or RTILs) [1]. Ionic liquids are typically formed by a combination of large organic cations, such as imidazolium, pyridinium or quaternary ammonium ions and anionic counterions as commonly halides or $[BF_4]^-$, $[PF_6]^-$ or $[CF_3SO_3]^-$. The appropriate choice of the anion–cation combination allows for tuning of many physical and chemical properties such as miscibility with water and other solvents, dissolving ability, polarity, viscosity or density. Thus ionic liquids are often addressed as designer solvents. They have gained great attention during the last few years especially in organic chemistry replacing conventional solvents as reaction media. In comparison with these, ionic liquids have many advantages—they do not only have negligible vapour pressures and are therefore considered environmentally safe, but as salts the cationic as well as the anionic component can be varied enabling all solvent properties to be tailored for a particular application or reaction. It has been shown that Lewis-acid catalyzed reactions for example with trivalent rare-earth metal cations give higher yields in carefully designed ionic liquids than in conventional organic solvents [2]. α-Aminophosphates, for instance, can be obtained with $M(OTf)_3$ (M = Sm, Dy, Yb, Sc) as Lewis-acid catalysts in 90% yield in $[BMI][PF_6]$ (BMI = 1-butyl-3-methylimidazolium) compared to 70% in CH_2Cl_2 [3]. Yet, the solvation and coordination effects in these solvents are poorly understood, although their knowledge is the key for an understanding of the reaction cycles and mechanisms.

We have therefore investigated the properties of LnI_3, Ln = (La, Er), in $[bmpyr][Tf_2N]$ (1,1-*n*-butyl-methylpyrrolidinium-bis(trifluoromethanesulfonyl)-amide) thoroughly. The triiodides are readily soluble in the ionic liquid and give characteristically coloured solutions. We were able to crystallize and structurally characterize a series of compounds with the general stoichiometry $[bmpyr]_4[LnI_6][Tf_2N]$ from these solutions.

---

* Corresponding author. Fax: +49 221 470 5083.
E-mail address: a.mudring@uni-koeln.de (A.-V. Mudring).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.08.088

2. Experimental

2.1. Synthesis

All preparations were carried out under argon atmosphere using a glovebox and standard Schlenk techniques. Special attention was paid to strictly anhydrous conditions as the lanthanide triiodides readily hydrolyze [4].

To synthesize the triiodides LnI_3, Ln = (La, Er), respective amounts of the elements were placed in silica tubes which were sealed under vacuum and subsequently heated for 30 h at 200 °C. The crude product was purified by sublimation under high vacuum at 800 °C [5].

The ionic liquid 1-butyl-3-methylpyrrolidinium bis(trifluoromethanesulfonyl)-amide, [bmpyr][Tf_2N], was synthesized following a literature procedure [6]. First, [bmpyr]Br was obtained by solvent-free alkylation of *N*-methylpyrrolidin with 1-bromobutane at 80 °C. The crude product was recrystallized from an acetonitrile–toluene mixture, dissolved in water and heated to 70 °C. One equivalent of lithium bis(trifluoromethanesulfonyl)-amide in water was added dropwise and the mixture was stirred for another 24 h at room temperature. The product, which formed a second phase to water, was purified by addition of activated charcoal and filtration through aluminium oxide. It was washed with small aliquots of water until no halide residues could be detected in the extract judged by the $AgNO_3$ test. The ionic liquid was dried for 120 h in an Schlenk tube at 150 °C under reduced pressure and rigorous stirring.

The triiodides LnI_3, Ln = (La, Er) (La ∼ 52 mg, Er ∼ 57 mg, both 0.1 mmol) were put into a silica tube (11 mm in diameter), then [bmpyr][Tf_2N] (∼0.5 ml, 0.75 g, 1.8 mmol) was added. The tube was sealed off under dynamic vacuum and heated to 120 °C until the rare-earth metal salts were completely dissolved. To obtain $[bmpyr]_4[LnI_6][Tf_2N]$, the solutions were subsequently cooled to room temperature (2 °C/min). Under these conditions, crystals of the composition $[bmpyr]_4[LnI_6][Tf_2N]$, Ln = La, Er, precipitated from the solution.

2.2. X-ray crystal structure determination

All data were collected on a Stoe IPDS-II single-crystal X-ray diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 170(2) K (Ln = Er) and 298(2) K (Ln = La). In case of the tetragonal lanthanum compound, analysis of the reflection conditions led to the two possible space groups $P4_12_12$ and $P4_32_12$. Structure solution [7] and refinement [8] succeeded in the space group $P4_32_12$ (no. 96). The reflection conditions of the data set of the also tetragonal erbium compound indicated the centrosymmetric space group $I4_1/a$ (no. 88). Crystal structure solution by direct methods using SHELXS-97 yielded in both cases the heavy atom positions. Subsequent difference Fourier analyses and least squares refinements revealed the remaining atom positions. Crystal data and structure refinement parameters of the two structures are summarized in Tables 1–4. Data reduction was carried out with the program package X-Red [9], numerical absorption corrections with the program X-Shape [10]. For crystal structure drawings the program Diamond was employed [11]. Further details on the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Center (CCDC, 12 Union Road, Cambridge CB2 1EZ, fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk), on quoting the depository numbers CCDC-273377 (Ln = La) and CCDC-273378 (Ln = Er), the authors and the journal citation.

Table 1
Crystal data and structure refinement parameters for $[bmpyr]_4[LaI_6][Tf_2N]$

Empirical formula	$La_1I_6S_2F_6O_4N_5C_{38}H_{80}$
Molecular mass (g/mol)	1749.50
Temperature (K)	298 (2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	$P4_32_12$ (no. 96)
Unit cell dimensions	$a = b = 1505.79(4)$ pm
	$c = 2826.2(1)$ pm
	$\alpha = \beta = \gamma = 90°$
Volume (pm^3)	$6408.1(3) \times 10^6$
Z	4
Density (calculated, mg/m^3)	1.813
Absorption coefficient (mm^{-1})	3.675
F(0 0 0)	3344
Crystal size	0.1 mm × 0.2 mm × 0.3 mm
θ-range for data collection	1.53–25.08°
Index ranges	$-17 \leq h \leq 17$
	$-17 \leq k \leq 17$
	$-33 \leq l \leq 30$
Reflections collected	61836
Independent reflections	5648 ($R_{int} = 0.0465$)
Completeness to $\theta = 29.61°$	99.4%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5648/51/173
Goodness-of-fit on F^2	0.926
Final R indices [$I > 2\sigma(I_o)$]	$R_1 = 0.0437$, $wR_2 = 0.1148$
R indices (all data)	$R_1 = 0.0628$, $wR_2 = 0.1231$
Largest diff. peak and hole	0.525 and −1.371e. Å^{-3}
Absolute structure parameter	0.09(6)
CCDC-no.	273377

Table 2
Crystal data and structure refinement parameters for $[bmpyr]_4[ErI_6][Tf_2N]$

Empirical formula	$Er_1I_6S_2F_6O_4N_5C_{38}H_{80}$
Molecular mass (g/mol)	1777.85
Temperature (K)	170 (2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	$I4_1/a$ (no. 88)
Unit cell dimensions	$a = b = 1464.8$ (2) pm
	$c = 2846.9$ (5) pm
	$\alpha = \beta = \gamma = 90°$
Volume (pm^3)	6134 (2) × 10^6
Z	4
Density (calculated, mg/m^3)	1.925
Absorption coefficient (mm^{-1})	4.511
F(0 0 0)	3388
Crystal size	0.1 mm × 0.2 mm × 0.2 mm
θ-range for data collection	1.56–27.28°
Index ranges	$-18 \leq h \leq 18$
	$-18 \leq k \leq 18$
	$-36 \leq l \leq 36$
Reflections collected	39416
Independent reflections	3415 ($R_{int} = 0.0452$)
Completeness to $\theta = 29.61°$	98.8%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3415/62/90
Goodness-of-fit on F^2	0.871
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0931$, $wR_2 = 0.1542$
R indices (all data)	$R_1 = 0.2723$, $wR_2 = 0.2117$
Largest diff. peak and hole	1.382 and −0.937e. Å^{-3}
CCDC-no.	273378

3. Results and discussion

Nearly colourless, transparent crystals of the general composition $[bmpyr]_4[LnI_6][Tf_2N]$, Ln = (La, Er), precipitate from solutions of the respective lanthanide triiodide in the ionic liquid [bmpyr][Tf_2N] according to the general reaction equation:

$$2LnI_3 + 5[bmpyr][Tf_2N] \rightarrow [bmpyr]_4[LnI_6][Tf_2N]\downarrow$$
$$+\ [bmpyr][Ln(Tf_2N)_4].$$

The lanthanum compound crystallizes in the axial space group $P4_32_12$ (no. 96) with four formula units in the unit cell

Table 3
Atomic coordinates ($\times10^4$) and equivalent isotropic displacement parameters (U_{eq}, Å^2 $\times$ 10^3) for $[bmpyr]_4[LaI_6][Tf_2N]$

	x	y	z	U_{eq}
La	7692 (1)	7692 (1)	5000	81 (1)
I1	7766 (1)	9760 (1)	5213 (1)	111 (1)
S1	1442 (17)	7640 (30)	1933 (13)	670 (40)
O1	1570 (40)	6730 (30)	1780 (30)	390 (30)
I2	7433 (1)	8003 (1)	3907 (1)	107 (1)
S2	2300 (20)	7270 (30)	2408 (7)	620 (30)
O2	0530 (20)	7830 (60)	2030 (20)	680 (70)
I3	7724 (1)	5608 (1)	4902 (1)	119 (1)
O4	2901 (14)	7581 (15)	2048 (8)	150 (6)
O5	1650 (40)	6650 (40)	2270 (30)	430 (50)
N10	9485 (7)	5764 (7)	3360 (4)	118 (3)
C10	9890 (16)	5023 (17)	3104 (9)	206 (8)
C11	8700 (20)	5510 (20)	3581 (11)	263 (13)
C12	9900 (30)	4760 (30)	3994 (15)	334 (19)
C13	400 (30)	4560 (30)	3563 (16)	320 (20)
C14	180 (30)	6110 (30)	3704 (13)	293 (16)
C15	9200 (30)	6470 (20)	3073 (14)	281 (14)
C16	9040 (20)	6780 (20)	2688 (11)	229 (10)
C17	8870 (40)	7720 (40)	2490 (20)	410 (30)
C18	8560 (30)	7580 (30)	2143 (18)	350 (20)
N20	4305 (8)	4591 (8)	1412 (4)	130 (3)
C20	4810 (20)	5330 (20)	1651 (11)	244 (11)
N21	2020 (20)	8130 (20)	2287 (4)	270 (20)
C21	8800 (20)	300 (20)	3812 (11)	241 (11)
C22	0540 (30)	410 (30)	1428(15)	320 (18)
C23	9830 (30)	310 (30)	1843 (14)	323 (19)
C24	8894 (19)	156 (18)	1538 (10)	223 (10)
C25	5760 (20)	6330 (20)	3229 (12)	254 (13)
C26	3150 (20)	4550 (20)	2008 (12)	246 (12)
C27	2580 (40)	4100 (40)	2350 (20)	400 (30)
C28	2130 (40)	4410 (40)	2665 (18)	370 (30)
C100	2449 (9)	7507 (8)	1558 (5)	101 (3)
F101	3292 (18)	7550 (30)	1680 (20)	440 (30)
F102	2160 (19)	8208 (14)	1327 (9)	211 (9)
F103	2160 (20)	6736 (14)	1407 (12)	250 (12)
C200	2233 (13)	7579 (13)	1768 (7)	143 (5)
F201	2770 (40)	6930 (30)	1880 (20)	480 (40)
F202	2560 (60)	8380 (30)	1840 (30)	620 (60)
F203	1730 (20)	7520 (30)	1383 (10)	289 (15)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Atomic coordinates ($\times10^4$) and equivalent isotropic displacement parameters (U_{eq}, Å^2 $\times$ 10^3) for $[bmpyr]_4[ErI_6][Tf_2N]$

	x	y	z	U_{eq}
Er	5000	2500	3750	60 (1)
I1	5000	2500	2682 (1)	75 (1)
I2	7018 (1)	2116 (1)	3784 (1)	73 (1)
N1	2881 (17)	4616 (17)	2272 (9)	96 (7)
C1	2240 (30)	3940 (30)	2433 (16)	135 (15)
C2	1820 (30)	5530 (30)	2481 (16)	141 (14)
C3	1640 (40)	4630 (40)	2722 (19)	180 (20)
C4	2480 (20)	5430 (20)	2030 (11)	96 (9)
C5	3400 (30)	4060 (30)	1864 (17)	156 (15)
C6	4070 (30)	4480 (30)	1671 (18)	165 (16)
C7	4470 (60)	3770 (50)	1230 (30)	270 (30)
C8	5080 (60)	3930 (50)	1090 (30)	270 (40)
C9	3470 (20)	4910 (20)	2685 (13)	106 (12)
S1	5350 (30)	7390 (40)	1712 (5)	420 (40)
N2	4750 (40)	6980 (20)	1301 (9)	40 (13)
C10	5420 (30)	7450 (40)	2216 (12)	150 (40)
O1	5550 (50)	6440 (30)	1700 (19)	230 (30)
O2	5920 (40)	7940 (40)	1420 (30)	270 (40)
F1	5340 (60)	6640 (40)	2400 (20)	580 (120)
F2	5250 (40)	8030 (50)	2555 (12)	360 (60)
F3	6260 (30)	7560 (50)	2100 (20)	270 (30)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

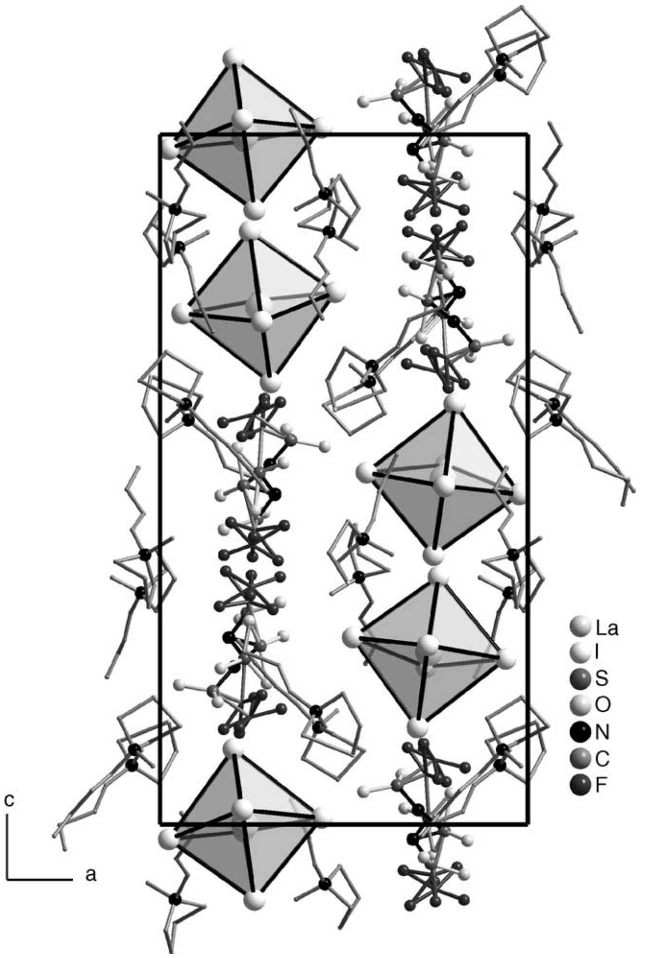

Fig. 1. Unit cell of $[bmpyr]_4[LaI_6][Tf_2N]$, projection along the crystallographic b-axis.

(Tables 1 and 3 and Fig. 1), while the erbium compound crystallizes in the centrosymmetric space group $I4_1/a$ (no. 88), with four formula units in the unit cell as well (Tables 2 and 4 and Fig. 2). In both cases, the asymmetric unit—corresponding to one formula unit of $[bmpyr]_4[LnI_6][Tf_2N]$—contains four cations of the ionic liquid, $[bmpyr]^+$, one (slightly distorted) $[LnI_6]^{3-}$ octahedron (c.f. Table 5) and one anion of the ionic liquid, Tf_2N^-. Formally, the compound can thus be seen as a solvent adduct of the pseudo-binary salt $[bmpyr]_3[LnI_6]$ with the ionic liquid $[bmpyr][Tf_2N]$ ("crystal solvent") itself according to the formula $[bmpyr]_3[LnI_6]\cdot[bmpyr][Tf_2N]$.

The local surrounding of each $[LnI_6]^{3-}$ octahedron is comparable for both compounds as four $[bmpyr]^+$ cations are situated above the faces of the $[LnI_6]^{3-}$ octahedra such that the pyrrolidinium rings are almost parallel to the octahedral faces (Fig. 3). In the erbium compound all alkyl chains adopt the same conformation (there is just one crystallographically

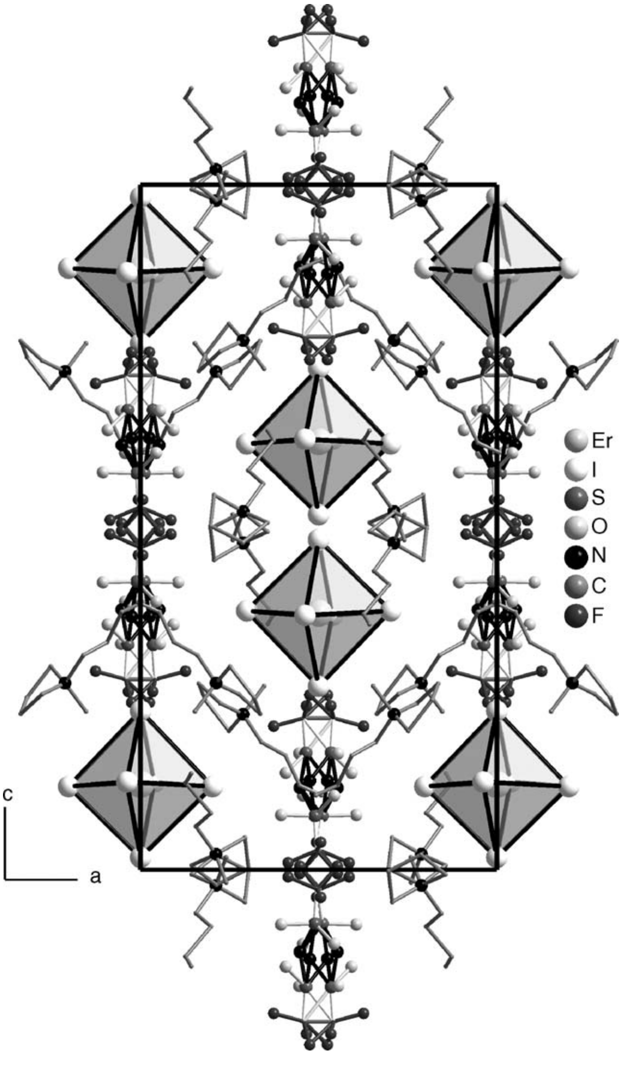

Fig. 2. Unit cell of [bmpyr]$_4$[ErI$_6$][Tf$_2$N], projection along the crystallographic *b*-axis.

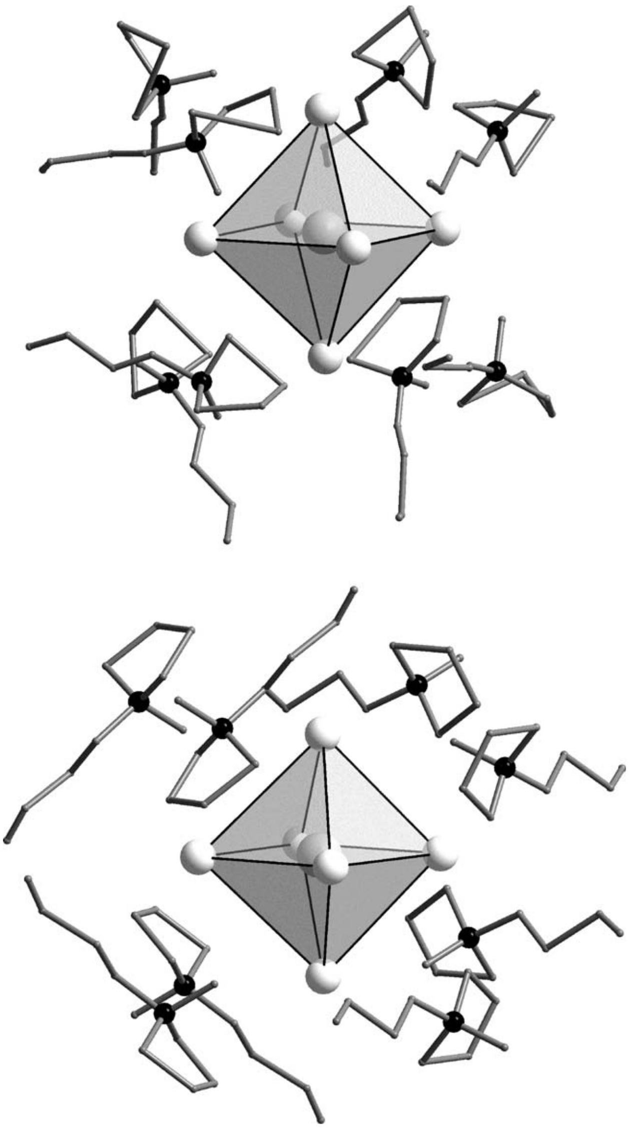

Fig. 3. Local surrounding of the [LnI$_6$]$^{3-}$ octahedral by eight [bmpyr]$^+$ cations in [bmpyr]$_4$[LaI$_6$][Tf$_2$N] (top) and [bmpyr]$_4$[ErI$_6$][Tf$_2$N] (bottom).

independent [bmpyr]$^+$ cation), in the lanthanum compound the two different [bmpyr]$^+$ cations can be distinguished by different conformations of the *n*-butyl side chains (Fig. 3). Molecular dynamic simulations predict a comparable local surrounding of [LnCl$_6$]$^{3-}$-units (Ln = La, Eu) by 1-butyl-3-methyl-imidazolium cations in the ionic liquids [bmim][PF$_6$] and [bmim][TCA] (bmim = 1-butyl-3-methylimidazolium and TCA = tetrachloroaluminate) [12].

In the lanthanum compound, the [LaI$_6$]$^{3-}$ octahedra wind themselves along the 4_3 screw axis parallel to the crystallographic *c*-axis. The octahedra are tilted from the *c*-axis as can be seen from Figs. 1 and 4. In case of the erbium compound, the [ErI$_6$]$^{3-}$ octahedra orient themselves parallel to the crystallographic *c*-axis. Thus, the latter compound has a higher symmetry and crystallizes in the space group $I4_1/a$, a supergroup of $P4_32_12$. In both crystal structures, Tf$_2$N$^-$ anions fill in the gaps between two [LnI$_6$] units along the crystallographic *c*-axes. It is therefore clear why the [LnI$_6$] octahedra are tilted in one compound and not in the other. In case of the smaller Er^{3+} cations the size between the $\{$[LnI$_6$] at 8 bmpyr$\}^{5+}$ units is just right to accommodate the Tf$_2$N$^-$ anions in the remaining voids, whereas in the larger La^{3+} analogue the cavity would be too large for the Tf$_2$N$^-$ groups. Thus, the space is reduced by tilting of the [LnI$_6$]$^{3-}$ octahedra to allow for an appropriate fit of the Tf$_2$N$^-$ unit. This assumption is supported by the observation that the analogous praseodymium compound [13] crystallizes isotypically with the quasi-ternary lanthanum iodide and that we were able to synthesize a neodymium compound [14], isotypic with the

Table 5
Selected bond lengths (pm) and angles (deg) for [bmpyr]$_4$[LnI$_6$][Tf$_2$N]

[bmpyr]$_4$[LaI$_6$][Tf$_2$N]			[bmpyr]$_4$[ErI$_6$][Tf$_2$N]		
La–I1	317.28 (9)	2	Er–I1	302.4 (2)	2
La–I2	314.73 (6)	2	Er–I2	302.5 (2)	4
La–I3	315.18 (9)	2			
I2–La1–I3	93.68 (2)		I1–Er–I1	180.0	
I3–La1–I1	173.42 (2)		I1–Er–I2	91.80 (4)	
I2–La1–I1	92.56 (2)				

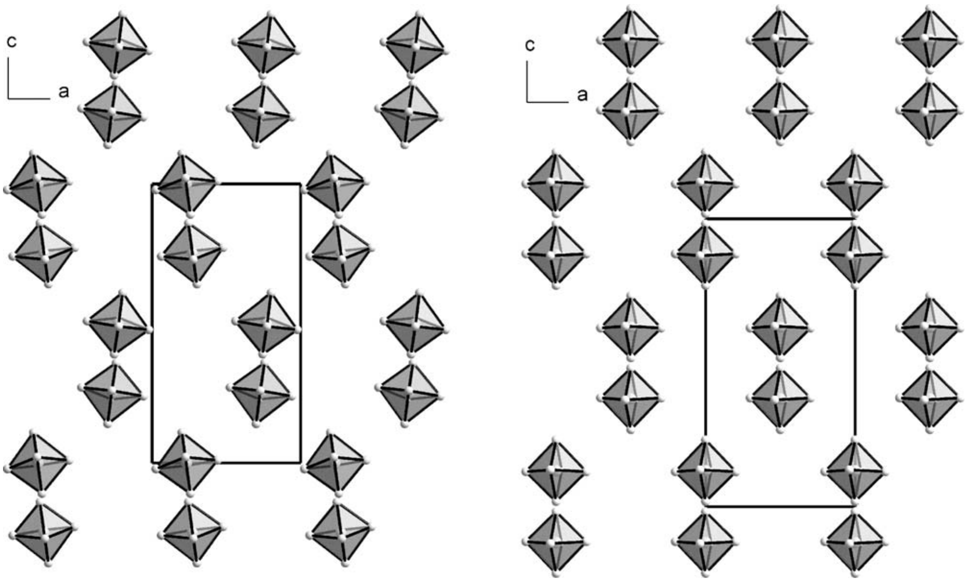

Fig. 4. Packing of the $[LnI_6]^{3-}$ octahedra in $[bmpyr]_4[LaI_6][Tf_2N]$ (left) and $[bmpyr]_4[ErI_6][Tf_2N]$ (right).

erbium analogue. Thus, the borderline for the structural transition from $P4_32_12$ to $I4_1/a$ of $[bmpyr]_4[LnI_6][Tf_2N]$ compounds lies between Pr^{3+} and Nd^{3+}.

The Tf_2N^- anions are incorporated in the crystal structures in a non-coordinating bonding mode. The bis(trifluoromethanesulfonyl)-amide anion, Tf_2N^-, belongs to the class of weakly coordinating anions (WCA). Only recently we were able to isolate the first lanthanide bis(trifluoromethanesulfonyl)-amide complex, $[mppyr]_2[Yb(Tf_2N)_4]$, mppyr = 1-methyl-1-propyl-pyrrolidinium [15]. The adopted trans conformation observed in both crystal structures has been shown by theoretical calculations to be the more stable one for the “free” anion [15]. The Tf_2N^- anions are strongly disordered in both the lanthanum and the erbium compound (Figs. 5 and 6). High conformational flexibility and a strong tendency to packing frustrations of the cation and the anion are believed to be the key to low melting salts and thus, to (room temperature) ionic liquids. Unfortunately, this makes it extremely difficult to obtain crystals of sufficient quality for single-crystal X-ray structure analysis. In our case, many specimens showed extreme disorder of both the cations and the anions belonging to the “solvent” and even at 170(2) K the displacement factors, as reported here, are unusually large.

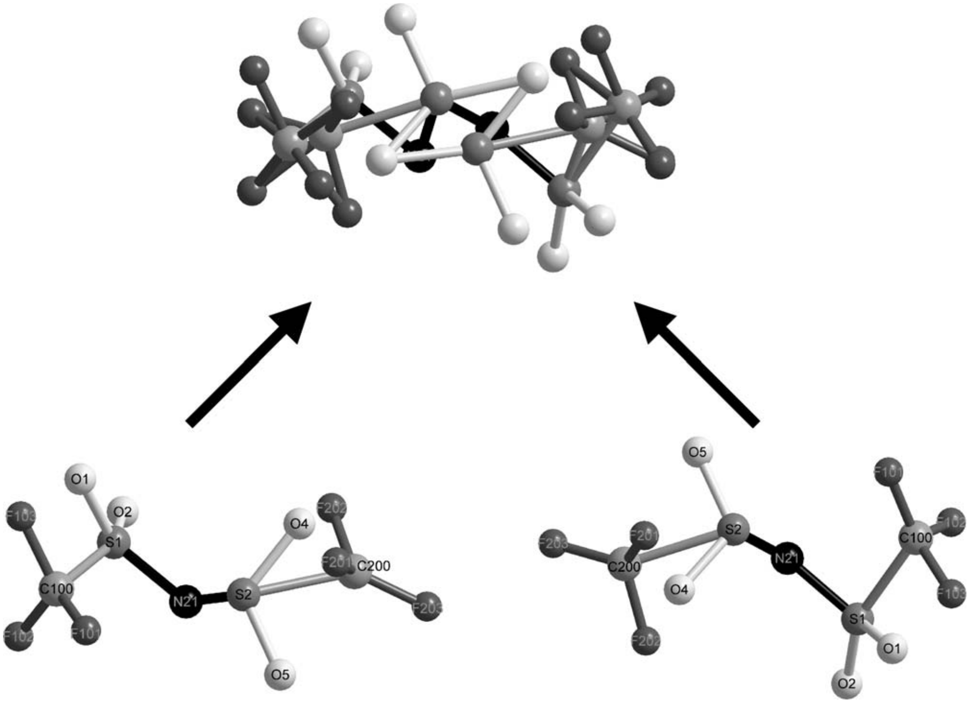

Fig. 5. Disorder of the Tf_2N^- anion in $[bmpyr]_4[LaI_6][Tf_2N]$.

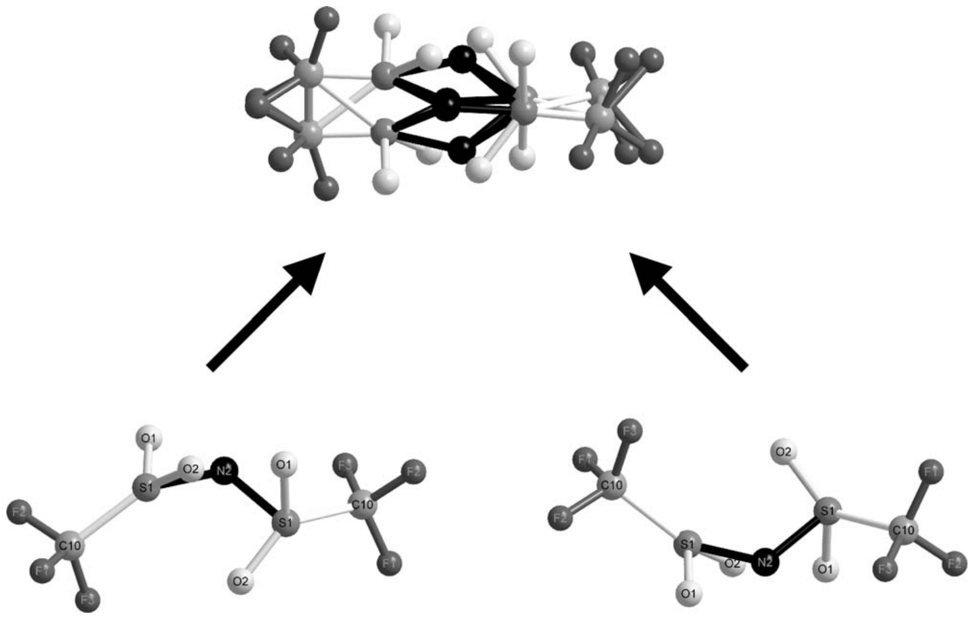

Fig. 6. Disorder of the Tf_2N^- anion in $[bmpyr]_4[ErI_6][Tf_2N]$.

4. Conclusions

Single-crystal X-ray structure analysis of compounds containing cations and anions of ionic liquids is extremely difficult. The properties of these ions used to design ionic liquids, namely the high conformational flexibility and the strong tendency to packing frustrations, lead, predominantly to crystals of poor quality for single-crystal X-ray structure analysis. In the present case, this fact becomes rather obvious through strong disorder of the non-coordinating bis(trifluoromethanesulfonyl)-amide anions in the crystal structures of the compounds $[bmpyr]_4[LnI_6][Tf_2N]$ (Ln = La, Er). However, the determination of these crystal structures was successful and, depending on the size of the lanthanide cation, optimal space filling for the Tf_2N^- anion is provided by the proper orientation of the $[LnI_6]^{3-}$ units involved.

Acknowledgements

The BMBF (Berlin/D) and Fonds der Chemischen Industrie (Frankfurt a.M./D) are acknowledged for a Liebig-fellowship to A.-V. Mudring, the Deutsche Forschungsgemeinschaft (Bonn/D) for grants (SPP 1166 – Lanthanoidspezifische Funktionalitäten) and Prof. Dr. G. Meyer (Universität zu Köln/D) his continuous support. Moreover, we would like to thank Dr. Christian Näther (Universität Kiel/D) for helpful comments.

References

[1] (a) P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. Engl. 39 (2000) 3772–3789;
P. Wasserscheid, W. Keim, Angew. Chem. 112 (2000) 3926–3945;
(b) P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, VCH-Wiley, Weinheim, 2003;
(c) T. Welton, Chem. Rev. 99 (1999) 2071–2083.
[2] M. Earle, A. Forestier, H. Olivier-Bourbigou, P. Wasserscheid, in: P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, VCH-Wiley, Weinheim, 2003.
[3] P. Kafarski, B. Lejczak, Phosphorous, Sulfur, Silicon 63 (1991) 193–215.
[4] (a) I. Billard, S. Mekki, C. Gaillard, P. Hesemann, G. Moutiers, C. Mariet, A. Labet, J.-C.G. Bünzli, Eur. J. Inorg. Chem. 6 (2004) 1190;
(b) S. Arenz, A. Babai, K. Binnemans, K. Driesen, R. Giernoth, A.-V. Mudring, P. Nockemann, Chem. Phys. Lett. 402 (2005) 75–79.
[5] (a) J.D. Corbett, Inorg. Synth. 22 (1983) 31–36;
(b) G. Meyer, in: G. Meyer, L.R. Morss (Eds.), Synthesis of Lanthanide and Actinide Compounds, Kluwer Academic Publishers, Dordrecht, NL, 1991, pp. 135–144.
[6] R. Giernoth, M.S. Krumm, Adv. Synth. Catal. 346 (2004) 989–992.
[7] SHELXS-97, W.S. Sheldrick, Universität Göttingen, 1997.
[8] SHELXL-97, W.S. Sheldrick, Universität Göttingen, 1997.
[9] X-RED, Stoe & Cie, Darmstadt, 2002.
[10] X-Shape, Stoe & Cie, Darmstadt, 2002.
[11] Diamond Version 2.1e, Crystal Impact GbR, 1996–2001.
[12] A. Chaumont, G. Wipff, J. Phys. Chem. B 108 (2004) 3311–3319.
[13] A. Babai, A.-V. Mudring, Chem. Mat. 17 (2005) 6230–6238.
[14] A. Babai, A.-V. Mudring, Angew. Chem. Int. Ed., submitted for publication.
[15] A.-V. Mudring, A. Babai, S. Arenz, R. Giernoth, Angew. Chem. Int. Ed. 44 (2005) 5485–5488.