Structural Diversity in Lewis-Base Complexes of Lithium Triflamide

Matthew G. Davidson,*[a] Paul R. Raithby,*[a] Andrew L. Johnson,[a] and Philip D. Bolton[a]

Dedicated to the memory of Dr Ron Snaith

Keywords: Lithium / Solid-state structures / Aggregation / Crystal engineering / Anions

Complexation of the salt lithium triflamide [$LiNTf_2$; NTf_2 = $N(SO_2CF_3)_2$], with a range of nitrogen donor ligands results in the formation of a series of coordination complexes [$(Tf_2N)Li{\cdot}N(H)PPh_2Me$] (**1**), [$(Tf_2N)Li{\cdot}N(H)PPh_3$] (**2**), [$(Tf_2N)Li{\cdot}TMEDA$] (**3**), [$(Tf_2N)Li{\cdot}PMDTEA$] (**4**) and [$(Bz\text{-}TAC)_2\text{-}Li][NTf_2$] (**5**). The molecular structures of **1**, **3**, **4** and **5** have been determined by single-crystal X-ray diffraction. The resulting solvated structures are discussed in terms of solvent-separated ion pairs, contact ion pairs and higher aggregates, with the degree of aggregation and ion contact being dependent on the relative coordinating abilities and steric demands of the donor ligand and the anion, and provide an insight into the possible structures of lithium aggregates present in complex systems such as polymer electrolytes and synthetic reaction media.

Introduction

The structural chemistry of organolithium compounds has attracted significant and sustained interest, primarily because of their extensive use as reagents in synthetic chemistry and the perceived close relationship between structure and reactivity.[1−6] Principles such as ring stacking and laddering[2,3] have been developed to explain the structural types of organolithiums that are found in the gas phase,[4] the solid state[5] and in solution.[6] Furthermore, these structures have been useful in accounting for the observed reactivity of even quite complex systems.[6] In contrast, the systematic study of simple inorganic lithium salts has attracted considerably less attention. The development of "in situ" synthetic routes (in particular the so-called "ammonium salt route")[7] has provided facile and high yielding methodologies for the controlled synthesis of hydrocarbon-soluble molecular complexes of inorganic lithium salts. However, these methodologies have yet to be fully exploited in terms of providing well-defined materials with specific reactivities and/or material properties.

Two areas of research that may benefit from systematic structural studies of inorganic lithium salts are polymer electrolytes[8] and Lewis acid-mediated organic synthesis.[1,9] Both of these areas utilise inorganic lithium salts containing weakly coordinating anions, such as $LiPF_6$, $LiClO_4$, $LiBF_4$ and $LiAsF_6$.

[a] Department of Chemistry, University of Bath, Claverton Down, Bath. BA2 7AY, UK
Fax: (internat.) +44-(0)1225/826-231
E-mail: M.G.Davidson@Bath.ac.uk
P.R.Raithby@Bath.ac.uk

In order to understand more fully the role of these weakly coordinated lithium salts in complex environments (such as in homogeneous liquid-phase reactions or a coordinating polymer electrolyte) it is useful to investigate systems in the solid state in which we can more easily and unambiguously assign the coordination geometry about the lithium ion and extrapolate these studies to "real" systems.

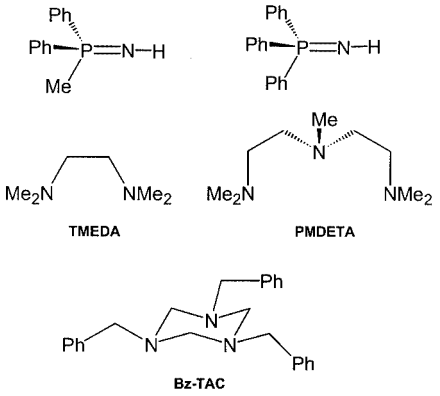
Of late, studies in these areas have begun to focus on salts that incorporate much more stable, larger and more weakly coordinating anions such as $CF_3SO_3^-$ (OTf^-, triflate), $[N(SO_2CF_3)_2]^-$ (NTf_2^-, triflamide), $[HC(SO_2CF_3)_2]^-$ and $[C(SO_2CF_3)_3]^-$, all of which show remarkable chemical and electrochemical stability, and provide alternatives to potentially dangerous salts such as $LiClO_4$.

In this context, we report herein a systematic study of the coordination chemistry of lithium triflamide. Although structural studies of the parent salt, $LiNTf_2$,[10] and its hydrate, $LiNTf_2{\cdot}H_2O$,[11] have been performed, this work represents the first systematic structural study of $LiNTf_2$ in the presence of a range of nitrogen-donor ligands, with the aim of investigating the extent and range of anion binding within these systems and their more general structural diversity.

Results and Discussion

In order to study the coordination chemistry between $LiNTf_2$ and donor ligand systems, and the extent of anion-cation contact in the presence of strongly competing donor ligands, we first chose specific donor ligands that could provide a varied number of coordination environments from

mono- to polydentate in order to mimic the possible coordination environments in systems such as conducting polymer electrolytes. The nitrogen-based ligands, selected on the basis of their synthetic utility and availability, are shown below.



All lithium complexes **1**−**5** were initially synthesised using the "ammonium-salt route",[7] in which ammonium triflamide, $[NH_4][NTf_2]$, and the ligand are combined in toluene and a stoichiometric amount of *n*-butyllithium is added. The ammonium triflamide was prepared by passing ammonia gas through a toluene solution of the parent acid, Tf_2NH (see Exp. Sect.).

In some scenarios, the "ammonium-salt route" is the only rigorous method of synthesis for complexes of lithium salts, e.g. halides.[7] However, direct methods, whereby solid salts are treated with the Lewis base (donor ligand), either neat or in hydrocarbon solution, can be applied to more soluble lithium salts, such as lithium triflamide. Both direct and in situ methods of lithium complex preparation were employed in our investigation in order to reveal any differences between the products formed by the two methods, i.e. stoichiometries, different ligand coordination modes, different polymorphs, etc.

Our investigation has shown that for the compounds discussed here, both methodologies (Scheme 1) are equally effective, and for comparable experiments, the products were found to be identical by multinuclear NMR spectroscopy, elemental analysis, melting point analysis and unit cell determination.

In solution, ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR experiments performed on complexes **1**−**5** indicate that, in all cases, on the NMR timescale, the lithium ion appears to remain coordinated to the nitrogen donor ligand in solution, as indicated by the moderate change in ^{1}H and ^{13}C NMR chemical shift between free and ligated nitrogen-donor ligand. As with the closely related triflate anions $[OTf]^-$, ^{19}F NMR experiments on **1**−**5** provide little information about the coordination state of the triflamide anion, $[NTf_2]^-$, in the solution state.[12]

Compound **1** was found to have the empirical formula $[(Tf_2N)Li{\cdot}N(H)PPh_2Me]$. Crystallisation of the complex from hot toluene resulted in the formation of colourless crystals. Single crystal X-ray diffraction experiments reveal the asymmetric unit cell of **1** to consist of a central lithium cation coordinated by both the nitrogen atom of the iminophosphorane ligand and one oxygen atom of the triflamide

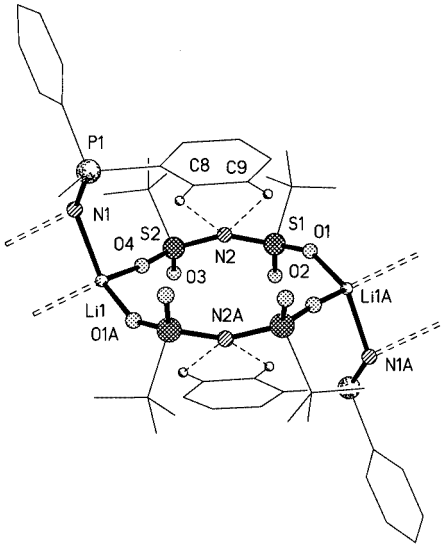
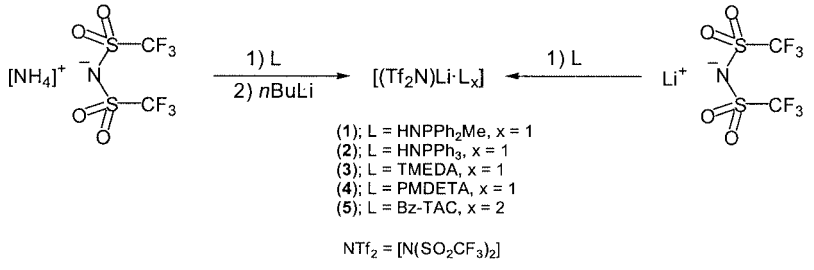


Figure 1. Molecular structure of (**1**), highlighting the weak N···H−C hydrogen bonding interaction between the C−H of a iminophosphorane bound phenyl group and the central nitrogen atom of the triflamide anion; CF_3 groups on the triflamide anion and the iminophosphorane ligand are shown as wire frames and hydrogen atoms omitted for clarity; symmetry transformations used to generate equivalent atoms: $(-x, -y+1, -z+2)$, $(x+1, y, z)$ and $(x-1, y, z)$; selected bond lengths (Å): Li(1)−N(1) 2.036(13), Li(1)−N(1A) 2.051(12), Li(1)−O(4) 1.980(13), Li(1)−O(1A) 1.934(12), O(1)−S(1) 1.427(5), O(2)−S(1) 1.415(5), S(1)−N(2) 1.562(6), N(1)−S(2) 1.573(5), S(2)−O(3), 1.424(5), S(2)−O(4) 1.429(5), P(1)−N(1) 1.589(6), P(1)−C(15) 1.782(7), P(1)−C(1) 1.806(7), P(1)−C(7) 1.805(7), C(8)−H(8) 0.93, N(2)−H(8) 2.79, C(8)−N(2) 3.465(9), C(9)−H(9) 0.93, N(2)−H(9) 2.96, C(9)−N(2) 3.541(9); selected bond angles (°): Li(1)−N(1)−Li(1A) 80.6(5), N(1)−Li(1)−N(1A) 99.4(5), O(4)−Li(1)−O(1A) 119.2(6), S(1)−N(2)−S(2) 127.5(3), C(15)−P(1)−N(1) 109.7(3) C(8)−H(8)−N(2) 130.7, C(9)−H(9)−N(2) 122.3



Scheme 1

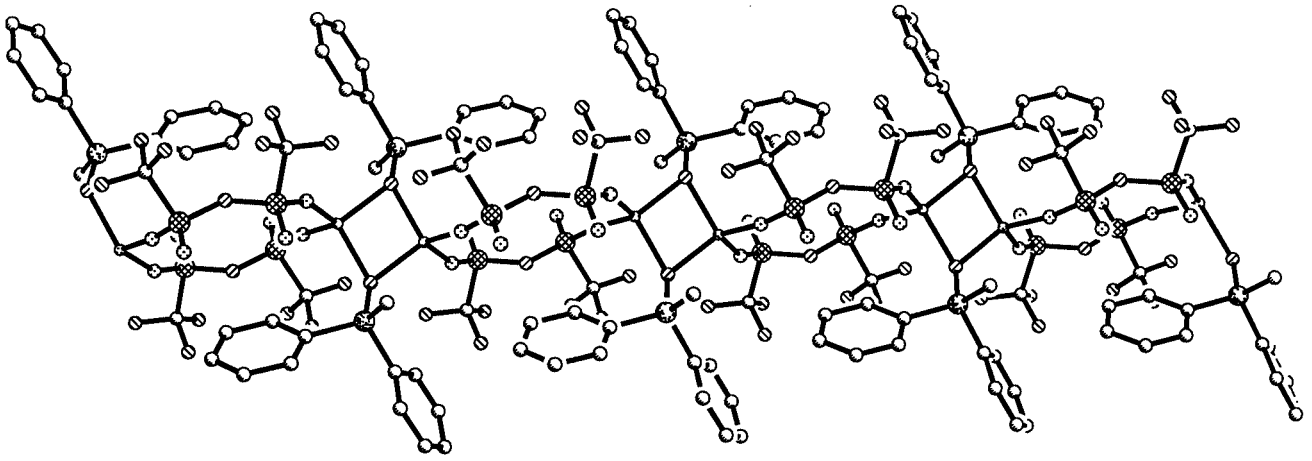


Figure 2. View of the polymeric chain in **1**

anion. Crystallographic symmetry renders the asymmetric unit part of an infinite polymeric chain, in which each lithium triflamide unit forms one half of a twelve-membered ring system (Figure 1). Each twelve-membered ring is subsequently linked by lithium-bridging iminophosphorane groups to propagate the polymeric chain through alternate, and approximately orthogonal, corner-sharing twelve-membered and four-membered rings (Figure 2).

Searches of the literature and the Cambridge Structural Database reveal this twelve-membered ring system to be unique in terms of both its composition and as a bonding mode for the triflamide anion.[13] The CF_3 groups of each NTf_2^- anion within the dimer are found to be mutually *cisoid* with respect to the twelve-membered ring, whereas those of different anions are mutually *transoid*. This unexpected conformation allows a close approach between one of the iminophosphorane-based phenyl groups and the lone pair of the central nitrogen atom of the triflamide anion, facilitating the formation of two C−H···N···H−C hydrogen bonds [C(8)···N(2): 3.464(9) Å; H(8)···N(2): 2.77 Å; C(8)−H(8)···N(2): 130.3°; and C(9)···N(2): 3.540(9) Å; H(9)···N(2): 2.94 Å; C(9)−H(9)···N(2), 122.0°; Figure 1].[14]

Neutral iminophosphorane ligands, which are isoelectronic with phosphane oxides,[15] have been observed previously as ligands to s-block metals.[15,16] The iminophosphorane P−N bond length [P(1)−N(1): 1.589(6) Å] is little changed on coordination to Li from that of the parent ligand,[17] [P−N: 1.563(4)], and in the solid state the ligands are arranged *trans* to each other across the $[Li_2N_2]$ core. Whilst the Li−N bond lengths in **1** [Li(1)−N(1): 2.036(13) Å; Li(1)−N(1A): 2.051(12) Å] are fairly typical of Li−N bonds in a wide range of compounds, the Li−O bonds [Li(1)−O(1): 1.934(12) Å; Li(1)−O(4): 1.980(13) Å] are longer than generally observed in systems containing oxygen-based anions, such as lithium aryloxides,[18] and are closer to typical bond lengths for Li···THF and Li···OEt_2 contacts, implying rather weak anion-cation interactions. The binding of triflamide to the lithium atoms via the oxygen atoms, and not the nitrogen, would suggest that the centre of electronegativity does not reside solely at the nitrogen centre, and close inspection of the bond lengths and bond angles in the triflamide anion reveals only a small degree of asymmetry.

We believe that the preference for Li−O rather than Li−N coordination is electronic in nature rather than steric. This theory is supported by both the structural characterisation of bulkier bis(fluorobenzylsuphonyl)imido systems, $[N(SO_2C_6H_4F)_2]^-$,[19] which possess M−N interactions and the observation by others that strong electron-withdrawing effects of the -CF_3 groups result in a large degree of pπ-dπ bonding within the N−S backbone, resulting in charge delocalisation over the whole of the anion.[20,21]

Compound **2**, $[(Tf_2N)Li{\cdot}N(H)PPh_3]_n$, was prepared in an identical manner to **1** using triphenyliminophosphorane as the nitrogen donor ligand. Characterisation by multinuclear NMR spectroscopy and elemental analysis showed **2** to have the empirical formula $[(Tf_2N)Li{\cdot}N(H)PPh_3]$. Single-crystal X-ray diffraction studies were not undertaken on **2**, but the complex is assumed to be isostructural with the methyldiphenyliminophosphorane complex **1**.

In order to examine further the coordination chemistry of the triflamide anion we reasoned that addition of a bidentate N-donor ligand would enable us to isolate and characterise a single dimeric $[Li_2(NTf_2)_2]$ twelve-membered ring system. Indeed, reaction of TMEDA with $LiNTf_2$ in toluene (or reaction of $[NH_4][NTf_2]$ with *n*BuLi in the presence of TMEDA) results in the isolation of the complex **3**, which has been shown by X-ray diffraction studies to be a discrete dimeric lithium species, $[(Tf_2N)Li{\cdot}TMEDA]_2$, as predicted (Figure 3).

The asymmetric unit of **3** contains half of the dimer, the second half being generated by a crystallographic centre of symmetry that lies at the centre of the twelve-membered $[Li_2(NTf_2)_2]$ ring such that the two lithium centres are bridged by two triflamide ligands as in **1**. However, unlike in **1**, distortion of the twelve-membered ring results in increased cation-anion contact, such that a secondary coordination of the triflamide ligand results, and the geometry about each lithium ion in **3** is pseudo-trigonal bipyramidal rather than the pseudo-tetrahedral geometry observed in **1**.

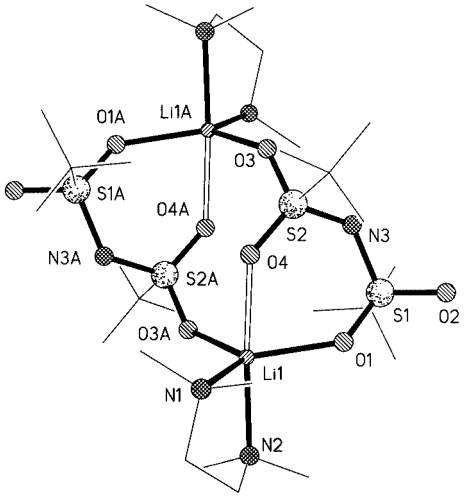


Figure 3. Molecular structure of **3**; symmetry transformations used to generate equivalent atoms: ($-x$, $-y$, $-z$); CF_3 groups and the TMEDA ligands are shown as wire frames and hydrogen atoms omitted for clarity; selected bond lengths (Å): Li(1)−N(1) 2.077(3), Li(1)−N(2) 2.175(3), Li(1)−O(1) 2.070(3), Li(1)−O(3A) 2.008(3), Li(1)−O(4) 2.230(3), O(1)−S(1) 1.4382(13), S(2)−O(3) 1.4332(12), S(2)−O(4) 1.4326(13), S(1)−N(3) 1.5779(15), S(2)−N(3) 1.5628(15); selected bond angles (°): N(1)−Li(1)−N(2) 86.63(12), O(1)−Li(1)−O(4) 79.66(12) O(1)−Li(1)−O(3A) 126.33(16), O(1)−Li(1)−N(1) 118.71(16), O(3A)−Li(1)−N(1) 113.68(15), N(2)−Li(1)−O(4) 175.53(17), S(1)−N(3)−S(2) 124.74(10)

The nitrogen atoms of the TMEDA ligand occupy equatorial and axial positions [Li(1)−N(1): 2.077(3) Å; Li(1)−N(2): 2.175(3) Å], with the axial Li−N bond being the longer. Each lithium centre within the dimer is also coordinated by two oxygen atoms of separate triflamide anions, creating the twelve-membered ring. These oxygen atoms occupy equatorial positions about the lithium ion [Li(1)−O(1): 2.007(3) Å; Li(1)−O(3A): 2.008(3) Å], leaving the axial position available for secondary coordination by an oxygen atom from one of the two bound triflamide anions. This axial Li−O distance [Li(1)−O(4): 2.230(3) Å] is significantly longer than any of the other interactions with lithium, implying a significantly weaker ligation compared to other Li−O contacts. These observations are in contrast to the related complex $[(Tf_2N)Li{\cdot}DME]_\infty$ [22] (DME = dimethoxyethane) in which the central lithium possesses a five-coordinate square-based pyramidal geometry with both the DME ligand and triflamide anion coordinating in an η^2-fashion to the lithium ion. The fifth coordination about the lithium ion site is filled by a long Li−O interaction from a neighbouring η^2-bound triflamide ligand. This bonding motif continues throughout the complex forming a polymeric chain of $[(Tf_2N)Li{\cdot}DME]$ units.[22]

In contrast to **1** the central nitrogen atom of the triflamide anion does not participate in any hydrogen bonding in the absence of suitable acidic C−H donor groups, and it is unclear whether the change in NTf_2^- coordination mode between **1** and **3** is a result of the lack of suitable hydrogen-bonding interactions or due to the steric differences in the N-donor ligands. The different conformations of the twelve-membered rings found in **1** and **3** are highlighted in Figure 4.

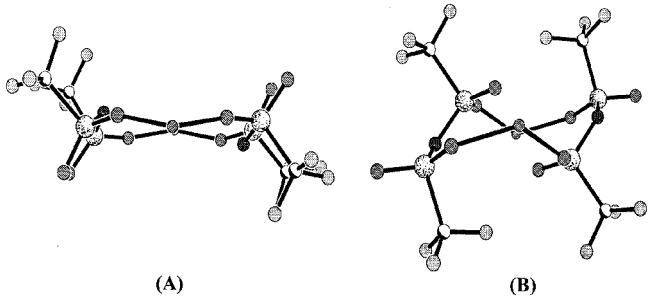


Figure 4. Structure of the central twelve-membered rings found in **1** (**A**) and **3** (**B**)

On changing the nitrogen donor ligand from bidentate TMEDA to the tridentate ligand PMDETA (pentamethyldiethylenetriamine), the aggregation state of the lithium triflamide is further reduced with the formation of a monomeric complex $[(Tf_2N)Li{\cdot}PMDETA]$ (**4**). The central lithium cation in this monomeric species possesses a five-coordinate pseudo-trigonal bipyramidal geometry as in **3** with the PMDETA ligand and the triflamide anion bound to the lithium centre in a tridentate and bidentate fashion, respectively. The molecular structure of **4** is shown in Figure 5.

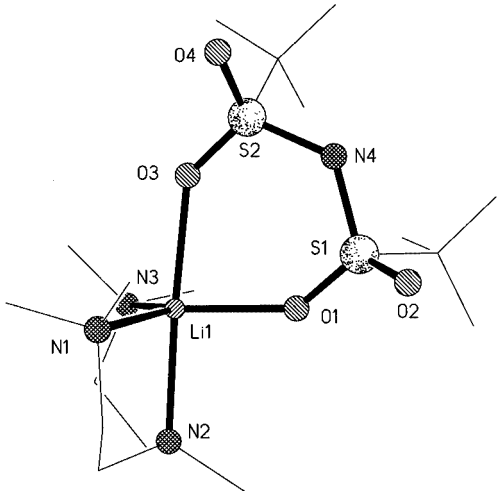


Figure 5. Molecular structure of **4** highlighting the coordination geometry about the central lithium ion; hydrogen atoms have been omitted and selected groups (PMDETA and CF_3) are shown as wire frames for clarity; selected bond lengths (A): Li(1)−N(1) 2.118(4), Li(1)−N(2) 2.173(4), Li(1)−N(3) 2.132(4) Li(1)−O(1) 1.997(4), Li(1)−O(3) 2.151(4), O(1)−S(1) 1.4251(17), S(2)−O(3) 1.4322(15), S(1)−N(4) 1.5705(17), S(2)−N(4) 1.5658(17); selected bond angles (°): O(1)−L(1)−O(3) 83.84(13), N(1)−Li(1)−N(3) 123.62(17), N(1)−Li(1)−N(2) 86.23(13), N(1)−Li(1)−N(3) 84.12(13), N(1)−Li(1)−O(1) 110.06(17), O(1)−Li(1)−N(3) 125.98(17), N(2)−Li(1)−O(3) 175.04(18), S(1)−N(4)−S(2) 126.99(11)

The distortion away from an ideal trigonal bipyramidal geometry in **4** is manifest in the axial-equatorial bond angles and is presumably the result of constrained bite angles within the PMDETA ligand and the triflamide anion [N(1)−Li(1)−N(2): 86.32(13)°; N(2)−Li(1)−N(3): 84.12(13)°; O(1)−Li(1)−O(3): 83.84(13)°]. However the

O−Li−N angle is close to linear [N(2)−Li(1)−O(3): 175.04(18)°].

The PMDETA ligand binds to the lithium in a facial configuration, with three Li−N contacts, two of which correspond to the outer nitrogen atoms [Li(1)−N(1): 2.118(4) Å; Li(1)−N(3): 2.132(4) Å] and lie in the equatorial plane of the trigonal bipyramid. The third nitrogen atom, which is the central nitrogen of the PMDETA ligand, occupies an axial position with a comparatively longer Li−N contact [Li(1)−N(2): 2.173(4) Å]. The triflamide anion, which binds to the lithium in an η^2-fashion [Li(1)−O(1): 1.997(4) Å; Li(1)−O(3): 2.151(4) Å] fills the remaining two coordination sites about the lithium ion, with the longer of the two Li−O contacts in the axial position. In the absence of any further intra- or intermolecular bonding the CF_3 groups of the triflamide anion maintain the *cis*- conformation observed in **1**.

It is noteworthy when considering the conceptual deaggregation of a dimeric complex containing a bidentate donor ligand, such as **3**, to a monomeric complex containing a tridentate donor ligand, such as **4**, that it is the short Li−O bond [Li(1)−O(3A) in **3**] that generates the dimer that is replaced rather than the longer (secondary) Li−O interaction [Li(1)−O(4) in **3**].

Finally, we wished to investigate the effect of variation in the nature of the tridentate donor ligand by synthesising complexes of *N*-tribenzyltriazocyclohexane (Bz-TAC). Although both PMDETA and Bz-TAC contain three donor atoms we expected the more compact ligand set of Bz-TAC relative to PMDETA to influence the nature of NTf_2^- coordination to the lithium ion.[23]

Attempted synthesis of the Bz-TAC analogues of **4**, using the direct addition of ligand to $LiNTf_2$ in toluene, were unsuccessful, with all stoichiometries of starting materials resulting in the isolation of the ion-separated bis-ligand complex $[(Bz\text{-}TAC)_2Li][NTf_2]$, (**5**), in which each lithium ion is coordinated by two TAC ligands.

Complex **5** was characterised by single-crystal X-ray diffraction (Figure 6). The asymmetric unit cell contains two independent half $[\eta^3\text{-}(Bz\text{-}TAC)_2Li]^+$ cations, with the Li atom in each case sitting on a centre of symmetry. The asymmetric unit is completed by one non-coordinating NTf_2^- anion. For both cations all Li−N distances are similar, spanning a small range [2.2411(15) to 2.3031(15) Å].

The six benzyl groups of the $[(Bz\text{-}TAC)_2Li]^+$ cation wrap around the central lithium ion and participate in an intricate *ortho*-(C−H···π) arene hydrogen bonding motif, in which each benzyl group is hydrogen bonded to its nearest neighbour on the other Bz-TAC ligand (Figure 7). The two ligands are thus interlocked in a paddlewheel motif about the central lithium ion.

$[(R\text{-}TAC)_2Li]^+$ cations, where R = Bz[24] or R = Me,[24,25] have been characterised previously, although the hydrogen-bonding network that is present in the benzyl system has not been commented upon. The presence of two TAC ligands around the lithium ion provides sufficient steric protection to preclude any cation-anion interactions in **5**.

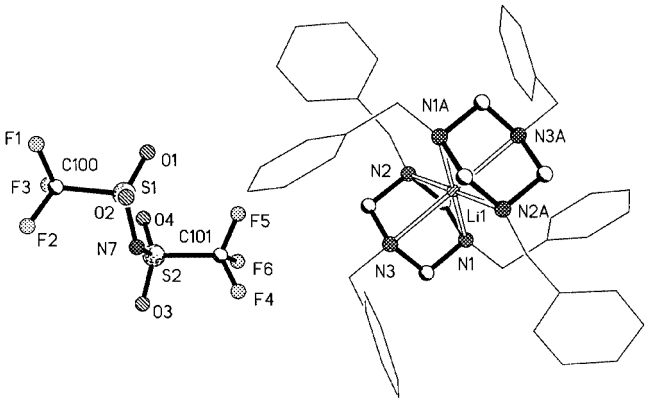


Figure 6. Molecular structure of one of the two centrosymmetric $[Li(Bz\text{-}TAC)_2]^+$ cations and an NTf_2^- anion in (**5**); symmetry transformations used to generate equivalent atoms: (x, y, z), & ($-x$, $-y$, $-z$); benzyl groups of the $[Li(Bz\text{-}TAC)_2]^+$ cation are shown as wire frames and hydrogen atoms omitted for clarity; selected bond lengths (Å): Li(1)−N(1) 2.2411(15), Li(1)−N(2) 2.2602(15), Li(1)−N(3) 2.2471(16), S(1)−N(7) 1.5731(17), S(2)−N(7) 1.5736(18), S(1)−O(1) 1.4259(16), S(1)−O(2) 1.4239(15), S(2)−O(3) 1.4286(15), S(2)−O(4) 1.4223(15); selected bond angles (°): N(1)−Li(1)−N(2) 63.64(6), N(1)−Li(1)−N(3) 63.53(6), N(2)−Li(1)−N(3) 63.06(6), S(1)−N(7)−S(2) 125.41(11)

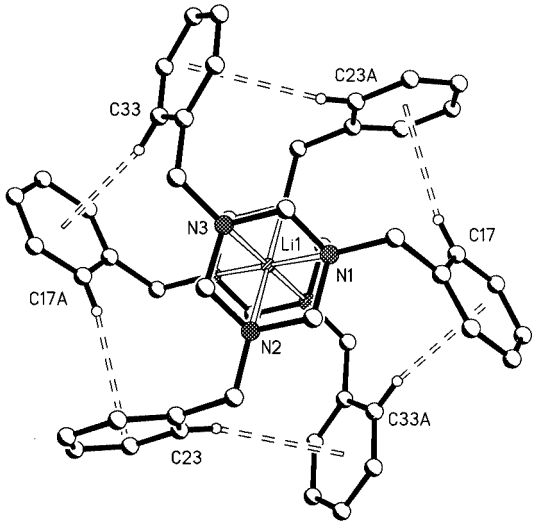


Figure 7. Diagram highlighting the C−H···π arene hydrogen-bonding network within one of the two centrosymmetric cations in **5**; hydrogen atoms not involved in the hydrogen-bonding network omitted for clarity; C−(H)···X distances (where X = centroid of the relevant aryl ring) (Å): C(17)−X 3.802, C(23)−X 3.956, C(33)−X 3.593; selected C−(H)···X angles (°): C(17)−H(17)−X 167, C(23)−H(23)−X 155, C(33)−H(33)−X 166

Close inspection of the bond lengths and angles about the NTf_2^- anion in **5** (Figure 6), shows a remarkable similarity to the coordinated anions in $[(Tf_2N)Li{\cdot}N(H)Ph_2Me]$, $[(Tf_2N)Li{\cdot}TMEDA]$, $[(Tf_2N)Li{\cdot}PMDETA]$, and other non-coordinated anions in complexes such as $[Li(12\text{-}C\text{-}4)_2][NTf_2]$,[26] $[Li(C\text{-}2,2,2)][NTf_2]$,[26] $[Mg(H_2O)_6][NTf_2]_2$,[27] $[Im][NTf_2]$,[28] $[R_4N][NTf_2]$[29] and $[Me_3NH][NTf_2]$.[30]

It is noteworthy that even using the high degree of control provided by the ammonium salt route, it has not been possible to isolate mono Bz-TAC complexes, such as [(*i*Pr-

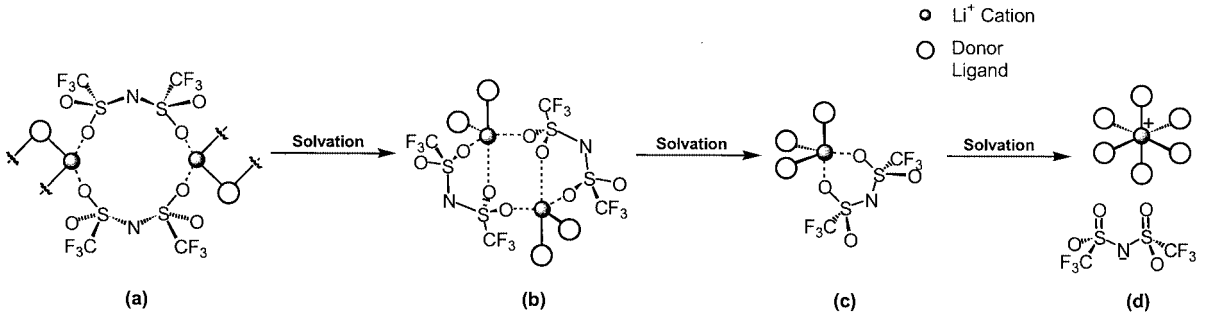


Figure 8. Schematic illustration of the sequential solvation and deaggregation of lithium triflamide complexes: (a) higher aggregate (polymeric) structures, (b) dimeric contact ion pair, (c) a contact ion pair and (d) donor ligand-separated ion pair

TAC)Li·BH_4]$_2$,[24] highlighting the high stability of the [(Bz-TAC)$_2$Li]$^+$ cation.

Conclusions

The single crystal structures of the four lithium triflamide salts have been determined. The resulting solvated structures can be thought of in terms of solvent-separated ion pairs, contact ion pairs and higher aggregates (Figure 8), with the degree of aggregation and ion contact being dependent on the relative coordinating abilities and steric demands of the donor ligand and the anion. These results provide an insight into the possible structures of lithium aggregates present in complex systems such as polymer electrolytes and synthetic reaction media.

The degree to which lithium ions will engage in intimate contact with the triflamide anions has little effect on the electronic structure of the anion, which remains reasonably impassive. However, conformational changes within the very flexible anion are observed.

The observation of ion separation in lithium triflamide salts contrasts directly with more coordinating (less delocalised) anions such as triflate, $CF_3SO_3^-$, in which contact between anion and cation persists to the extent that the coordination number of the metal cation is expanded rather than loss of contact with the anion.

Experimental Section

General Remarks: All manipulations were carried out under an atmosphere of dry argon using standard Schlenk and glove-box techniques. Solvents were purified by conventional procedures and distilled prior to use. $LiNTf_2$ was purchased from Aldrich and used as received, without further purification. The ligand systems were prepared using standard literature techniques or purchased from Aldrich.

Solution ^{1}H, ^{19}F and ^{31}P NMR experiments were performed at ambient temperature using a Varian 400 or a Bruker Advance-300 Spectrometer. ^{1}H NMR chemical shifts are referenced to $SiMe_4$, and ^{31}P NMR shifts relative to 85% H_3PO_4. All chemical shifts (δ) are in ppm and coupling constants in Hz.

[NH_4][NTf_2]: Ammonia gas was bubbled through an ethereal solution (50 mL) of bis(trifluoromethylsulfonyl)amine (Tf_2NH; 10 mmol, 2.8 g) for 10 min. The solvent was then allowed to evaporate at room temperature, yielding a white crystalline material which was isolated and washed with hexane (3 × 5 mL). Yield: 2.9 g (98%). Colourless blocks. $C_2H_4F_6N_2O_4S_2$ (298.2): calcd. C 8.1, H 1.4, N 9.4; found C 8.1, H 1.3, N 9.9.

The lithium complexes **1**−**5** were prepared using standard procedures for both the direct and in situ synthesis, examples of both procedures are given below.

[(Tf_2N)Li·N(H)Ph_2Me] (1). (in situ Method): Methyldiphenyliminophosphorane (0.22 g, 1 mmol) was added to a suspension of ammonium trifluoromethanesulfonimide (0.30 g, 1 mmol) in 5 mL of toluene. The mixture was stirred for 20 min at room temperature, and then cooled to −78 °C. One mole-equivalent of *n*BuLi (0.63 mL, 1.6 M) was then added to the cooled suspension. Warming to room temperature caused the solution to undergo several colour changes, and a fine colourless precipitate to be deposited on the walls of the vessel. The precipitate was re-dissolved by heating, and the solution was left to cool to room temperature to yield a crop of crystals, which where isolated by filtration and washed with 5 mL of cold hexane and dried in vacuo. Yield: 0.30 g (60%). Colourless blocks. Mp: 120−122 °C. $C_{15}H_{14}F_6LiN_2O_4P_1S_2$ (502.3): calcd. C 35.9, H 2.8, N 5.6; found C 36.2, H 3.2, N 4.9. ^{1}H NMR (400 MHz, 23 °C, C_6D_6): δ = 1.11 (s, 1 H, N*H*), 1.45 (d, $^2J_{P,H}$ = 13.3 Hz, 3 H, P−CH_3), 6.8−7.0 (m, 6 H, *m*- & *p*- aromatic C*H*), 7.1−7.3 (m, 4 H, *o*-aromatic C*H*) ppm. ^{19}F NMR (376 MHz, 23 °C, C_6D_6): δ = −79.9 (s, CF_3) ppm. ^{31}P NMR (162 MHz, 23 °C, C_6D_6): δ = 33.7 (s, Ph_2Me*P*NH) ppm.

(Direct Method): A toluene solution (2 mL) of methyldiphenyliminophosphorane (0.22 g, 1 mmol) was added to a sample of *N*-lithiotrifluoromethanesulfonimide (0.29 g, 1 mmol) in 2 mL of toluene. The reaction was stirred for 1 h under an argon atmosphere and a further 3 mL of toluene was added. The mixture was then heated to reflux, to aid dissolution, and the solution left to crystallise at room temperature to yield a crop of crystals suitable for X-ray analysis, which where isolated by filtration and washed with 5 mL of cold hexane and dried in vacuo. Yield: 0.36 g (71%). Analysis showed the product to be identical to that prepared by the in situ method.

[(Tf_2N)Li·N(H)PPh_3] (2): Triphenyliminophosphorane (0.28 g, 1 mmol). in situ method: yield 0.30 g (60%); direct method: yield 0.37 g (73%). Colourless blocks. Mp: 85−87 °C. $C_{20}H_{16}F_6Li_1N_2O_4P_1S_2$ (564.4): calcd. C 42.5, H 2.9, N 5.0; found C 43.2, H 3.34, N 4.8. ^{1}H NMR (400 MHz, 23 °C, C_6D_6): δ = 1.35 (s, 1 H, N*H*), 7.0−7.2 (m, 9 H, *m*- & *p*- aromatic C*H*), 7.4−7.6 (m, 6 H, *o*-aromatic C*H*) ppm. ^{19}F NMR (376 MHz, 23 °C, C_6D_6): δ = −79.7 (s, CF_3) ppm. ^{31}P NMR (162 MHz, 23 °C, C_6D_6): δ = 33.0 (s, Ph_3*P*NH) ppm.

Table 1. Crystallographic data for $[NH_4][NTf_2]$ and compounds **1**, **3**, **4** and **5**

Compound	$[NH_4][NTf_2]$	$[(Tf_2N)Li{\cdot}N(H)PPh_2Me]$ (1)	$[(Tf_2N)Li{\cdot}TMEDA]$ (3)	$[(Tf_2N)Li{\cdot}PMDETA]$ (4)	$[(Bz\text{-}TAC)_2Li][NTf_2]$ (5)
Formula	$C_2H_4F_6N_2O_4S_2$	$C_{15}H_{14}F_6LiN_2O_4PS_2$	$C_{16}H_{32}F_{12}Li_2N_6O_8S_4$	$C_{11}H_{23}F_6LiN_4O_4S_2$	$C_{50}H_{54}F_6LiN_7O_4S_2$
Molecular weight	298.19	502.31	806.64	460.39	1002.06
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Orthorhombic	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	*Pnba*	$P\bar{1}$	$P\bar{1}$	*Pcab*	$P\bar{1}$
a (Å)	13.0150(2)	8.988(4)	8.9560(2)	13.48100(10)	11.2890(2)
b (Å)	13.8460(2)	11.094(4)	9.6970(2)	16.4720(2)	11.6820(2)
c (Å)	22.1410(3)	11.858(5)	10.7950(3)	18.3100(2)	21.1100(5)
α (°)		67.90(3)	81.4230(10)		97.5620(10)
β (°)		77.14(2)	75.6930(10)		97.1280(10)
γ (°)		69.02(2)	70.9400(10)		111.8580(10)
U (Å^3)	3989.93(10)	1017.6(7)	856.23(4)	4065.90(7)	2515.60(9)
Z	16	2	1	8	2
D_c (g cm^{-3})	1.986	1.639	1.564	1.504	1.323
μ (mm^{-1})	0.629	0.420	0.389	0.339	0.179
F(000)	2368	508	412	1904	1048
Crystal size (mm)	0.32 × 0.20 × 0.10	0.20 × 0.10 × 0.10	0.25 × 0.15 × 0.13	0.13 × 0.10 × 0.08	0.38 × 0.25 × 0.25
Theta range (°)	3.81 to 25.57	3.66 to 24.28	3.77 to 27.47	3.75 to 27.50	3.78 to 27.47.
Reflections collected	39131	4004	12900	73535	39239
Independent reflections	3705 [*R*(int) = 0.0532]	2864 [*R*(int) = 0.0448]	3903 [*R*(int) = 0.0492]	4657 [*R*(int) = 0.0828]	11382 [*R*(int) = 0.0866]
Reflections [$I > 2\sigma(I)$]	3096	2221	3328	3748	6163
Data/restraints/parameters	3705/0/322	2864/0/286	3903/0/222	4657/0/259	11382/0/635
Goodness-of-fit on F^2	1.056	1.132	1.041	1.034	0.967
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0329, 0.0770	0.0852, 0.1851	0.0395, 0.1005	0.0427, 0.1032	0.0536, 0.1037
Final *R*1, *wR*2 (all data)	0.0425, 0.0828	0.1124, 0.2010	0.0475, 0.1066	0.0583, 0.1125	0.1272, 0.1250
Max, min diff. (e·Å^{-3})	0.444, −0.395	0.394, −0.406	0.564, −0.390	0.604, −0.491	0.325, −0.500

$[(Tf_2N)Li{\cdot}TMEDA]$ (3): *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (0.15 mL, 0.12 g, 1 mmol); in situ method: yield 0.28 g (69%); direct method: yield 0.4 g (85%). Colourless blocks. Mp: 110−112 °C. $C_8H_{16}F_6Li_1N_3O_4S_2$ (403.3): calcd. C 23.8, H 4.0, N 10.4, Found: calcd. C 23.6, H 4.0, N 10.9. ^{1}H NMR (400 MHz, 23 °C, C_6D_6): δ = 1.8 (br. s, 4 H, NCH_2CH_2N), 1.9 (br. s, 12 H, N−CH_3) ppm. ^{19}F NMR (376 MHz, 23 °C, C_6D_6): δ = −80.0 (s, CF_3) ppm.

$[(Tf_2N)Li{\cdot}PMDETA]$ (4): *N*,*N*,*N*′,*N*′′,*N*′′-Pentamethyldiethylenetriamine (0.20 mL, 0.17 g, 1 mmol); in situ method: yield 0.34 g (74%); direct method: yield 0.38 g (83%). Colourless blocks. Mp: 122−123.5 °C. $C_{11}H_{23}F_6LiN_4O_4S_2$ (460.4): calcd. C 28.7, H 5.0, N 12.2; found C 28.8, H 5.1, N 12.3. ^{1}H NMR (400 MHz, 23 °C, C_6D_6): δ = 2.19 (s, 12 H, NMe_2), 2.23 (s, 3 H, N*Me*), 2.28−2.56 [br. m, 8 H, (Me_2NCH_2CH_2)NMe] ppm. ^{19}F NMR (376 MHz, 23 °C, C_6D_6): δ = −78.9 (s, CF_3) ppm.

$[(Bz\text{-}TAC)_2Li][NTf_2]$(5): *N*-tribenzyltriazocyclohexane (0.36 g, 1 mmol); in situ method: yield 0.36 g (36% with respect to Li); direct method: yield 0.48 g (48% with respect to Li). Colourless blocks. Mp: 141−143 °C. $C_{50}H_{54}F_6Li_1N_7O_4S_2$ (1002.1): calcd. C 59.9, H 5.4, N 9.8; found C 59.9, H 5.6, N 9.8. ^{1}H NMR (400 MHz, 23 °C, $CDCl_3$): δ = 3.32 (br. s, 12 H, N−CH_2-N), 3.46 (br. s, 12 H, N−CH_2-Ph), 7.1−7.4 (br. m, 30 H, aromatic-C*H*) ppm. ^{19}F NMR (376 MHz, 23 °C, $CDCl_3$): δ = −78.8 (s, CF_3) ppm.

X-ray Crystallographic Study: Suitable single crystals of $[NH_4][NTf_2]$ and compounds **1**, **3**, **4** and **5** were mounted on glass fibres using perfluoroether oil. Data collections were carried out on an Enraf Nonius Kappa CCD diffractometer, equipped with a Oxford Cryosystems cooling device, and graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). Data were corrected for Lorentz and polarisation effects and for absorption. The structures were solved by direct methods, and refined using full-matrix least-squares on F^2 with all non-hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms were included at calculated positions throughout and refined using a riding model, with U_{iso} set to 1.2-times (1.5-times for methyl-H) U_{equiv} of the carrier atom, with the exception of the nitrogen-bound hydrogen atoms in $[NH_4][NTf_2]$. In the final stages of refinement a weighting scheme was introduced and refinement continued until convergence was achieved. Programs used were SHELXS-86[31] and SHELXL-97.[32] Experimental data relating to all the structure determinations are presented in Table 1.

CCDC-212575−212579 ($[NH_4][NTf_2]$, **1**, **3**, **4** and **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors would like to thank the EPSRC (studentship to P.D.B, JREI Award for M.G.D.) and the Royal Society (Industrial Fellowship for M.G.D.).

[1] [1a] *Organometallics in Synthesis* (Ed.: M. Schlosser), J. Wiley & Son, New York, 1994. [1b] E. Weiss, *Angew. Chem.* **1993**, *105* 1565−1587; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1501−1523.

[2] [2a] D. R. Armstrong, D. Barr, R. Snaith, W. Clegg, R. E. Mulvey, K. Wade, D. Reed, *J. Chem. Soc., Dalton Trans.* **1987**, 1071−1081. [2b] R. E. Mulvey, *Chem. Soc. Rev.* **1991**, *20*, 167−209. [2c] R. E. Mulvey, *Chem. Soc. Rev.* **1998**, *27*, 339−346.

[3] *Lithium Chemistry* (Eds.: A. M. Sapse and P. von R. Schleyer), Wiley Interscience, New York, London, Sydney, 1996, and references cited therein.

[4] For recent examples see: [4a] L. M. Pratt, A. Streitwieser, *J. Org. Chem.* **2003**, *68*, 2830−2838. [4b] K. W. Henderson, A. R. Kennedy, D. J. MacDougall, *Inorg. Chem.* **2003**, *42*, 2736−2741. [4c] O. Parisel, C. Fressigne, J. Maddaluno, C. Giessner-Prettre, *J. Org. Chem.* **2003**, *68*, 1290−1294.

[5] For recent examples see. [5a] A. Johansson, O. Davidsson, *Chem. Eur. J.* **2001**, *7*, 3461−3465. [5b] A. E. H. Wheatley, *Chem. Soc. Rev.* **2001**, *30*, 265−273. [5c] G. C. Forbes, F. R. Kenley, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, J. A. Parkinson, *Chem. Commun.* **2003**, 1140−1141. [5d] D. R. Armstrong, S. C. Ball, D. Barr, W. Clegg, D. J. Linton, L. C. Kerr, D. Moncrieff, P. R. Raithby, R. J. Singer, R. Snaith, D. Stalke, A. E. H. Wheatley, D. S. Wright, *J. Chem. Soc., Dalton Trans.* **2002**, 2505−2511.

[6] For recent examples see: [6a] H. J. Reich, W. S. Goldenberg, A. W. Sanders, K. L. Jantzi, C. C. Tzschucke, *J. Am. Chem. Soc.* **2003**, *125*, 3509−3521. [6b] J. L. Rutherford, D. Hoffmann, D. B. Collum, *J. Am. Chem. Soc.* **2002**, *124*, 264−271. [6c] R. L. Parsons, J. M. Fortunak, R. L. Dorow, G. D. Harris, G. S. Kauffman, W. A. Nugent, M. D. Winemiller, T. F. Briggs, B. S. Xiang, D. B. Collum, *J. Am. Chem. Soc.* **2001**, *123*, 9135−9143. [6d] I. Keresztes, P. G. Williard, *J. Am. Chem. Soc.* **2000**, *122* 10228−10229.

[7] R. Snaith, D. S. Wright, *Lithium Chemistry* (Eds.: A. M. Sapse and P. von R. Schleyer), Wiley Interscience, New York, London, Sydney, 1996, chapter 8, p 227−293.

[8] [8a] W. H. Meyer, *Adv. Mater.* **1998**, *10*, 439−448. [8b] R. Frech, S. Chintapalli, P. G. Bruce, C. A. Vincent, *Chem. Commun.* **1997**, 157−158. [8c] A. Lauenstein, J. Tegenfeldt, *J. Phys. Chem. B* **1998**, *102*, 6702−6709. [8d] P. G. Bruce, *Phil. Trans. R. Soc., Lon. A* **1996**, *354*, 415−436.

[9] [9a] J. S Yadav, B. V. S. Reddy, D. Narsimhaswamy, K. Narsimulu, A. C. Kunwar, *Tetrahedron. Lett.* **2003**, *44*, 3697−3700. [9b] B. Karimi, W. Maleki, *Tetrahedron. Lett.* **2002**, *43*, 5353−5355. [9c] *Lewis Acids in Organic synthesis* (Ed.: H. Yamamoto), Wiley-VCH, New York, **2000**.

[10] J. L. Nowinski, P. Lightfoot, P. G. Bruce, *J. Mater. Chem.* **1994**, *4*, 1579−1580.

[11] L. Xue, C. W. Padgett, D. D. DesMarteau, W. T. Pennington, *Solid State Sci.* **2002**, *4*, 1535−1545.

[12] G. A. Lawrance, *Chem. Rev.* **1986**, *86*, 17−33.

[13] [13a] F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, *8*, 1. [13b] F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, *8*, 31.

[14] G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond*, Oxford Science Publications, Oxford, **1999**.

[15] A. S. Batsanov, M. G. Davidson, J. A. K. Howard, S. Lamb, C. Lustig, R. D. Price, *Chem. Commun.* **1997**, 1211−1212.

[16] D. R. Armstrong, M. G. Davidson, D. Moncrieff, *Angew. Chem.* **1995**, *107* 514−517; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 478−481.

[17] P. D. Bolton, M. G. Davidson, unpublished results.

[18] *Alkoxo and Aryloxo Derivatives of Metals* (Eds.: D. C. Bradley, R. C. Mehrotra, I. P. Rothwell, A. Singh), Academic Press, London, **2001**.

[19] O. Moers, A. Blaschette, P. G. Jones, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2409−2418.

[20] J. Foropoulos, D. D. DesMarteau, *Inorg. Chem.* **1984**, *23*, 3720−3723.

[21] D. W. Cruickshank, *Inorganic Sulfur Chemistry* (Ed.: G. Nickless) Elsevier, Amsterdam, **1998**.

[22] D. Brouillette, D. E. Irish, N. J. Taylor, G. Perron, M. Odziemkowski, J. E. Desnoyers, *Phys. Chem. Chem. Phys.* **2002**, *4*, 6063−6071.

[23] Indeed, gas-phase ab initio calculations of lithium with PMDETA, and its parent complex DTA, have shown them to have a much greater ability to solvate lithium ions than the TAC [$(CH_2NH)_3$] and Me-TAC [$(CH_2NMe)_3$] ligands. See: E. Kaufmann, J. Gose, P. von R. Schleyer, *Organometallics* **1989**, *8*, 2577−2584.

[24] H. H. Giese, T. Habereder, J. Knizek, H. Nöth, M. Warchhold, *Eur. J. Inorg. Chem.* **2001**, 1195−1205.

[25] [25a] W. Uhl, R. Gerding, F. Hannemann, *Z. Anorg. Allg. Chem.* **1998**, *624*, 937−944. [25b] W. Uhl, F. Hannemann, W. Saak, R. Wartchow, *Eur. J. Inorg. Chem.* **1998**, 921−926. [25c] W. Uhl, M. Koch, S. Pohl, W. Saak, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1619−1626. [25d] M. Westerhausen, B. Rademacher, W. Schwartz, S. Henkel, *Z. Naturforsch., Teil B* **1994**, *49*, 199−210. [25e] W. Uhl, M. Koch, J. Wagner, *Z. Anorg. Allg. Chem.* **1995**, *621*, 249−257. [25f] W. Uhl, U. Schutz, W. Kaim, E. Waldhor, *J. Organomet. Chem.* **1995**, *501*, 79−85.

[26] R. E. A. Dillon, C. L. Stern, D. F. Shriver, *Solid State Ionics* **2000**, *133*, 247−255.

[27] A. Haas, Ch. Klare, P. Betz, J. Bruckmann, C. Kruger, Y. H. Tsay, F. Aubke, *Inorg. Chem.* **1996**, *35*, 1918−1925.

[28] D. R. McFarlane, J. Sun, J. Golding, P. Meakin, M. Forsyth, *Electrochim. Acta* **2000**, *45*, 1271−1278.

[29] D. R. McFarlane, J. Huang, M. Forsyth, *Nature* **1999**, *402*, 792−794.

[30] C. M. Forsyth, D. R. McFarlane, J. Golding, J. Huang, J. Sun, M. Forsyth, *Chem. Mater.* **2002**, *14*, 2103−2108.

[31] G. M. Sheldrick (**1986**). SHELX-86. Program for the solution of crystal structures, Univ. of Göttingen, Germany.

[32] G. M. Sheldrick (**1997**). SHELX-97. *Program for crystal structure refinement*, Univ. of Göttingen, Germany.

Received June 17, 2003

