

Dissolution of Metal Salts in Bis- (trifluoromethylsulfonyl)imide Based Ionic Liquids: Studying the Affinity of Metal Cations Towards a “Weakly Coordinating” Anion

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ABSTRACT. Despite the weakly coordinating ability of the bis-(trifluoromethylsulfonyl)imide anion ($[\text{Tf}_2\text{N}]^-$) the corresponding ionic liquids (ILs) are able to dissolve relevant amounts of metal salts having the same anion, $\text{M}[\text{Tf}_2\text{N}]_x$. To better understanding the metal dissolution process we evaluated the interaction ability of a set of metal cations (Y(III), Al(III) Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Li(I) and Na(I)) towards the $[\text{Tf}_2\text{N}]^-$ anion measuring the relative aptitude to give the corresponding anionic mono-charged complex, $[\text{M}(\text{Tf}_2\text{N})_{x+1}]^-$ using the ESI-MS technique. UV-Vis and NMR measurements were carried out to verify the consistence

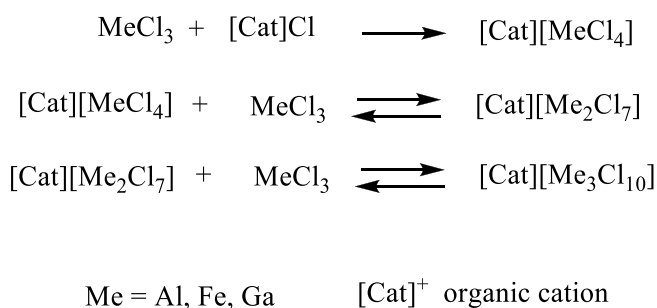
between liquid and gas phase. DFT calculations have been used to identify the metal-containing species and determine their relative stability. An interesting correlation between interaction ability and chemical properties (Lewis acidity) was found.

Keywords: ionic liquids, metal ions, coordinating anion

Introduction

Ionic liquids (ILs) are compounds composed exclusively by ions (usually a bulk organic cation and an inorganic or organic anion) liquid at/or near room temperature, which have received in the last ten years increasing interest due to their attractive and peculiar properties: they have been proposed as alternative media or additive in various areas, such as organic synthesis,^{1,2} catalysis,³ electrochemical devices,⁴ extraction processes.⁵ ILs are frequently labeled as “tailored”, “tunable”, “task-specific” or “designer” solvents due to the possibility to modify all the physico-chemical properties in function of each specific application, varying cation and/or anion structure or adding suitable compounds.^{1,6} Tailored-ILs are able to dissolve organic, inorganic and polymeric compounds offering an unique environment for their transformation. A simple approach to modify drastically the main properties of an IL, contemporaneously inducing new abilities, is represented by the addition of metal salts. The process, which is completely different from the dissolution of inorganic salts in water or other solvents, (“solute” and “solvent” are indeed in this case meaningless terms), generally produces complex mixtures of ions.⁷ The presence of specific functional groups (OH, CN, COOH) on IL cation or the use of ILs having coordinating anions generally favors the metal salt dissolution contemporaneously determining the chemical structure of the resulting liquid. The addition of a proper amount of a metal halide to a chloride or bromide based IL is indeed a simple and efficient way to obtain halometallates

ILs able to act as solvents and Lewis acids.⁸ The reaction mixture may contain, depending on reagents concentration and temperature, beside a well-defined cation, halide and one or more halometallates in a dynamic equilibrium with each other. These equilibria represent the main peculiarity of these ILs and it must be stressed that anion speciation (and consequently the IL catalytic activity⁹) can be significantly different depending on metal features (Scheme 1).¹⁰



Scheme 1. Metal (III) chloride speciation in chloride based ILs, [Cat]Cl.

Chlorometallated ILs based on aluminium have been extensively investigated since the early 1980s.¹¹ Subsequently, other metal halides (indium(III), gallium(III) and iron(III), iron(II), copper(II), tin(II) and zinc(II)) have been used to prepare ILs, and their anionic speciation has been studied.¹²⁻¹⁶ A reactive dissolution of metal salts can however occur also in ILs constituted by less coordinating anions, such as bis-(trifluoromethylsulfonyl)imide, [Tf₂N]⁻. X-ray crystallographic data indicate indeed that in the solid state this anion is able to coordinate metal centers¹⁷ and spectroscopic measurements show that this ability characterizes also the liquid state, even if a change in the coordination number cannot be excluded *a priori* on going from a situation to the other one.¹⁸ Recently, we have shown that concentrated solutions of metal salts in [Tf₂N]⁻ based ILs can be obtained simply dissolving in these media the inorganic salts having the same anion, M[Tf₂N]_x.¹⁹ Angle resolved XPS (AR-XPS) measurements, carried out on several

metal ions in 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide, [bmim][Tf₂N], showed significant variations in the coordination sphere depending on the metal nature.¹⁹ Since the coordination sphere can affect the properties of a metal center, acting as a catalyst or undergoing reduction, we decided to investigate the relative binding ability of several metal cations towards [Tf₂N]⁻ through competition experiments, using electrospray ionization mass spectrometry (ESI-MS). Although mass spectrometry has been widely used as a tool for ILs characterization, it has been recently stressed that it is not suitable for speciation studies, having led in the case of some chlorometallated systems to confusion and erroneous conclusions.²⁰ Therefore, we decided to use exclusively the information arising from competition experiments,²¹ carried out by introducing contemporaneously two metal-containing mixtures in the gas phase, with the intent to develop a relative binding affinity scale of metal cations towards the low coordinating [Tf₂N]⁻ anion. The competition experiments were performed on eluting solutions of M(Tf₂N)_x couples, dissolved in the same IL, in different relative compositions in order to safeguard from deviating ESI response factors. Subsequently, anion speciation data arising from these experiments have been analyzed and compared with information related to liquid phase, obtained from UV-vis and NMR experiments. All the findings were supported by DFT calculations, which aimed to identify plausible metal-containing species and determine their relative stabilities. Particularly intriguing is the presently found correlation between the qualitative order of metal affinity to [Tf₂N]⁻ and the catalytic ability of the related solutions when used as media in Lewis acid catalyzed processes.

Results and Discussion

ESI-MS Experiments

The relative affinity of selected cations for bis-(trifluoromethylsulfonyl)imide $[\text{Tf}_2\text{N}]^-$ anion has been obtained from $[\text{bmim}][\text{Tf}_2\text{N}] + \text{M}(\text{Tf}_2\text{N})_x$ and $[\text{bm}_2\text{im}][\text{Tf}_2\text{N}] + \text{M}(\text{Tf}_2\text{N})_x$ mixtures ($\chi_{\text{M}(\text{Tf}_2\text{N})_x} = 0.1$) with $x=1-3$ depending on the metal, *i.e.* $x=1$ for $\text{Ag}(\text{Tf}_2\text{N})$, $\text{Li}(\text{Tf}_2\text{N})$, $\text{Na}(\text{Tf}_2\text{N})$; $x=2$ for $\text{Co}(\text{Tf}_2\text{N})_2$, $\text{Zn}(\text{Tf}_2\text{N})_2$, $\text{Ni}(\text{Tf}_2\text{N})_2$, $\text{Cu}(\text{Tf}_2\text{N})_2$ and $x=3$ for $\text{Al}(\text{Tf}_2\text{N})_3$, $\text{Y}(\text{Tf}_2\text{N})_3$. In a preliminary screening on bmim-based ionic liquids, the mixtures were dissolved in CH_3OH in concentrations of *ca.* 5×10^{-4} M and analyzed both in positive and negative ion modes. For all tested compositions, the most intense peaks in the (+)-ESI spectra correspond to the molecular peak of the heterocyclic cation, $[\text{bmim}]^+$ at m/z 139, and to clusters with bis-(trifluoromethylsulfonyl)imide, $[(\text{bmim})_2\text{Tf}_2\text{N}]^+$ m/z 558. In negative-ion mode, all the spectra show the presence of the free bis-(trifluoromethylsulfonyl)imide $[\text{Tf}_2\text{N}]^-$ at m/z 280, of its dimeric form in coordination with $[\text{bmim}]^+$, *i.e.* $[\text{bmim}(\text{Tf}_2\text{N})_2]^-$ at m/z 699 and of $[\text{Tf}_2\text{N}]^-$ in coordination with the metal $[\text{M}(\text{Tf}_2\text{N})_{n+1}]^-$. The composition of the latter ionic species depends on the oxidation state of M, as shown in Figure 1 for Ag(I) and Zn(II) mixtures. Except for Ag(I) and Al(III), the $[\text{M}(\text{Tf}_2\text{N})_{n+1}]^-$ ionic species is always the most abundant peak of the spectrum. No signals corresponding to oxidation or reduction of the metal centers are observed.

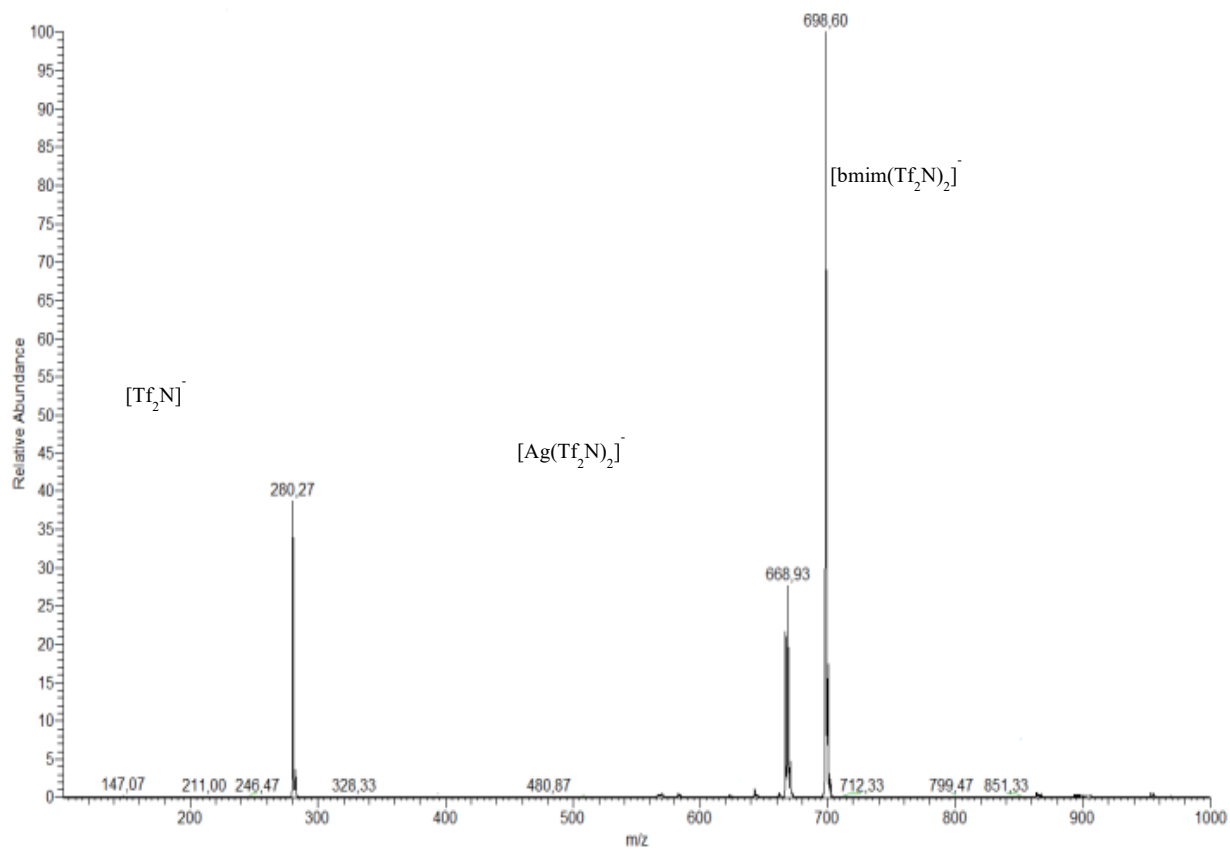
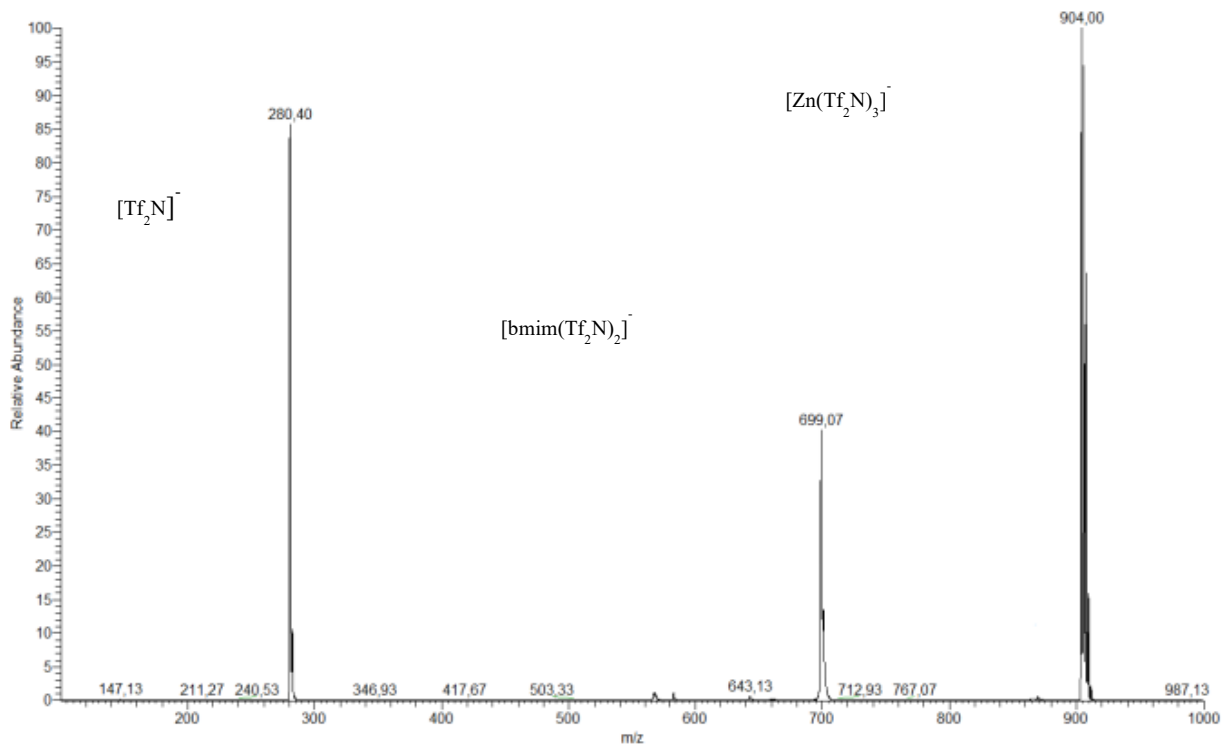


Figure 1. Full scan ESI mass spectra of [bmim][Tf₂N]+Ag(Tf₂N) and [bmim][Tf₂N]+Zn(Tf₂N)₂ acquired in negative-ion mode

In a second set of experiments the relative affinity of the different cations with respect to [Tf₂N]⁻ has been evaluated. Proper mixtures of solutions of different metal cations (M(Tf₂N)_x) in the same [Tf₂N]⁻ based ionic liquid were used for the competition experiments. As an example, [bmim][Tf₂N] + Co(Tf₂N)₂ and [bmim][Tf₂N] + Cu(Tf₂N)₂ were dissolved in a relative ratio 1:1 in CH₃OH and the resulting solution analyzed by (-)-ESI-MS in order to measure the relative abundance of [Co(Tf₂N)₃]⁻ (m/z 899) with respect to [⁶³Cu(Tf₂N)₃]⁻ (m/z 903) ions. As depicted in Figure 2, the cobalt derivative possesses higher affinity than copper for [Tf₂N]⁻, as showed by the much higher intensity of the related peak.

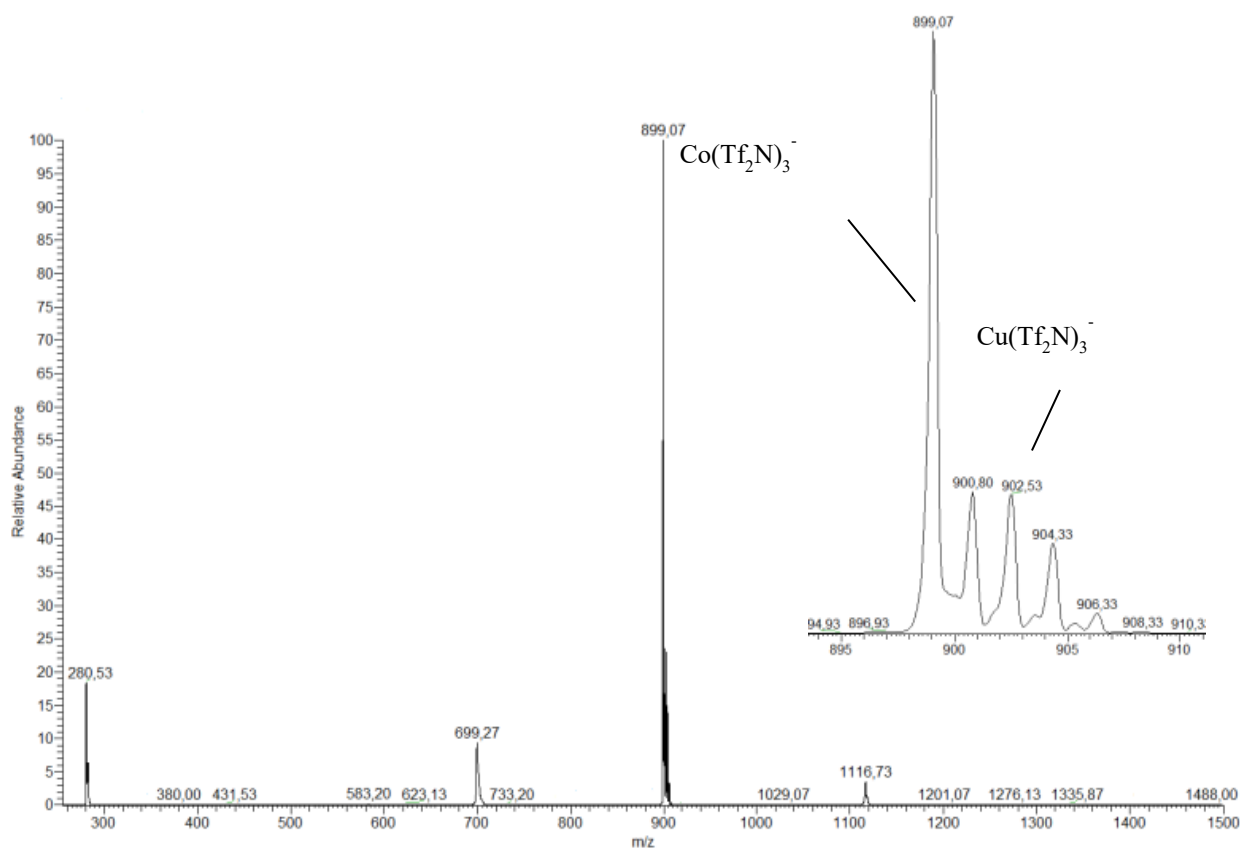


Figure 2. Competitive experiments between 1:1 mixtures of [bmim][Tf₂N] + Co(Tf₂N)₂ (m/z 899) and [bmim][Tf₂N] + Cu(Tf₂N)₂ (m/z 903) in CH₃OH; m/z values refer to the most abundant isotope

Each [bmim][Tf₂N] + M(Tf₂N)_x sample has been crossed with the almost entire set of the metal containing mixtures. For example, [bmim][Tf₂N] + Co(Tf₂N)₂ has been subsequently analyzed in the presence of [bmim][Tf₂N] + Y(Tf₂N)₃, [bmim][Tf₂N] + Zn(Tf₂N)₂, [bmim][Tf₂N] + Ni(Tf₂N)₂ and [bmim][Tf₂N] + Ag(Tf₂N), respectively. Furthermore, since recent studies claim that the relative heights of the MS peaks are dependent on the nature of the solvent used,²² we have repeated most of the competition experiments also in CH₃CN and CH₂Cl₂. Our tests confirm that the solvent plays an important role in determining the relative heights of the peaks due to specific solvation strengths. As an example, in the competition between Co vs. Zn, the relative abundance of Co[(Tf₂N)₃]⁻ in the full scan mass spectrum is 100% in CH₃OH as eluting solvent, 60% in CH₂Cl₂ and 15% in CH₃CN. However, the concurrent presence of the two metal species experimenting the same conditions safeguards from these effects and the relative intensities of Co[(Tf₂N)₃]⁻ and Zn[(Tf₂N)₃]⁻ remain practically unchanged in the three solvents, as shown in Figure 3.

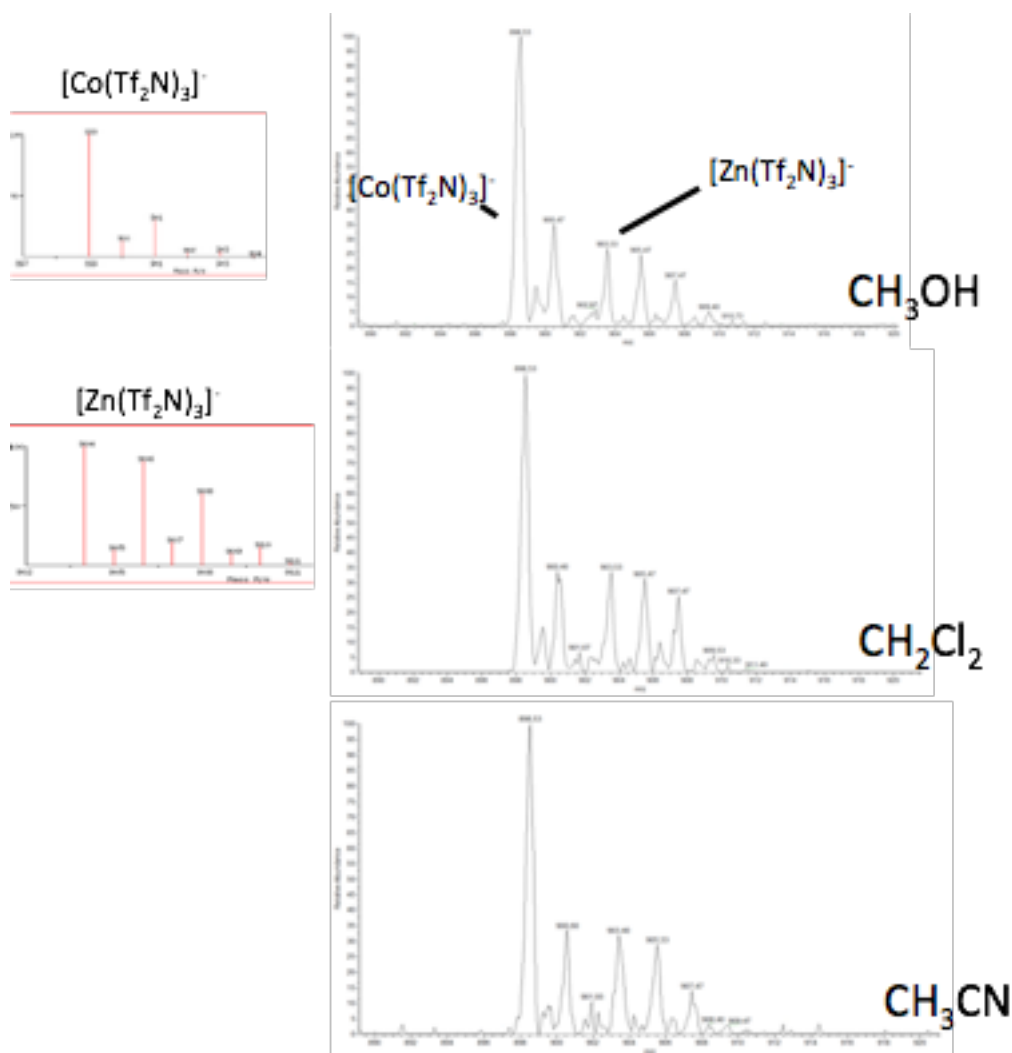
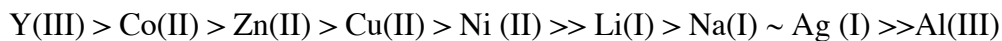


Figure 3. Competitive experiments between 1:1 mixtures of [bmim][Tf₂N] + Co(Tf₂N)₂ (m/z 899) and [bmim][Tf₂N] + Zn(Tf₂N)₂ (m/z 904) in different eluting solvents; m/z values refer to the most abundant isotope; inserts are the theoretical isotope patterns for the two clusters.

Finally, since differences in ESI signal intensities do not necessarily reflect the actual differences of concentration (deviating ESI response factors of the different species can affect this parameter) we have refined the comparison performing the same measurements for relative

ratios of 1:5 and 5:1, with respect to the metals under investigation.²³ Hence, the resulting relative affinity sequence of the different cations for $[\text{Tf}_2\text{N}]^-$, from high to low, is:



Practically, no peak attributable to Al(III) complexes of the type $[\text{M}(\text{Tf}_2\text{N})_{x+1}]^-$ has been observed. Further validation of this sequence is provided by similar measurements carried out on the same metal salts $\text{M}(\text{Tf}_2\text{N})_x$ dissolved in a slightly different ionic liquid $[\text{bm}_2\text{im}][\text{Tf}_2\text{N}]$ *i.e.* 1,2-dimethyl-3-butylimidazolium bis-(trifluoromethylsulfonyl)imide.

UV-vis and NMR Measurements

With the exception of Al(III), the ESI-MS experiments suggested that the dissolution of metal salts, $\text{M}(\text{Tf}_2\text{N})_x$, in $[\text{Tf}_2\text{N}]^-$ -based ILs leads to negatively mono-charged metal ion carrying species, $[\text{M}(\text{Tf}_2\text{N})_{x+1}]^-$. To confirm the presence of these species also in the liquid phase, the UV-vis spectra of $\text{Co}(\text{Tf}_2\text{N})_2$ and $\text{Ni}(\text{Tf}_2\text{N})_2$ in $[\text{bmim}][\text{Tf}_2\text{N}]$ were registered at room temperature (Figure 4). Both samples showed intense absorption bands in the visible region which can be attributed, by comparison with the corresponding spectra in water solution, to six-coordinated clusters of the metal ions accommodated in an octahedral ligand field with three $[\text{Tf}_2\text{N}]^-$ anions: *i.e.* $[\text{Co}(\text{Tf}_2\text{N})_3]^-$ and $[\text{Ni}(\text{Tf}_2\text{N})_3]^-$, respectively. The registered spectra were identical to those recently reported for same salts in a phosphonium based IL, $([\text{P}_{2225}][\text{Tf}_2\text{N}])$.²⁴

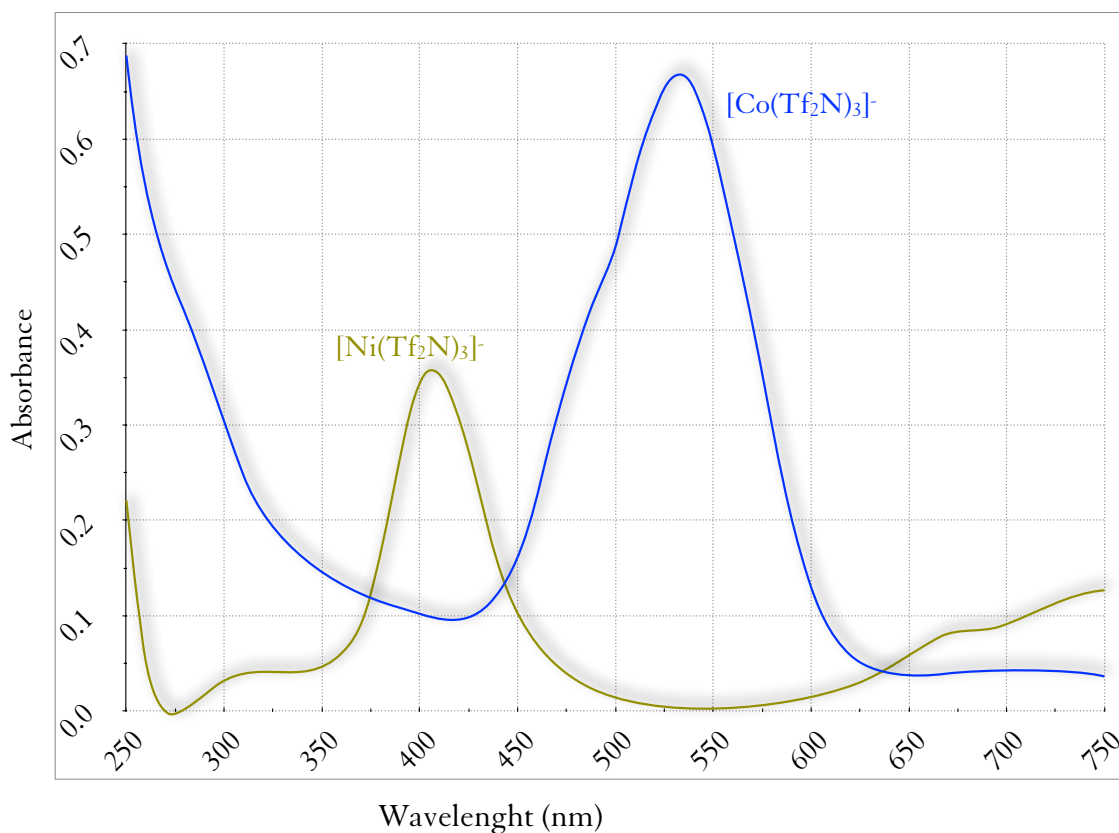


Figure 4. UV-vis spectra of Ni(Tf₂N)₂ and Co(Tf₂N)₂ in [bmim][Tf₂N].

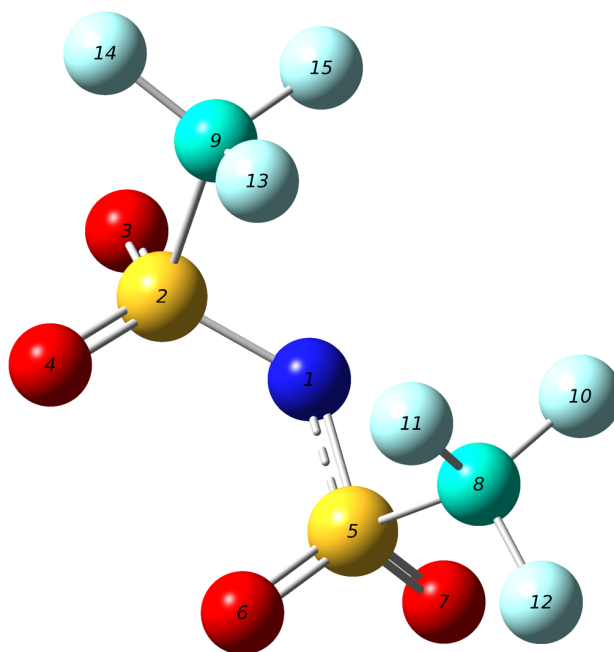
On the other hand, the dominance of species containing two [Tf₂N]⁻ anions in the first solvation sphere of the lithium ion in [Tf₂N]-based ILs has been recently established²⁵ on the basis of IR and Raman spectra, although other techniques (in particular, ion conductivity measurements and diffusion NMR spectroscopy support also the presence of higher-order complexes.²⁶ These latter species can be however due to the presence of “bystander” ions, *i.e.* “free” anions and “free” cations of the IL matrix, which can contribute to the total ion conductivity.

Finally, to verify if the peculiar behavior of Al(III) emerging from ESI-MS experiments represents also the situation in the liquid phase, we decided to employ the ^{27}Al NMR spectroscopy. Chemical shift can indeed be used to obtain information about the environmental chemistry of aluminium. The ^{27}Al spectrum of $\text{Al}(\text{Tf}_2\text{N})_3$ in $[\text{bmim}][\text{Tf}_2\text{N}]$ is characterized by the exclusive presence of an intense broad signal (due to an efficient nuclear quadrupolar relaxation) at *ca.* -18 ppm, attributable to aluminium-containing species with octahedral symmetry: *i.e.* the *transoid* and *cisoid* isomers of the neutral salt $\text{Al}(\text{Tf}_2\text{N})_3$.²⁷ Therefore, ^{27}Al NMR spectrum confirms the absence of clusters in solution.

DFT Calculations

The affinity of $[\text{Tf}_2\text{N}]^-$ for the above reported metal cations was also investigated through DFT calculations. We considered exclusively the metal- $[\text{Tf}_2\text{N}]^-$ complexes of the type $[\text{M}(\text{Tf}_2\text{N})_{x+1}]^-$, being these the sole species revealed by ESI-MS and UV-vis spectroscopy for all the investigated metals (with the exception of Al(III)). The starting structures of these complexes have been sketched with a molecular geometry editor. Although the $[\text{Tf}_2\text{N}]^-$ anion should have two possible coordination modes, *i.e.* through the central nitrogen atom (that carries the formal negative charge) or through the two oxygen atoms each belonging to one of the two SO_2 groups, preliminary calculations have shown that the first mode does not lead to stable structures. This topic has been also extensively discussed¹⁸ by Mudring *et. al.* showing that the approach of the nitrogen atom is sterically hindered and disfavored by the shape of the molecular electrostatic potential. Consequently, in this investigation $[\text{Tf}_2\text{N}]^-$ has to be considered as a bidentate ligand, focalizing initially our attention on the free rotation around the two N-S bonds. This conformational mobility is indeed able to modify the distance between the oxygen atoms and the

relative position in the space of the two CF_3 groups thus allowing this anion to chelate metal cations of different sizes (Figure 5).



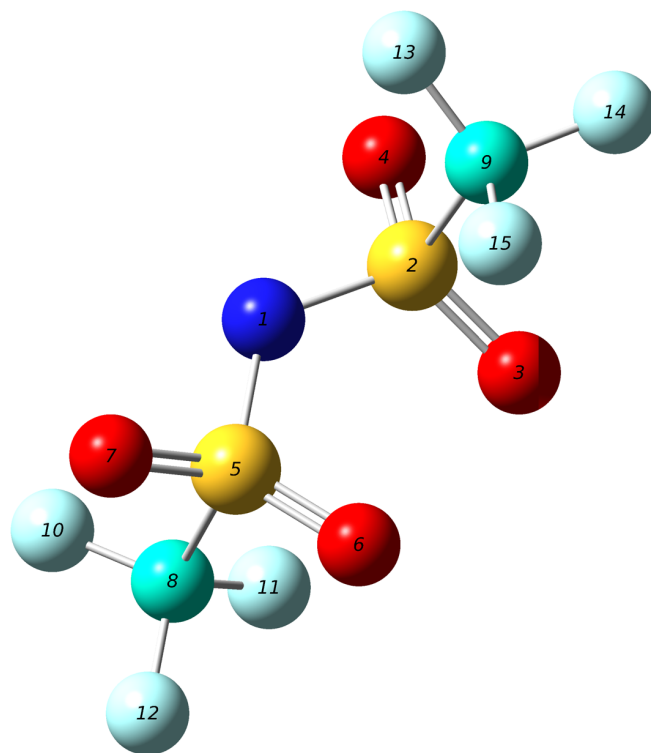


Figure 5. The conformational dihedral angle is defined by the atoms O(4)-S(2)-S(5)-O(7). Top: $[\text{Tf}_2\text{N}]^-$ anion in *cisoid* conformation (135°). Bottom: $[\text{Tf}_2\text{N}]^-$ anion in *transoid* conformation (305.1°).

It is noteworthy that, due to the symmetry of the $[\text{Tf}_2\text{N}]^-$ anion, the rotations around the two N-S bonds are equivalent and rotations of the same entity (and sign) around these two bonds lead to a rotation of the whole molecule. Therefore, in the conformational analysis we have used the torsion angle $\text{O}=\text{S}\cdots\text{S}=\text{O}$ as variable, the oxygen atoms here considered being the two not involved in the coordination process. If we imagine to handle the $[\text{Tf}_2\text{N}]^-$ anion as a mechanical tool, employing as levers the two S=O groups, it is possible to modify the distance between the other two oxygen atoms facing and interacting with the metal center. Figure 5 reports a graphical

representation of the two conformers and of the selected torsion angle, whereas the potential energy scan from 0° to 360° (each step corresponding to 15°) is reported in Figure 6.

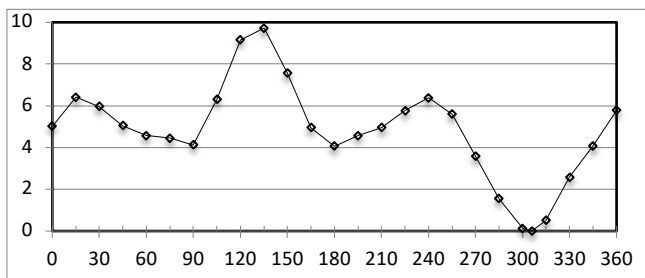


Figure 6. Conformational energy of $[\text{Tf}_2\text{N}]^-$ in kJ/mol versus the value of the $\text{O}=\text{S}\cdots\text{S}=\text{O}$ torsion angle. All other geometrical parameters has been optimized. The conformation with a 305.1° angle (absolute minimum) is taken as zero. The torsion angle is defined in the text and in Figure 5.

The lowest energy conformation, at 305.1° , corresponds to a *transoid* arrangement of the two CF_3 groups. The potential well around this conformation extends roughly from 240° to 360° . A peak of energy is localized between 90° and 180° . This region corresponds to a *cisoid* arrangement of the sterically hindering CF_3 groups. The energy variation associated with the conformational changes is however small, thus allowing to the $[\text{Tf}_2\text{N}]^-$ anion to adopt the proper coordination geometry required by the metal ion under consideration. Most of the investigated $[\text{M}(\text{Tf}_2\text{N})_{x+1}]^-$ complexes are characterized by a torsion angle that lies in the *transoid* region. In Figure 7 is reported the variation of the O-O distance in function of the torsional angle in the

180°-360° range. This distance changes from a minimum of 2.98 Å to a maximum of 4.14 Å, allowing to the $[\text{Tf}_2\text{N}]^-$ anion to adapt to all the coordination geometries proposed in this paper.

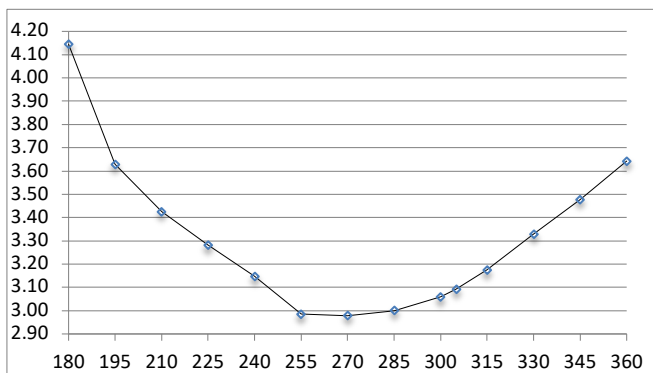


Figure 7. Distance between the two coordinating oxygen atoms in function of the $\text{O}=\text{S}\cdots\text{S}=\text{O}$ torsion angle. Angles in degrees, distance in Å. These quantities are defined in the text and in Figure 5.

Some energetic and geometric quantities related to the optimized complexes are reported in Table 1, whereas the molecular structures are reported in Figure 8. The x value corresponds to the fraction of the total coordination bonds present in the complex that must be broken to remove a single $[\text{Tf}_2\text{N}]^-$ ligand. It is equivalent to the inverse of the number of ligands with the exception of $[\text{Al}(\text{Tf}_2\text{N})_4]^-$. The peculiarities of this complex with respect to the other ones investigated in this paper will be discussed in detail below.

The reduced energy $x\Delta(E_0+\text{ZPE})$ is an evaluation of the dissociation energy of the complex (assuming that all the coordination bonds have the same strength) and therefore it is a useful quantity to compare the complexes stabilities.

The first group of complexes considered in this work has $[M(\text{Tf}_2\text{N})_2]^-$ structure, $M = \text{Li(I)}$, Na(I) , Ag(I) . These complexes are characterized by the smallest values of the $\text{O}=\text{S}\cdots\text{S}=\text{O}$ torsion angles; they are practically equidistant from the limit *cisoid* and *transoid* structures. The structure of $[\text{Li}(\text{Tf}_2\text{N})_2]^-$ is reported in Figure 8a. *Ab-initio* calculations at the MP2 level of theory using the same basis set employed in this paper, associated to Raman spectroscopy measurements, have been recently reported by Umebayashi *et al.* for $\text{Li}(\text{Tf}_2\text{N})$ in $[\text{bmim}][\text{Tf}_2\text{N}]$.²⁸

Table 1. Energetic and geometric quantities of the optimized complexes.				
Energies in KJ/mol. Angles in degrees.				
Complex	$\Delta(E_0+\text{ZPE})$	x	$x\Delta(E_0+\text{ZPE})$	$\text{O}=\text{S}\cdots\text{S}=\text{O}$
$[\text{Li}(\text{Tf}_2\text{N})_2]^-$	-194.92	1/2	-97.46	210
$[\text{Na}(\text{Tf}_2\text{N})_2]^-$	-168.75		-84.37	205
$[\text{Ag}(\text{Tf}_2\text{N})_2]^-$	-172.06		-86.03	200
$[\text{Co}(\text{Tf}_2\text{N})_3]^-$	-594.14	1/3	-198.05	255
$[\text{Ni}(\text{Tf}_2\text{N})_3]^-$	-602.75		-200.92	255
$[\text{Cu}(\text{Tf}_2\text{N})_3]^-$	-602.83		-200.94	260
$[\text{Zn}(\text{Tf}_2\text{N})_3]^-$	-571.46		-190.49	245
$[\text{Al}(\text{Tf}_2\text{N})_3]$	-1224.56	1/3	-408.19	265
$[\text{Y}(\text{Tf}_2\text{N})_4]^-$	-1001.92	1/4	-250.48	270
$[\text{Al}(\text{Tf}_2\text{N})_4]^-$	-1205.92	1/6	-200.99	300

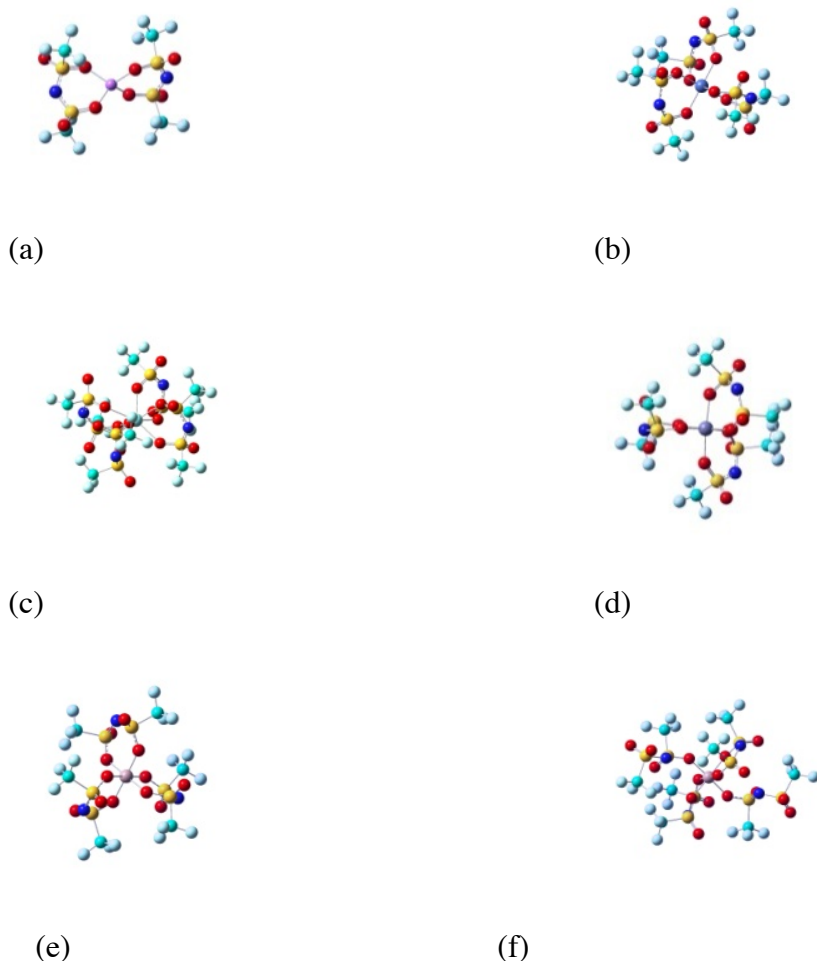


Figure 8. Geometrical structures of some $[M(\text{Tf}_2\text{N})_{x+1}]^-$ complexes and neutral Al(III) salt: (a) $[\text{Li}(\text{Tf}_2\text{N})_2]^-$; (b) $[\text{Ni}(\text{Tf}_2\text{N})_3]^-$; (c) $[\text{Y}(\text{Tf}_2\text{N})_4]^-$; (d) $[\text{Zn}(\text{Tf}_2\text{N})_3]^-$; (e) $[\text{Al}(\text{Tf}_2\text{N})_3]^-$; (f) $[\text{Al}(\text{Tf}_2\text{N})_4]^-$.

In the above cited paper both the *cisoid* and *transoid* $[\text{Li}(\text{Tf}_2\text{N})_2]^-$ complexes (with $[\text{emim}]^+$ as model cation in the second solvation sphere) have been considered: the *cisoid* structure appeared more stable than the *transoid* one by about 4 kJ/mol. The higher stability of the *cisoid* structure was attributed to a better interaction of two not coordinating oxygen atoms (one for each ligand) with the $[\text{emim}]^+$ cation. However, if the stability of the *cisoid* complex is determined by the interaction metal ligand-IL cation, it is possible to hypothesize that in the presence of more

hindered cations, or simply when a larger model system (including more cations around the complex) is considered for calculations, the order of stability of the *cisoid* and *transoid* forms may be inverted. The structure of $[M(\text{Tf}_2\text{N})_2]^-$ complex, found in our investigation not considering the counteranion, is exactly in the middle between the *cisoid* and *transoid* limit structures.

Very interestingly, the qualitative order of “stability” arising from ESI-MS measurements ($\text{Li(I)} > \text{Na(I)} \sim \text{Ag(I)}$) found a complete correspondence in our calculations. The second group of examined complexes is that having $[M(\text{Tf}_2\text{N})_3]^-$ structure, $M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II) . These four metal cations are homogeneous from the point of view of charge and coordination structure, octahedral, which is moreover consistent with their coordination chemistry in water. With the exception of d^{10} Zn(II) , all these ions are paramagnetic. Furthermore, whereas the d^9 Cu(II) cation is likely in the singlet state, the d^7 Co(II) and d^8 Ni(II) cations should be in their high spin state, considering $[\text{Tf}_2\text{N}]^-$ a weak ligand, probably weaker than acetylacetonate anion (acac). Calculations have been however performed also for the corresponding low spin complexes; these complexes resulted significantly less stable than the high spin ones.

In these complexes, the O-O distances are close to the minimum and the ligands are disposed in the *transoid* conformation that allows a reduction of the steric hindering in the external part of the complex, where each of the large CF_3 groups stands in front to an equal group on the another ligand. An accurate examination of the $[\text{Ni}(\text{Tf}_2\text{N})_3]^-$ structure, reported in Figure 8b, evidences two kinds of geometrical patterns: inside, the coordination center shows an octahedral structure; outside, the ligands, which are in a *Z* shaped *transoid* conformation, are stacked to form a band-

like structure. Double patterns characterize also the structure of the $[Y(Tf_2N)_4]^-$ complex (Figure 8c): in this case the external band is aligned with the square antiprismatic structure.

The $[Y(Tf_2N)_4]^-$ complex is more stable, according to ESI-MS measurements, than the octahedral $[M(Tf_2N)_3]^-$ species, with $M = Co(II), Ni(II), Cu(II)$ and $Zn(II)$, and these latter are more stable than the tetrahedral $[M(Tf_2N)_2]^-$ complexes. The stability order of the octahedral $[M(Tf_2N)_3]^-$ complexes, arising from ESI-MS measurements, however does not exactly match that obtained from calculations (the differences among the calculated energies are however small), suggesting that the formation of these complexes is probably affected by the electrostatic parameter. Finally, a peculiar behavior characterizes $Al(III)$. For this cation, we have performed calculations on two species of different stoichiometries: the charged complex $[Al(Tf_2N)_4]^-$ and the neutral salt $[Al(Tf_2N)_3]$. For steric reasons it is impossible to arrange four chelating $[Tf_2N]^-$ anions around this metal cation. Furthermore, a coordination number of eight has never been reported for $Al(III)$. The sole possibility therefore to insert four $[Tf_2N]^-$ ligands around the $Al(III)$ cation is to consider an hypothetical structure in which two chelating $[Tf_2N]^-$ anions are on the same plane and the other two give each a single bond at the opposite vertices of the octahedron (8f). This is a very unusual and sterical hindered structure, although the calculated dissociation energy of this complex is not very different from those found for the other octahedral $[M(Tf_2N)_3]^-$ complexes. However, since there are not evidences of the formation of this species both in the ESI-MS and ^{27}Al NMR spectra we retain that its formation is probably kinetically disfavored. An hypothetical square pyramidal $[Al(Tf_2N)_3]$ salt, with one of the $[Tf_2N]^-$ ligand singly coordinated, probably rearranges more easily to a fully chelated structure (*i.e.* that of neutral $[Al(Tf_2N)_3]$) rather than to coordinate a further ligand. The $[Al(Tf_2N)_3]$ salt (see Figure 8e) shows indeed a D_3 symmetry (the symmetry has not been tracked in our calculations) with

three equivalent *transoid* [Tf₂N]⁻ ligands. In Table 2, we report a comparison between the calculated Raman absorption frequencies and the experimental value reported²⁸ by Umebayashi *et al.*. The assignment of the normal modes to the frequencies has been performed visually using a molecular graphics package. The substantial agreement between the two series of values, in particular if we consider the different environment (*in vacuo* and condensed phase), supports the validity of DFT calculations to identify plausible metal containing species.

Related to the *transoid* conformation adopted by the [Tf₂N]⁻ anion in [Al(Tf₂N)₃] and in most of the other examined metal complexes, some comments are probably necessary. A completely *transoid* structure, analogous to that reported in this paper, has been proposed also by Krossing *et al.* for [Al(Tf₂N)₃],³⁰ on the basis of DFT calculations (BP86/TZVP) and by Rocheret *et al.*,²⁷ on the basis of NMR, Raman and DFT results. Actually, the crystal structure of [Al(Tf₂N)₃], reported by Krossing *et al.* in 2009³⁰, evidences the presence of two molecular sites constituting the unit cell. The first one is characterized by a 9:1 prevalence of a completely *transoid* structure over a structure where the two ligands are both *transoid* and *cisoid*. The second one presents one ligand in a disordered state and the other two almost divided between *transoid* and *cisoid* structure. Four chelating [Tf₂N]⁻, all adopting a *transoid* conformation with respect the CF₃-groups, typify also the Y(III) complex, [bmim][Y(Tf₂N)₄], at the solid state.³¹ On the other hand, a *cisoid* conformation characterizes the crystal structure of double charged Yb(III)-Tf₂N complex, (1-methyl-1-propylpyrrolidinium)₂[Yb(Tf₂N)₄].¹⁸ In this case, however, this conformation is the sole able to guarantee two pairs of outward pointing oxygen atoms, in an ideal position to interact with the pyrrolidinium cations. Since in the crystalline structure anions and cations have a well-defined collocation in the space, this structural peculiarity might represent an energetic feature favoring the *cisoid* conformation. At variance, in the less ordered

liquid phase the interaction between cation and anion might become less important and the internal steric hindering of the *cisoid* structure can be at the origin of the preferential *transoid* conformation. The balance between electrostatic and sterical factors can therefore modify the order of stability of these two kinds of structures. The neutral $[\text{Al}(\text{Tf}_2\text{N})_3]$, in which the electrostatic repulsion and the M-O distance (1.90\AA) reaches the minimum value, presents all the ligands in a *transoid*-like conformation according to both calculation and crystal structures.^{28,30}

Table 2. Raman frequencies of $\text{Al}(\text{Tf}_2\text{N})_3$.

motion	exp. ^a	calc. ^b
$\delta(\text{SO}_2)_1$	259.8	248.5
$\delta(\text{SO}_2)_2$	308.0	293.4
$\delta(\text{SNS})$	452.7	454.9
$\nu(\text{AlO})$	660.0	651.7
$\nu(\text{SNS})$	761.0	742.2
$\nu(\text{SO}_2)$	1131.5	1100.9

^aFrom ref. 28. ^bScaled by a factor of 0.9682

according to 29. Frequencies in cm^{-1}

It is noteworthy that despite to the recently expressed doubts about the possibility to obtain information on anionic speciation in solution in the case of chlorometallated ILs through ESI-MS techniques, UV-vis measurements and DFT calculations confirm that monocharged complexes, $[\text{M}(\text{Tf}_2\text{N})_{x+1}]^-$, are for most of the investigated metal salts the sole species detectable also in the liquid phase. On the other hand, the inability to identify in the ESI-MS spectra of $\text{Al}(\text{Tf}_2\text{N})_3$ in

[bmim][Tf₂N] an anionic species containing the metal is in agreement with the ²⁷Al NMR data, showing the presence of the octahedral neutral salt [Al(Tf₂N)₃], and with the recent AR-XPS measurements¹⁹ indicating a weak coordination sphere around the metal cation that allows to this latter to reach the physical surface of the liquid.

Surely, the fact that [Tf₂N]⁻ is a weakly coordinating anion, which prefers to act as a bidentate ligand, significantly reduces the number of possible negatively charged species arising from the solvation process compared to the spherical and small chloride anion. Consequently, also the possibility of variation in speciation on going from crystal to liquid and gas phase is diminished even if the flexibility of the [Tf₂N]⁻ anion and its steric requirements can generate, for each complex having a well-defined stoichiometry, more isomers in dynamic equilibrium: the question of the preference between *cisoid* and *transoid* conformation of the ligand and its dependence on the physical state (solid or liquid) is still open.

The most relevant and surprising result arising from the present investigation is however the concordance between the relative affinity sequence of the different metal cations for [Tf₂N]⁻ (*i.e.* Y(III) > Co(II) > Zn(II) > Cu(II) > Ni(II) >> Al(III)) and the catalytic ability of the related solutions in [Tf₂N]-based ILs when used as media in some Lewis acid catalyzed processes. Indeed, on the basis of a recent patent,³² cobalt displays a superior catalytic activity than zinc in the reaction of benzoic acid with *m*-xylene. Furthermore, better results were obtained in the Friedel-Crafts acylation of toluene with benzoyl chloride in [emim][Tf₂N], when employing Co(II) compared to Ni(II), and Zn(II) with respect to Cu(II) metal catalysts.³² On the other hand, the modest activity of aluminium bis-triflimide suggested a “*chemistry different from conventional*” in these media.³²

Indubitably, these data suggest that *in situ* formed negatively charged species ($[M(Tf_2N)_{x+1}]^-$) do not prevent the catalytic role of the metal. Furthermore, it is well known that their formation positively affects also the electrochemical behavior of the related solutions. In the case of Al(III), the peculiar stability of the neutral salt having an octahedral structure with three chelate $[Tf_2N]^-$ anions, avoiding the formation of the corresponding $[Al(Tf_2N)_4]^-$ complex, not only reduces the Lewis acidity of the metal center but also impedes Al deposition.³³ On the other hand, it is noteworthy that whereas $Al(Tf_2N)_3$ cannot be electrodeposited in $[Tf_2N]^-$ based ILs, negatively charged mixed complexes, in which $[Tf_2N]^-$ anion acts a monodentate ligand ($[AlCl_3Tf_2N]^-$), or bidentate ligand ($[AlCl_2Tf_2N]_2^-$), are electroactive species.³³

In principle, this sort of “metal cation-availability”, which probably determines also the electrochemical behavior of the negatively charged ($[M(Tf_2N)_{x+1}]^-$) species, might be attribute to aputative dynamic flexibility of these complexes. Indeed, an analysis of the low frequency normal modes of complexes shows that there is still a certain degree of flexibility of the ligand about the metal center that depends on structure. Octahedral complexes, especially the aluminium one, are more rigid than tetrahedral and anti-prismatic (yttrium) ones. This flexibility is an index of dynamicity in the metal environment: $[Tf_2N]^-$ ligands can be easily replaced by “by-standing” $[Tf_2N]^-$ anions or by other eventually present species (Lewis bases). Thus, a Lewis acidic catalytic activity is still possible notwithstanding the metal center is fully coordinated.

Conclusion

Bis-(trifluoromethylsulfonyl)imide anion is one of the most common building blocks used in ILs. Many ILs that contain this anion have melting points below 0 °C, low viscosities, and high conductivities. Moreover, despite the weak coordinating ability of the $[Tf_2N]^-$ anion, attributable

to its sterically demanding and electron withdrawing trifluoromethyl groups, the corresponding ILs are able to dissolve relevant amounts of metal salts having the same anion, $M[\text{Tf}_2\text{N}]_x$. Metal salts dissolution in ILs is a process completely different from the corresponding situation in molecular solvents since it generally determines the creation of new metal ion containing species. The interaction between the metal cation and the IL anions, together with those originating from the metal salt, fulfill indeed the metal solvation sphere, in agreement with its preferred coordination number, giving negatively charged species. The chemistry of the metal cations is determined by the formed species. Thus, to better understanding the metal dissolution process we have evaluated the interaction ability of a set of metal cations towards the $[\text{Tf}_2\text{N}]^-$ anion through the measure of the relative attitude to give the corresponding anionic mono-charged complexes. This has been done through ESI-MS, UV-vis and NMR measurements: these latter techniques have been employed to verify the consistence between gas and liquid phase. Furthermore, DFT calculations have been carried out to identify the metal-containing species and determine their relative stability. These studies have confirmed that monocharged complexes, $[\text{M}(\text{Tf}_2\text{N})_{x+1}]^-$ are for most of the investigated metal salts the sole species detectable both in the gas and liquid phase. An interesting correlation between the affinity of the metals to $[\text{Tf}_2\text{N}]^-$ and the Lewis acid activity has been found.

Experimental Section

The metal salts $\text{Ag}(\text{Tf}_2\text{N})$, $\text{Li}(\text{Tf}_2\text{N})$, $\text{Co}(\text{Tf}_2\text{N})_2$, $\text{Zn}(\text{Tf}_2\text{N})_2$, $\text{Ni}(\text{Tf}_2\text{N})_2$, $\text{Cu}(\text{Tf}_2\text{N})_2$, $\text{Al}(\text{Tf}_2\text{N})_3$, $\text{Y}(\text{Tf}_2\text{N})_3$ (Solvionic, 99% pure) and $\text{Na}(\text{Tf}_2\text{N})$ (Aldrich, 97% pure) were always dried (70 °C) under vacuum ($\approx 10^{-5}$ Pa, for 10 h) before use. The ionic liquids 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide $[\text{bmim}][\text{Tf}_2\text{N}]$, and 1-butyl-2,3-dimethylimidazolium bis-(trifluoromethylsulfonyl)imide, $[\text{bm}_2\text{im}][\text{Tf}_2\text{N}]$, were synthesized as previously reported.³⁴ To

remove traces of water and volatile compounds ILs were dried before use at moderate temperature (≈ 70 °C) and at high vacuum ($\approx 10^{-5}$ Pa) for a minimum period of 48 h under constant stirring. The mass spectrometric experiments were obtained using a LCQ Duo (ThermoQuest, San Jose, CA, USA), equipped with an electrospray ionization source operating in both positive and negative-ion mode, by introducing the single metal containing ionic liquid dissolved in methanol or a mixture of two different [bmim][Tf₂N]+M(Tf₂N)_x samples, using the value of $5 \cdot 10^{-4}$ M as reference concentration. Different ratios of two diverse metal containing ILs have been prepared by increasing the concentration of the component in excess up to $2.5 \cdot 10^{-3}$ M. Instrumental parameters for the negative-ion mode conditions: capillary voltage -10 V, spray voltage 4.50 kV, capillary temperature of 150 °C, mass scan range was from m/z 100 to 1200 ; N₂ was used as sheath gas. The samples were injected into the ESI source by a syringe pump at a constant flow rate of $8 \mu\text{L}/\text{min}$. UV spectra were registered on a UV-Vis Agilent Cary 300 at 25 °C.

Computational details

Calculations have been performed using the Gaussian 09 package (release C.01),³⁵ at DFT theory level with the B3LYP functional. The basis set 6-311G (d,p) has been used for second and third row elements (C, N, O, F, S, Li, Na, Al), while LANL08 for transition elements.³⁶ The ultrafine grid has been used for the integration of the functional. All the geometries has been optimized coherently with the level of the theory and characterized as minima with analytical frequencies calculation. The calculations have been performed on a dual Intel Xeon E5430 based server with 16Gb RAM. The installed operating system was Linux Centos 5 (final release).

Supporting information (SI).

Table S1: Absolute energies of the complexes (Table S1). Table S2: Absolute energies of the Tf_2N^- conformers (Table S2). Geometries in XYZ format of all the molecular systems considered in the paper are provided as supporting information.

References

1. Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*, 2nd Edition, Wiley-VCH, 2007, vol.
2. Hallett, J. P.; Welton T, Room Temperature Ionic Liquids: Solvents for Synthesis and Catalysis. 2, *Chem Rev.* **2011**, *111*, 3508-3576.
3. Parvulescu, V. I.; Hardacre, C. Catalysis in Ionic Liquids *Chem Rev.* **2007**, *107*, 2615-2165.
4. Ohno, H. *Electrochemical Aspects of Ionic Liquids*, Wiley Interscience, New York, 2005; P. Hapiot and C. Lagrost, Electrochemical Reactivity in Room Temperature Ionic Liquids *Chem. Rev.* **2008**, *108*, 2238-2264.
5. Esser, J.; Wasserscheid, P.; Jess A. Deep Desulfurization of Oil Refinery Streams by Extraction with Ionic Liquids *Green Chem.* **2004**, *6*, 316-322.
6. a) Chiappe, C.; Pieraccini, D. Ionic Liquids: Solvent Properties and Organic Reactivity *J. Phys. Org. Chem.* **2005**, *18*, 275-296; b) Chiappe, C.; Rajamani, S. Structural Effects on the Physico-Chemical and Catalytic Properties of Acidic Ionic Liquids: An Overview *Eur. J. Org. Chem.* **2011**, 5517-5539.
7. Chiappe, C.; Malvaldi, M. Highly Concentrated "Solutions" of Metal Cations in Ionic Liquids: Current Status and Future Challenges *Phys.Chem.Chem.Phys.* **2010**, *12*, 11191-11196.

8. Welton, T. Ionic Liquids in catalysis *Coord. Chem Rev.* **2004**, *248*, 2459-2477.
9. Wasserscheid, P.; Keim, W. Ionic Liquids – “New Solutions” for Transition Metal Catalysis *Angew. Chem. Int. Ed.* **2000**, *39*, 3772-3789.
10. a) Wilkes, J. S.; Levisky, A. J.; Wilson R. A.; Hussey, C. L. Dialkylimidazolium Chloroaluminate Melts: a New Class of Room-Temperature Ionic Liquids for Electrochemistry, Spectroscopy and Synthesis *Inorg. Chem.*, **1982**, *21*, 1263-1264; b) Estager, J.; Oliferenko, A. A.; Seddon, K. R.; Swadzba-Kwasny, M. Chlorometallate(III) Ionic Liquids as Lewis Acidic Catalysts – a Quantitative Study of Acceptor Properties *Dalton Trans.* **2010**, *39*, 11375-11382.
11. a) Hussey, C. L. In *Adv. Molten Salt Chem.* **1983**, *5*, 185; b) Tsuda, T.; Hussey C. L. In *Modern Aspects of Electrochemistry*, White, R. L.; Vayenas, C. G.; Gamboa-Adelco M. E., Eds. Springer: Dordrecht, The Netherlands, 2009; Vol. 45, p 63.
12. a) Wicelinski, S. P.; Gale, R. J.; Wilkes, J. S. Low Temperature Chlorogallate Molten Salt Systems *J. Electroch. Soc.* **1987**, *134*, 262-263; b) Wicelinski, S. P.; Gale, R. J.; Wilkes J. S., Differential Scanning Calorimetric Study of Low Melting Organic Chlorogallate Systems *Thermochim. Acta* **1988**, *126*, 255-263; c) Hardacre, C.; Murphy, R. W.; Seddon, K. R.; Swadzba-Kwasny, M. Speciation of Chlorometallate Ionic Liquids Based on Gallium(III) and Indium(III) *Aust. J. Chem.* **2010**, *63*, 845-848; d) Sitze, M. S.; Schreiter, E. R.; Patterson, E. V.; Freeman, R. G. Ionic Liquids Based on FeCl₃ and FeCl₂. Raman Scattering and Ab Initio Calculations *Inorg. Chem.* **2001**, *40*, 2298-2304.

13. Currie, M.; Estager, J.; Licence, P.; Men, S.; Nockemann, P.; Seddon, K. R.; Swadźba-Kwaśny, M.; Terrade, C. Chlorostannate(II) Ionic Liquids: Speciation, Lewis Acidity, and Oxidative Stability *Inorg. Chem.*, **2013**, *52*, 1710-1721.
14. Estager, J. ; Nockmann, P.; Seddon, K. R.; Swadźba-Kwaśny, M.; Tyrrell, S. Validation of Speciation Techniques: A Study of Chlorozincate(II) Ionic Liquids *Inorg. Chem.* **2011**, *50*, 5258-5271.
15. Coleman, F.; Feng, G.; Murphy, R. W.; Nockemann, P.; Seddon, K. R.; Swadźba-Kwaśny, M. Lead(II) Chloride Ionic Liquids and Organic/Inorganic Hybrid Materials - a Study of Chloroplumbate(II) Speciation *Dalton Trans.*, **2013**, *42*, 5025-5035.
16. Caporali, S.; Chiappe, C.; Ghilardi, T.; Pomelli, C. S.; Pinzino C. Coordination Environment of Highly Concentrated Solutions of Cu^{II} in Ionic Liquids Through a Multidisciplinary Approach *Chem. Phys. Chem.* **2012**, *13*, 1885-1892.
17. a) Earle, M. J.; Hakala, U.; McAuley, B. J.; Nieuwenhuyzen, M.; Ramani A.; Seddon, K. R. Metal Bis{(trifluoromethyl)sulfonyl}amide Complexes: Highly Efficient Friedel–Crafts Acylation Catalysts *Chem. Commun.*, **2004**, 1368-1369; b) Mudring, A. V.; Babai, A.; Arenz S.; Giernoth, R. The “Noncoordinating“ Anion Tf₂N⁻Coordinates to Yb²⁺: A Structurally Characterized Tf₂N-Complex from the Ionic Liquid [mppyr][Tf₂N] *Angew. Chem., Int. Ed.*, **2005**, *44*, 5485-5488.
18. Tang, S.; Babai A.; Mudring, A. V. Europium-Based Ionic Liquids as Luminescent Soft Materials *Angew. Chem., Int. Ed.*, **2008**, *47*, 7631-7634.

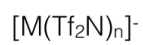
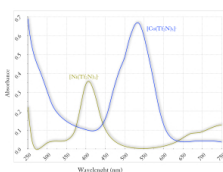
19. a) Chiappe, C.; Malvaldi, M.; Melai, B.; Fantini, S.; Bardi, U.; Caporali, S. An Unusual Common Ion Effect Promotes Dissolution of Metal Salts in Room-Temperature Ionic Liquids: a Strategy to Obtain Ionic Liquids Having Organic–Inorganic Mixed cations *Green Chem.* **2010**, *12*, 77-88; b) Chiappe, C.; Pomelli, C. S.; Bardi, U.; Caporali S. Interface Properties of Ionic Liquids Containing Metal Ions: Features and Potentialities *Phys. Chem. Chem. Phys.* **2012**, *14*, 5045-5051.
20. Estager, J.; Holbrey, J. D.; Swadzba- Kwasny, M. Halometallate Ionic Liquids – Revisited *Chem. Soc. Rev.* **2014**, *43*, 847-886.
21. Daniel, J. M.; Friess, S. D.; Rajagopalan, S.; Wendt, S.; Zenobi R. Quantitative Determination of Noncovalent Binding Interactions Using Soft Ionization Mass Spectrometry *Int. J. Mass Spectrom.* **2002**, *216*, 1; b) Paul, L. E. H.; Therrien, B.; Furrer J. Investigation of the Reactivity between a Ruthenium Hexacationic Prism and Biological Ligands *Inorg. Chem.* **2012**, *51*, 1057-1067;
22. Fei, Z.; Zhu, D.-R.; Yan, N.; Scopelliti, R.; Katsuba, S. A.; Laurency, G.; Chisholm, D. M.; McIndoe, J. S.; Seddon, K. R.; Dyson P. J. Electrostatic and Non-Covalent Interactions in Dicationic Imidazolium-Sulfonium Salts With Mixed Anions *Chem. Eur. J.* **2014**, *20*, 4273-4283.
23. Leito, I.; Herodes, K.; Huopola, M.; Virro, K.; Künnapas, A.; Krüge, A.; Tanner R. Towards the Electrospray Ionization Mass Spectrometry Ionization Efficiency Scale of Organic Compounds *Rapid Commun. Mass Spectrom.* **2008**, *22*, 379-384.

24. Matsumiya, M.; Kamo, Y.; Hata, K. Tsunashima K. Solvation Structure of Iron Group Metal Ion in TFSA-Based Ionic Liquids Investigated by Raman Spectroscopy and DFT Calculations *J. Mol. Struct.* **2013**, *1048*, 59-63.
25. a) Lassègues, J. C.; Grondin, J.; Talaga D. Lithium Solvation in Bis(trifluoromethanesulfonyl)imide-Based Ionic Liquids *Phys. Chem. Chem. Phys.* **2006**, *8*, 5629-5632; b) Umebayashi, Y.; Mitsugi, T.; Fukuda, S.; Fujimori, T.; Fujii, K.; Kanzaki, R.; Takeuchi, M.; Ishiguro, S.-I. Lithium Ion Solvation in Room-Temperature Ionic Liquids Involving Bis(trifluoromethanesulfonyl) Imide Anion Studied by Raman Spectroscopy and DFT Calculations *J. Phys. Chem. B* **2007**, *111*, 13028-13032; c) Duluard, S.; Grondin, J.; Bruneel, J. L.; Pianet, I.; Groelard, A.; Campet, G.; Delville, M. H.; Lassègues, J. C. Lithium Solvation and Diffusion in the 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide Ionic Liquid *J. Raman Spectrosc.* **2008**, *39*, 627-632; d) Duluard, S.; Grondin, J.; Bruneel, J. L.; Campet, G.; Delville, M. H.; Lassègues, J. C. Lithium Solvation in a PMMA Membrane Plasticized by a Lithium-Conducting Ionic Liquid Based on 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide *J. Raman Spectrosc.* **2008**, *39*, 1189-1194; e) Lassègues, J. C.; Grondin, J.; Aupetit, C.; Johansson, P. Spectroscopic Identification of the Lithium Ion Transporting Species in LiTFSI-Doped Ionic Liquids *J. Phys. Chem. A* **2009**, *113*, 305.
26. a) Hayamizu, K.; Aihara, Y.; Nakagawa, H.; Nukuda, T.; Price, W. S. Ionic Conduction and Ion Diffusion in Binary Room-Temperature Ionic Liquids Composed of [emim][BF₄] and LiBF₄ *J. Phys. Chem. B* **2004**, *108*, 19527-19532; b) Saito, Y.; Umecky, T.; Niwa, J.; Sakai, T.; Maeda, S. Existing Condition and Migration Property of Ions in Lithium Electrolytes with Ionic Liquid Solvent *J. Phys. Chem. B* **2007**, *111*, 11794-11802; c) Umecky, T.; Saito, Y.; Okumura, Y.; Maeda, S.; Sakai, T. Ionization Condition of Lithium Ionic Liquid Electrolytes under the

- Solvation Effect of Liquid and Solid Solvents *J. Phys. Chem. B* **2008**, *112*, 3357-3364. d)
- Freomling, T.; Kunze, M.; Scheonhoff, M.; Sundermeyer, J.; Roling, B. Enhanced Lithium Transference Numbers in Ionic Liquid Electrolytes *J. Phys. Chem. B* **2008**, *112*, 12985-12990. e)
- Andriola, A.; Singh, K.; Lewis, J.; Yu, L. Conductivity, Viscosity, and Dissolution Enthalpy of LiNTF₂ in Ionic Liquid BMINTF₂ *J. Phys. Chem. B* **2010**, *114*, 11709-11714.
27. a) Rocher, N.M.; Izgoridina, E.I.; R  ther, T.; Forsyth, M.; MacFarlane, D.R.; Rodopolus, T.; Horne M.D.; Bond, A.M. Aluminium Speciation in 1-Butyl-1-Methylpyrrolidinium Bis(trifluoromethylsulfonyl)amide/AlCl₃ Mixtures *Chem. Eur. J.* **2009**, *15*, 3435-3447.
28. Umebayashi, Y.; Mori, S.; Fujii, K.; Tsuzuki, S.; Seki, S.; Hayamizu, K.; Ishiguro S. Raman Spectroscopic Studies and Ab Initio Calculations on Conformational Isomerism of 1-Butyl-3-methylimidazolium Bis-(trifluoromethanesulfonyl)amide Solvated to a Lithium Ion in Ionic Liquids: Effects of the Second Solvation Sphere of the Lithium Ion *J. Phys. Chem. B* **2010**, *114*, 6513-6521.
29. Merrick, J.P.; Moran, D.; Radom L. An Evaluation of Harmonic Vibrational Frequency Scale Factors *J. Phys. Chem. A* **2007**, *111*, 11683-11700.
30. Eiden, P.; Liu, Q.; El Abedin, S. Z.; Endres F.; Krossing I. An Experimental and Theoretical Study of the Aluminium Species Present in Mixtures of AlCl₃ with the Ionic Liquids [BMP]Tf₂N and [EMIm]Tf₂N *Chem. Eur. J.* **2009**, *15*, 3426-3434.
31. Babai, A.; Mudring, A.-V. The First Homoleptic Bis(trifluoromethanesulfonyl)amide Complex of Yttrium: [bmim][Y(Tf₂N)₄] *Z. Anorg. Allg. Chem.* **2008**, *634*, 938-940.

32. Earle, M. J.; McAuley, B. J.; Ramani, A.; Seddon, K. R.; Thomson J. M. World Patent WO 02, 072519 (2002).
33. Rodopolus, T.; Smith, L.; Horne, M.D.; R  ther, T. Speciation of Aluminium in Mixtures of the Ionic Liquids [C₃mpip][NTf₂] and [C₄mpyr][NTf₂] with AlCl₃: An Electrochemical and NMR Spectroscopy Study *Chem. Eur. J.* **2010**, *16*, 3815-3826.
34. Bini, R.; Chiappe, C.; Llopolis, V.; Pomelli, C. S.; Welton, T. A Rationalization of the Solvent Effect on the Diels–Alder Reaction in Ionic Liquids Using Multiparameter Linear Solvation Energy Relationships *Org. Biomol. Chem.* **2008**, *6*, 2522-2529.
35. Gaussian 09, Revision C.01, Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G. E.; Robb, A. Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H. et al. . Gaussian, Inc., Wallingford CT, 2009.
36. Hay P. J.; Wadt, W. R. *Ab Initio* Effective Core Potentials for Molecular Calculations. Potentials for the Transition Metal Atoms Sc to Hg *J. Chem. Phys.* **1985**, *82*, 270-283.

TOC Image



Li(I) Na(I) Ag(I)
Ni(II) Co(II) Zn(II)
Al(III) Y(III)

