"Potassium Potassates" Based on Dihydrotriazinide Ligands: Syntheses, Crystal Structures, and Comparison with Other Alkali Metal Dihydrotriazinide Compounds

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A series of dihydro-s-triazinidopotassium complexes have been synthesised and structurally characterised by X-ray diffraction. Two of them, the sesqui-pyridine solvate **2** and the mono-THF solvate **3**, can be classified *in formal terms* as "potassium potassates" in conforming to the structural pattern established previously for the sesqui-THF solvate **1**, the first reported 'ate of this type. Formally complex $[(R_2K)^-]$ anions are linked to K^+ cations in polymeric, zig-zag chain arrangements. Solvate **3** also possesses a unique RK coordination as a direct result of having fewer solvent ligands. DMSO analogue **4** deviates from this uniformity in adopting a centrosymmetric, dimeric $(OK)_2$ ring structure featuring both terminal and bridging DMSO ligands. The dihydro-s-triazinidosodium tris(THF) solvate **5** is found to be a monomer. For comparative purposes, the metal-free, parent triazine molecule **6** has also been subjected to an X-ray crystallographic study: it displays a 1,2-dihydro ring setup as opposed to the 1,4-dihydro alternative existing in the metallo examples. Triazine **6** is also found to form a N−H···Br bridge in the dimeric structure of the lithium bromide bis (THF) solvate **7**, a suspected hydrolysis product from the reaction of dihydro-s-triazinidolithium **8** and magnesium bromide bis(ether) adduct.

Introduction

Primarily through a thirty year long campaign by the Weiss group[1], crystalline organometallate compounds combining an alkali metal with another metal (e.g., Al, Be, Cu, Ga, Mg, Tl, Zn) are now well established. In contrast, 'ate formulations containing an alkali metal in both their cation and anion moieties are meagre by comparison. Only as recently as 1983 was the first lithium lithate, $[Li(THF)_4]^+[R_2Li]^-$ [R = $C(SiMe_3)_3$][2] (notable for its linear C−Li−C anion), structurally characterised. The following year witnessed the structure of the ketimine-based 'ate, $[Li(HMPA)_4]^+[R_6Li_5(HMPA)]^-$ (R = $N{=}CPh_2$), with its contrasting pentanuclear clustered anion[3]. Since then a modest number of other 'ate compositions have appeared including the sodium sodate $[Na(TMEDA)_2(Et_2O)]^+$-$[R_2Na]^-$ [R = $C(SiMe_3)_3$][4] and the sodium lithate $[Na(THF)_6]^+[R_2Li]^-$ [R = (2-pyr)CH(2-pyr)][5]. This paper focuses on "potassium potassates". Characterised by having two distinct types of K centre, this new category of 'ate complex was introduced by our group in 1994 through a communication on the triazine derivative **1**[6]. Unlike the aforementioned 'ates which exist as solvent-separated ion pairs, in formal terms **1** forms a contact ion pair polymer of K^+ cations and $(R_2K)^-$ anions propagated through N−K−N interactions in a zig-zag chain arrangement. Hoping to establish that **1** was not a one-off, we subsequently attempted to prepare a series of such compounds. The results of this study are presented herein. Incidentally, we note that in the intervening period a second potassium potassate has appeared in the literature: $[K(C_6H_6)]^+$-$[\{PhMe_2Si(Me_3Si)_2C\}_2K]^-$ exhibits C_6H_6−K, Ph−K, and C(alkyl)−K interactions in another chain-like polymer[7].

In this paper we describe the synthesis and crystal structure of a further two dihydro-*s*-triazinidopotassium compounds which can be similarly classified as potassium potassates, since their gross structural features and dimensions conform to the pattern found in **1**. Both contain the same substituted triazine ring system as in **1**. Furthermore, the sesquipyridine solvate **2** matches **1** exactly in terms of stoichiometry with pyridine ligands replacing THF ones. Interestingly, the other new potassium potassate **3** is also a THF solvate, but differs from **1** in its K/THF ratio of 2:2 (cf. 2:3 in **1**): however, an analysis of bond lengths and the presence of a unique third type of K centre reveals that it is a genuinely distinct structure, and not simply **1** having "lost" a loosely-bound THF ligand. In a surprising twist, we also report that the DMSO analogue **4** does not belong to this potassium potassate family: its structure departs from the

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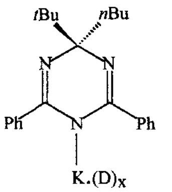
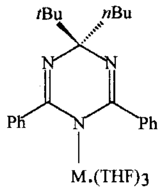


1 : D = THF; x = 1.5

2 : D = Pyr; x = 1.5

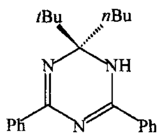
3 : D = THF; x = 1

4 : D = DMSO; x = 2



5 : M = Na

8 : M = Li



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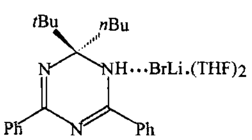

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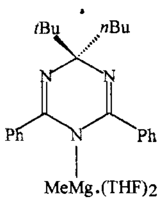

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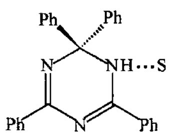


10 : S = EtOH

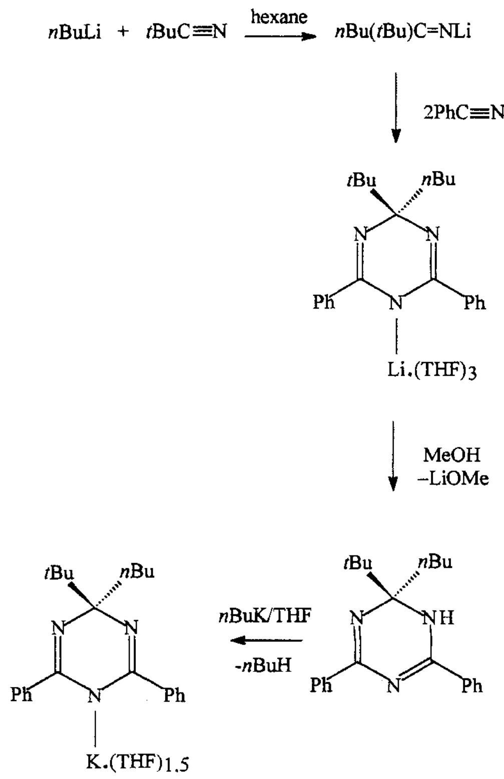
polymeric arrangement of **1**−**3** to a dimeric alternative with a single type of K centre. For comparative purposes, we have additionally examined the corresponding dihydro-*s*-triazinidosodium THF solvate **5**, establishing that its structure has more in common with the previously-reported lithium and magnesium analogues[8], which are both monomeric, than with the aggregated potassium structures. Since all of the aforementioned metallotriazine species are based on the same triazine system, we deemed it appropriate, for completeness, to also record the crystal structure of the metallo-free triazine compound **6** where the metal atom has been replaced by a hydrogen atom. Finally, to our surprise, this neutral triazine molecule also appears in the lithium bromide/THF solvate **7**, an unexpected product from the reaction of the dihydro-*s*-triazinidolithium tris(THF) solvate (containing an anionic triazine ligand) with magnesium bromide bis(ether) adduct: the crystal structure of **7** provides an interesting contrast with those of **1**−**5** as the triazine molecule bonds not to the metal atom, but to the halogen atom through a N−H···Br hydrogen bond.

Results and Discussion

Syntheses

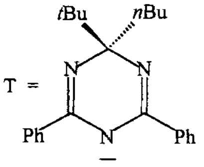
Scheme 1 outlines the general method employed to generate the potassio triazines. It may appear an unduly long-winded approach, preparing a metal triazinide initially only to destroy it subsequently with methanol to afford the dihydrotriazine, which is then remetallated; but our main concern was purity. The cyclotrimerisation process in the first step is not a clean reaction, a problem we found to be greatly exacerbated on using the more reactive *n*-butylsodium or *n*-butylpotassium in place of *n*-butyllithium. Though in the chosen route a mixture of products exists in solution, the dihydro-*s*-triazinidolithium selectively crystallises from it in the form of the tris (THF) solvate **8** in decent yields (70−75%). By isolating these crystals and utilising them in the second step (methanolysis), a pure, preformed dihydro-*s*-triazine ring system, free of contamination by side products of the cyclotrimerisation process, is ensured. Following removal of the lithium methoxide by filtration, protic triazine **6** could be purified itself by recrystallisation from a toluene/THF solvent mixture: the crystals had to be vacuum dried thoroughly to remove weakly bound solvate molecules (methanol and/or THF). Butylpotassium could then be added to **6** at this stage to effect the H/K substitution, which in the presence of about a ten-fold molar excess of THF produced the sesqui-THF solvate **1**. This compound served as the starting material for the preparation of all the other dihydro-*s*-triazinidopotassium compounds. A simple (donor) solvent displacement approach proved successful in forming **2** and **4** from **1**, in which THF was displaced by the more polar solvents pyridine and DMSO, respectively. While this approach failed with 1,4-dioxane, which is still more polar than THF but less so than the other solvent pair, interestingly, however, partial desolvation (formally a loss of 0.5 molar equivalents of THF per K) occurred instead to produce solvate **3**. More conventionally, the well-established transmetallation procedure used to generate alkylsodium compounds from lithium congeners was exploited in preparing the sodium compound **5** from the lithium analogue **8** and sodium *tert*-butoxide.

Scheme 1



Digressing from the study of alkali metal systems, we also explored the possibility of forming a bis(dihydro-*s*-triazinido) magnesium complex through the simple metathetical reaction outlined in Equation 1. This attempted synthesis was prompted by our earlier report of the first crystallographically characterised mono(dihydro-*s*-triazinido) magnesium species **9**[8]. Having already filtered the reaction solution once to remove solid lithium bromide, we were surprised to learn that the crystalline material obtained after work-up was the lithium bromide solvate **7**. Presumably this low-yield product (ca. 8%) originates from (unintentional) hydrolysis. Hitherto, we have not investigated this possibility nor repeated the reaction under more stringently dry conditions. However, since **7** contains a dihydro-*s*-triazine molecule, we decided to determine its crystal structure in order to allow a comparison with the anionic variations in **1**–**5** and with the metal free specimen **6**.

$$2LiT.(THF)_3 + MgBr_2.(Et_2O) \longrightarrow MgT_2 + 2LiBr$$



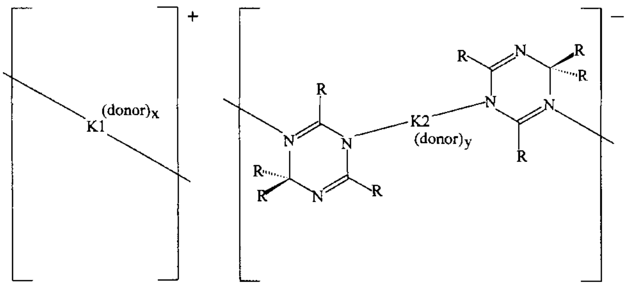
Crystal Structures

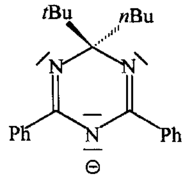
Experimental data for the X-ray crystallographic studies of compounds **2**–**7** are listed collectively in Table 1. Tables 2, 3, and 5–8 give selected bond lengths and bond angles for each individual compound.

Potassio Triazines Belonging to the Potassate Family

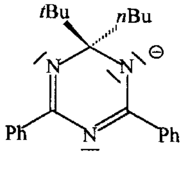
A dihydro-*s*-triazinidopotassium complex can be classified as a potassium potassate if it conforms to the general structural plan (Figure 1), first established by the earlier crystal structure report of the sesqui-THF solvate **1**[6]. To elaborate, there are two distinct K centres: K(1) is a cation as it binds only to formally neutral donor atoms, while K(2) is directly attached to two formally anionic N centres and so belongs within a $[R_2K]^-$ complex anion. In this description, the triazine molecules must exist in a 1,4-dihydro state with the negative charge formally localised on the N site opposite to the saturated C centre, as depicted in the structural formula of **1**. Of course it must be stressed that delocalisation does occur within the π-system of the C_3N_3 ring along the lines suggested by other possible mesomeric forms such as **1b**, **1c**, and **1d**, i.e. all three N centres must carry a partial negative charge in reality. However, the key point in our interpretation is that mesomeric form **1a** dominates, by virtue of the fact that in known molecular alkali metal triazinide structures the metal preferentially binds to the "N^-" site (see also the structure of **4** described later), indicating that it represents the seat of highest electron density. In this sense we feel the description "potassium potassate" is justified. The structures of **2** and **3** fulfil these requirements; therefore, both can be classified as potassium potassates. With regard to the general plan (Figure 1), the only distinction between the structures of **1**–**3** concerns the solvent ligands. In **1**, a single THF molecule binds to K(1), while two bind to K(2). This pattern is repeated in **2** substituting pyridine ligands for THF ones. In contrast, **3** only has two solvent ligands, one on each type of K centre: though as in **1** the solvent is THF, clear differences in the bonding and dimensions of **3**, as discussed below, sets it apart as a separate solvate wholly distinct from **1**.

Figure 1. General plan of dihydrotriazine-based potassium potassate structures marked by two distinct K^+ centres, one anion-free, the other part of a complex $(R_2K)^-$ ion

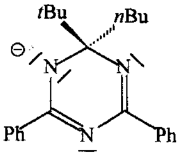




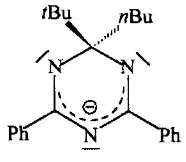
1a



1b



1c



1d

The actual crystal structures of **2** and **3** are shown in Figures 2 and 3 respectively. Both form polymeric zig-zag chains propagated through bis-monodentate, coordination (not chelation) of the triazine ligands via N–K–N interactions. This arrangement leaves one triazine N atom [e.g. N(3)] on each C_3N_3 ring unligated. Consistent with Figure 1, K(1) represents the solvated cation and K(2) belongs within the $[R_2K]^-$ anion: the cation and anion moieties link together to form the contacted ion-pair polymer. Five atoms lie within the coordination sphere of K(1) in both crystal structures: for **2**, 2 N(triazine), 1 N(pyr), and 2 C(*o*Ph); for **3**, 2 N(triazine), 1 O(THF), and 2 C(*o*Ph). The N–K(1)–N chain links are bent by about 30° from linearity. Positioned adjacent to the saturated C atom within the C_3N_3 ring, these N atoms are formally neutral not anionic, in keeping with the solvated cation description of K(1). Additional ligation is provided by one pyridine molecule (in **2**) or one THF molecule (in **3**), and there are also two short K(1)···C(*o*Ph) contacts in each structure. Turning to K(2), this is also five coordinate in both structures, interacting with 2 N(triazine), 2 N(pyr), and 1 C(*o*Ph) atom in **2** and 2 N(triazine), 1 O(THF), and 2 C(*o*Ph) atoms in **3**. It is at this metal centre where the molecular distinction between **3** and the sesqui-solvates **1** and **2** occurs as the former carries only one solvent ligand here whereas the latter pair carry two. To compensate for the "loss" of the solvent ligand, there is an additional K(2)···C(*o*Ph) interaction in **3**. Both N centres within the N−K(2)−N chain links of **2** and **3** are anionic since they sit opposite to the saturated C atom within the dihydro triazine ring. These anionic chain links are also bent, but more so than those involving K(1). Discussion now focuses on key dimensions associated with the metal centres in these structures, and on a comparison with those in **1**.

Figure 2. Section of the polymeric structure of **2**, without hydrogen atoms and with key atoms labelled. Short K···C contacts are indicated by broken lines

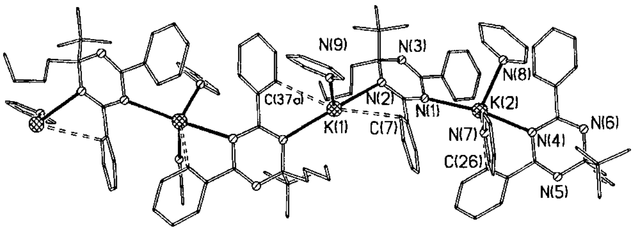
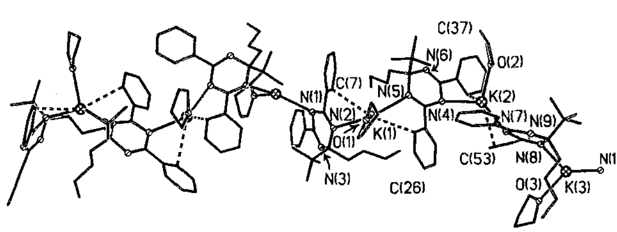


Figure 3. View of a section of 3 similar to that for **2**, but also showing the unique K(3) coordination



Dealing firstly with the K(1)−N(triazine) bond lengths, they cover a narrow range [2.755(2)−2.788(3) Å] over the three potassium potassate structures. Slightly more variation exists in the K(1)−C(*o*Ph) bond lengths of which there are two in each structure (mean values: 3.192, 3.260, and 3.130 Å for **1**, **2**, and **3** respectively). Structure **3** is unique as it also contains a chemically distinct K(3) centre, giving rise to a $-K^+-R_2K^--RK-K^+-R_2K^--RK-$ sequence rather than a $-K^+-R_2K^--K^+-R_2K^--$ one. The bonding at this centre is intermediate to that at K(1) and K(2) as it includes an interaction with one anionic N centre [N(1b): bond length, 2.769(2) Å] and one neutral N centre [N(8): bond length, 2.793(2) Å] (Figure 4). Furthermore, though K(3) like the K(1) centres is ligated by one solvent molecule [THF: bond length, 2.660(2) Å], the nearest C(Ph) atom to it [C(49)] lies over 3.4 Å away, a considerably longer distance than the K(1)−C ones mentioned above. This departure from having two distinct K centres can be directly attributed to the smaller number of solvent ligands attached to K(2) in **3**, i.e., one, compared to two each in **1** and **2**. To make up for this solvation imbalance, in **3** K(2) exerts a greater pull on the adjacent triazine molecule [the one bridging to K(3)] in comparison to that in **1** and **2**: this is manifested in a short K(2)−N(7) bond [length, 2.749(2) Å] (corresponding bonds in **1** and **2** are 2.769(8) and 2.762(3) Å respectively), but more particularly in an additional K(2)−C(53) contact [length, 3.242(3) Å] for which there are no corresponding contacts in the other structures. Hence this leads to a reorganisation of the triazine molecule bridging K(2) and K(3) in **3**, which in turn gives K(3) a unique coordination shell; whereas in **1** and **2**, the metal centre occupying this position is simply the symmetrical equivalent of K(1), i.e., K(1′). Turning next to the K(2)−N(triazine) bond lengths, these cover a wider range over the three structures [2.730(2)−2.869(8) Å] than do those involving K(1). Though these bonds formally contain N anions and not neutral N atoms as in K(1)−N(triazine) bonds, a comparison of mean lengths reveals no marked shortening; indeed, two of the three structures show a modest-lengthening (i.e. 2.837, 2.782, and 2.739 Å cf. 2.766, 2.774, and 2.739 Å, for **1**, **2**, and **3**, respectively). This, coupled with the fact that in both **1** and **2** the two solvent ligands are attached to K(2) in an asymmetric manner [bond lengths: in **1**, K−O, 2.770(11) and 2.703(9); in **2**, K−N(pyr), 2.888(5) and 2.813(7) Å], indicates that the steric environment about K(2) in each structure is extremely delicate, necessitating a compromise between maximising K−heteroatom bonding and minimising van-der-Waals repulsions of the three distinct types of ring system in close proximity. The subtle differences in bond lengths extends to the K(2)···C(*o*Ph) contacts: in **1** the closest contact is 3.433(12) Å, whereas in **2** it is markedly shorter [3.280(4) Å]. However, there is a predictable order to bond dimensions in **3**: two short K(2)···C(*o*Ph) contacts [lengths, 3.242(3) and 3.243(2) Å] are present, a logical consequence of the lower solvation at this site, and the solitary K−O(THF) bond is also shorter [length, 2.651(3) Å] than the pair of such bonds in **1**.

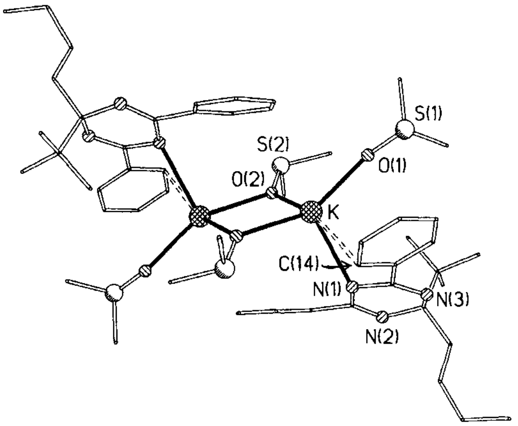
There is a definite pattern to the N−K−N (chain links) bond angles. Without exception, the cationic ones involving K(1) [angles: 147.4(2), 148.40(9), and 150.09(6)° for **1**, **2**, and **3**, respectively] are decidedly more open than the corresponding anionic N−K(2)−N ones [values: 131.8(2), 141.02(9), and 133.16(6)°]. Clearly the discriminating factor here is the steric bulk of the substituents attached to the C atoms directly adjacent to the triazine N atoms concerned: around K(1) sites there are two highly-branched *t*Bu(*n*Bu) and two Ph substituents, which require more room than the four Ph substituents surrounding K(2) sites. Close to only one *t*Bu(*n*Bu) and three Ph substituents, K(3) would be expected to display an angle intermediate to that of K(1) and K(2) in **3**, and this is indeed the case [i.e., 138.81(6)°]. Each pair of K centres in the three structures straddle the mean plane of the μ-C_3N_3 ring they share. The extent of this deviation from planarity varies substantially, ranging from 0.995–2.134 Å, and is generally more pronounced for K(2) centres (mean deviation, 1.669 Å) than for K(1) centres (1.308 Å). In the case of the unique K(3) centre in **3**, the deviations are 1.700 and 2.134 Å. The C_3N_3 rings themselves are not strictly planar, though only in **3** does the distortion appear significant, the largest mean deviation of the ring atoms being 0.083 Å for N(1)C(1)N(2)C(15)N(3)C(8), which significantly binds to K(3) [through N(1)]. Attached Ph substituents tilt out of the C_3N_3 ring planes as evidenced by torsion angles of the type N(1)C(8)C(9)C(14) in **2** (31.7°): the ranges of like torsion angles are 20.3–44.7, 29.5–41.6, and 22.4–33.9° for **1**, **2**, and **3**, respectively.

Table 4 lists the sum of bond angles at each distinct (ligating) dihydro-*s*-triazinide N centre within the three structures, an important consideration in the interpretation of them as potassium potassates. Formally, it could be argued that in an idealised model the neutral donor N centres, participating in C=N double bonds, would assume trigonal planar geometries; while the N anions would be pyramidal. However, in the real systems, the fact that the triazine rings pucker slightly and that the C-attached substituents are bulky mitigates against perfect trigonal planar N geometries, as does the π-delocalisation mentioned earlier. Given these complications the data in Table 4 fit the model rather well in that generally the N "donor" atoms have values approaching 360°, while the N "anions" have considerably lower values indicative of greater pyramidal character. Only donor atom N(2) in structure **3** appears somewhat out of step as its value overlaps with that of anionic N(7). A full analysis of the dimensions within the triazine rings of **1**–**3** is considered separately, further on in the discussion, so as all the triazine entities, including **4**–**7**, can be examined together.

Dihydro-*s*-triazinidopotassium Complex Not Part of the Potassate Family

Bis-DMSO solvate **4** is not a potassium potassate for the simple reason that it contains only one type of K centre within its centrosymmetric structure (Figure 4). It is further distinct in being dimeric (the first alkali metallo triazine reported to be so) rather than polymeric, with self-association occurring through μ-DMSO ligands. Another DMSO ligand binds terminally to the K cation, the four-coordinate environment of which is completed by a single N atom from the triazine molecule. Note that this is the anionic N centre, and as in **1**–**3**, the triazine exists in a 1,4-dihydro state. The remaining two triazinide N atoms are unligated. Another distinctive feature is the central, planar $(OK)_2$ four-membered ring. Whilst generally it is unusual within alkali metal aggregates for solvent molecules to serve as bridges in preference to constituent anions, it is not unprecedented[9]. Indeed, the situation found in **4** mimics that previously established for the sodium phenoxide solvate $[\{Na(OC_6H_3tBu\text{-}2,6)(\mu\text{-}DMSO)(DMSO)\}_2]$[10]. Matilainen and coworkers report in the same paper that DMSO fails to bridge in the corresponding lithium phenoxide solvated dimer (note, however, that the metal:DMSO ratio is 1:1, cf. 1:2 for the Na and K examples). Clearly, this bridging ability of DMSO, made possible by its high polarity, is more likely to be realised where anions are excessively bulky and where cation-cation separations are large (i.e., with heavier alkali metals). The steric bulk of the substituted-triazine anion in **4** can be gauged by its inability to bridge two metal centres through a single N component in the dihydro-*s*-triazinido-metal structures thus far elucidated.

Figure 4. Molecular structure of **4** without hydrogen atoms, showing the atom-numbering scheme. The short K···C(*o*Ph) interaction is highlighted



Two distinct O–Na bond lengths (difference, 0.082 Å) were noted within the central $(\mu\text{-}DMSO\text{-}Na)_2$ ring of the aforementioned phenoxide structure[10]. In contrast, asymmetry in the corresponding $(\mu\text{-}O\text{-}K)_2$ ring of **4** is essentially negligible (difference in bond lengths, 0.014 Å: see Table 5). Its more nearly square appearance is also reflected in the small variation in the endocyclic bond angles [at K, 87.64(6)°; at O, 92.36(6)° cf. in the former structure, at Na, 84.5(2)°; at O, 95.5(2)°]. As expected the terminal DMSO ligand in **4** forms a shorter bond to the K centre (by 0.13 Å on average) than the bridging type. The solitary N–K bond has a length [2.762(2) Å] within the range of (triazine) N–K bond lengths encountered in **1**–**3**. Structure **4** also contains one short K···C(*o*Ph) contact for each metal, measuring 3.324 Å [to C(14)]. Note that the K atom lies 2.069 Å out of the mean plane of the triazine ring (RMS deviation, 0.055 Å), and the dihedral angle between this plane and the strictly planar K_2O_2 ring is 48.1°.

Dihydro-*s*-triazinidosodium Complex

Switching the metal from potassium to sodium profoundly alters the metal triazine structure. Thus, contrary to the polymeric arrangements of THF solvates **1** and **3**, this (THF) solvate **5** prefers a discrete, molecular, contact ion-pair structure with a single metal centre (Figure 5: two independent molecules sharing the same gross structural features were found in the unit cell, but, for brevity, only one is shown). Since **5** is structurally analogous to the Li (**8**) and alkyl Mg (**9**) derivatives, the structural demarcation of alkali metals in this particular series of compound is presumably LiNa/KRbCs as opposed to Li/NaKRbCs, which one might reasonably predict on the basis of the anomalous behaviour of Li quoted often in textbooks[11] (note that we intend to explore the Rb and Cs systems in a follow-up study). It is extremely rare for sodium organics and their lithium congeners to be isostructural: the larger radius of sodium often results in aggregation state differences and/or higher coordination numbers[12]. The similarity observed here is primarily dictated by the special steric characteristics of the substituted triazine anion: the two Ph substituents α to the anionic N centre prevent aggregation and partially shield the metal centre, and by doing so limit the number of solvent ligands that can enter the metal's coordination sphere. With the even larger potassium cation, the steric influence of the Ph substituents is reduced but the solvent–metal interactions are weaker, so stabilisation is not gained through additional solvent ligands but through bridging triazine–K–triazine linkages.

Occupying a distorted tetrahedral environment, the Na$^+$ cation in **5** binds to the triazine's anionic N centre as well as to the O centre of three THF ligands. Table 6 lists the key dimensions pertaining to each independent molecule of this structure: generally there is good agreement between the two corresponding sets of data, but overall they are unremarkable. The only substantial difference is in the extent to which each Na$^+$ cation sits out of the mean triazine ring plane: 1.299 Å for Na(1); 1.800 Å for Na(2) (RMS deviation of ring plane 0.049 Å and 0.066 Å respectively). This means that the incline of the N–Na bonds with respect to the mean ring planes are approximately 33.5° and 50.4° respectively. Corresponding values for the N–Li bond in **8** and the N–Mg bond in **9** are 36.7° and 26.4° respectively.

Lithium Halide Complex Containing the Neutral Triazine Molecule

The protonated (neutral) triazine molecule appears in the crystal structure of the lithium bromide THF-solvated dimer **7**. Now that a proton has formally replaced a metal cation, the triazine ring switches from the 1,4-dihydro state observed in **1**–**5** to the 1,2-dihydro state of the free dihydrotriazine molecule **6** (see below). In earlier work based on ab initio MO calculations, we rationalised this switch in terms of the mechanism of the Li$^+$/H$^+$ exchange process[8]. To elaborate, while the 1,4-dihydro state is thermodynamically favoured irrespective of the identity of the cation, the 1,2-dihydro alternative occurs because the proton source (modelled by MeOH in the calculations) is blocked from attacking the anionic N by the presence of the attached solvated Li$^+$ cation. Instead, it attacks a neutral N atom, initially forming a N···H–OMe hydrogen bond, that develops into the new N–H bond and releases MeO$^-$, which in turn forms MeOLi (see Scheme 1). Trace quantities of water, accidentally left following the drying process, could effect a similar mechanism here in the formation of **7** from the lithio precursor **8**, with the intermediate appearance of a N···H–OH linkage. Metal-free triazine compounds are known to form linkages of this type in adducts with protic acids, e.g. as in the EtOH adduct of tetraaryl-substituted **10**[13].

Figure 6 shows the crystal structure of **7**. A rhomboidal (LiBr)$_2$ ring lies at the core of the discrete centrosymmetric dimer, each Li of which is solvated by a pair of THF ligands. Neutral triazine molecules normally function as N donors in metal complexes as established by a number of crystal structure determinations (e.g., where M = Al[14], Co[15], Cu[16], Pt[17], or Ru[18]). Here, in a departure from this role, there is no contact with the metal centre, instead the dihydro-*s*-triazine molecule binds to the Br$^-$ anion through a N–H···Br hydrogen bond.

Figure 5. One of the independent molecules occupying the unit cell of the crystal structure of **5** (without hydrogen atoms), showing the atom-numbering scheme

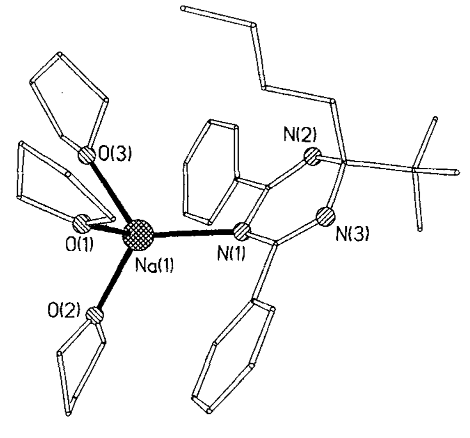


Figure 6. Molecular structure of **7** without C–H hydrogen atoms, showing the atom-numbering scheme. The N–H···Br bridge is highlighted

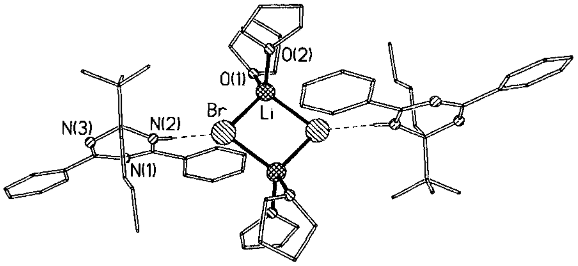
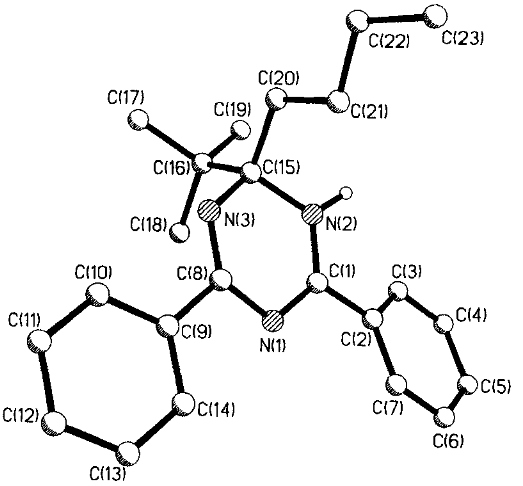


Table 7 lists the key dimensions of **7**. There is no significant variation in the lengths of the two distinct bonds making up the (LiBr)$_2$ ring, with the mean value (2.512 Å) being close to the combined ionic radius for Li$^+$Br$^-$ (i.e. 0.60 + 1.95 = 2.55 Å). Deviation from a square is considerably more pronounced within its endocyclic bond angles, which are sharper at the anionic corners by 23°. Surveying other dimeric lithium bromide complexes, it is apparent that such rings can have a flexible geometry depending on the steric and electronic nature of attached substituents, and therefore on the coordination numbers of the cation and anion. For example, five-coordination of Li$^+$ and two-coordination of Br$^-$ in the triamine adduct [(LiBr · PMDETA)$_2$][19] leads to more unsymmetrical ring edges (i.e., 2.51/3.20 Å; 2.57/2.87 Å: note that two independent dimers occupy the unit cell), and to nearly perpendicular corners (i.e., bond angles: at Li$^+$, 87.7 or 91.5°; at Br$^-$, 92.3 or 88.5°), indicative of reduced Br$^-$···Br$^-$ transannular repulsions. Dimensions within the dimeric (LiBr)$_2$ subunits of the polymeric "broken cube" structure of $[(LiBr \cdot THF)_\infty]$[20], on the other hand, closely resemble those of **7** (i.e., Li−Br bond lengths, range 2.518−2.530 Å: mean endocyclic angles, Li−Br−Li, 78.1°; Br−Li−Br, 101.8°). Clearly the difference in aggregation state here [n = 2 or $(2)_\infty$] is not as important as the similarity in coordination numbers (4 for Li^+ and 3 for Br^- in each structure): this equivalence occurs because the bonds exclusive to **7**, the second Li−O (THF) one and the Br···N−H hydrogen bond, are replaced by a pair of interdimer Li−Br bonds in the polymer. The similarity extends to the Li−O(THF) bond lengths: 1.921 Å (mean) in the former; 1.904 Å in the latter. Coordination effects in other LiBr complexes have been noted by Veith in his discussion of bimetallic $[\{Sn_2[N(H)tBu]_2Br_2\}_2 \cdot Li_2Br_2 \cdot 4\ tBuNH_2]$[21], which is notable for having short hydrogen bridges [2.85(3) Å] to Br of type Br···H−N. Such bridges are also a feature of **7**: their shortness (Br···H, 2.658 Å) reflects the low coordination number of the anion, and the hydrogen-bonding ability of dihydrotriazine molecules, previously demonstrated in a series of crystallographically-characterised solvates. The Br···H−N bond angle is 167.4°. Longer Br···H−N interactions (mean length, 3.0 Å) have also been found in the polymeric chain structure of $[(LiBr \cdot H_2NCH_2CH_2NH_2)_\infty]$[22]. Note also that the RMS deviation of the six atoms of the triazine ring is 0.076 Å. Excluding the saturated C atom [C(15)] the other five atoms are almost coplanar (RMS deviation 0.026 Å), and C(15) lies 0.290 Å out of this plane, giving an envelope appearance for the ring. The phenyl substituents are twisted by 4.5° and 15.6° relative to the mean C_3N_3 ring plane.

Parent Dihydrotriazine Molecule and Comparison with C_3N_3 Rings of 1−5 and 7

The crystal structure of the parent dihydro triazine **6** revealed a 1,2-dihydro arrangement (Figure 7), consistent with that identified in the lithium bromide complex **7**. Again the C_3N_3 ring is not quite planar (RMS deviation, 0.065 Å). Without the saturated C atom [C(15)], the other five ring atoms form a better plane (RMS deviation falling to 0.014 Å): C(15) lies 0.264 Å out of this plane to give the ring an envelope appearance with the flap at this atom. The phenyl substituents are twisted by 10.1° and 19.4° relative to the mean C_3N_3 ring plane. Unlike in **7**, no hydrogen-bonding is present, and there are no significant intermolecular interactions except normal van der Waals contacts.

Figure 7. Molecular structure of **6** showing the atom-numbering scheme. All hydrogen atoms except the N−H one are omitted



Turning to bond lengths within the C_3N_3 ring, Table 9 compares the values obtained for each individual type of C−N bond over the complete series of *n*-butyl-*tert*-butyl-bis(phenyl)-substituted dihydro triazine compounds. Ranging from 1.289−1.308 Å, the short double bonds can be clearly identified, their positions confirming the distinction between the 1,2-dihydro and 1,4-dihydro set-ups. The mean bond lengths listed for the latter compounds are remarkably consistent, a measure of the insensitivity of the triazine anion to the identity of the attached cation (Na^+ or K^+) and to the number of N centres ligating these cations (1 or 2). Thus the bonding is essentially ionic. As far as the former compounds are concerned, the major point of interest is the substantial contraction (by 0.138 Å) of the bond labelled "6-1", produced when the parent triazine molecule **6** forms the N−H···Br bridge to the lithium bromide THF solvate **7**. This is consistent with the development of a polarised $N^{\delta-}-H^{\delta+}$ linkage, and delocalisation of the additional negative charge through the π-system to the adjacent sp^2 C atom (the alternative adjacent C atom, which is chiral, is sp^3 hybridised and saturated). No other ring bonds are affected by this hydrogen-bonding action, as evidenced by the near-equivalence in the lengths of the corresponding bonds in **6** and **7**. This similarity extends to the angular dimensions within their $C_3N_3(H)$ rings, with values for each corresponding bond angle being within experimental error of each other (compare Table 7 and 8). Those at the N corners divide into three distinct categories: large at the N(H) position, intermediate at the other N centre adjacent to the sp^3 C atom, and small at the remaining N atom (mean values over the two structures, 122.0, 118.8, and 114.4°). Bond angles at the C corners are similarly distinct: mean values 127.8, 123.2°, and at the sp^3 centre 109.9°. Angular dimensions across the series of metallo 1,4-dihydro C_3N_3 rings also show little variation, as evidenced by the data listed in Tables 2, 3, 5, and 6. Each distinct ring displays the following pattern: anionic N corner (typically 112°), two remaining N corners (both typically about 117°), sp^3 C corner (typically 115°) and two remaining C corners (both typically about 128°). The main distinction with the aforementioned bond angles of **6** and **7** is the greater tetrahedral distortion at the saturated C atom, which is a logical consequence of having two adjacent Ph substituents as opposed to one Ph and one hydrogen substituent.

We express our gratitude to the *EPSRC* for financial support and to a very thorough referee for his helpful comments.

Experimental Section

Syntheses and Analyses: Solvents were dried by standard techniques and reagents were purchased from the Aldrich Chemical Co. and used as supplied. All manipulations were carried out under a

Table 1. Crystallographic data for compounds **2**–**7**

Compound	**2**	**3**	**4**	**5**	**6**	**7**
formula	$C_{61}H_{71}K_2N_9$	$C_{81}H_{108}K_3N_9O_3$	$C_{54}H_{80}K_2N_6O_4S_4$	$C_{35}H_{52}N_3NaO_3$	$C_{23}H_{29}N_3$	$C_{62}H_{90}Br_2Li_2O_4$
formula weight	1008.5	1373.1	1083.7	585.8	347.5	1157.1
crystal size [mm]	0.47×0.36×0.35	0.78×0.66×0.22	0.61×0.60×0.42	0.47×0.42×0.20	0.80×0.53×0.52	0.80×0.69×0.66
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	Pc	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a [Å]	11.179(2)	21.0635(10)	9.1469(8)	21.283(4)	12.1441(15)	10.9816(9)
b [Å]	18.472(3)	10.0194(5)	19.138(2)	15.864(3)	12.3859(15)	25.377(2)
c [Å]	27.950(5)	20.3912(10)	17.178(2)	21.847(4)	13.099(2)	11.2391(9)
β [°]	93.880(5)	115.298(2)	93.730(2)	109.549(3)	91.608(3)	99.984(2)
V [Å^3]	5758.4(17)	3890.7(3)	3000.7(5)	6951(2)	1969.5(4)	3084.7(4)
Z	4	2	2	8	4	2
density (calcd) [g/cm^3]	1.163	1.172	1.199	1.120	1.172	1.246
μ [mm^{-1}]	0.210	0.227	0.343	0.081	0.069	1.363
F(000)	2152	1476	1160	2544	752	1224
θ_{max} [°]	26.46	26.36	25.51	25.58	25.58	25.71
maximum indices hkl	13, 22, 34	26, 12, 25	11, 22, 19	25, 19, 26	13, 13, 15	13, 30, 13
reflections measured	30848	21061	12450	29537	8311	13424
unique reflections	11541	13022	4940	11597	3198	5297
weighting parameters a, b	0.0520, 6.8947	0.0306, 1.3884	0.0348, 2.7079	0.0692, 10.0717	0.0392, 0.5237	0.0385, 1.9065
refined parameters	668	888	345	861	243	351
R_w (all data)	0.2069	0.0898	0.1174	0.2387	0.0958	0.0922
R (observed data)	0.0783 (7405)	0.0354 (12331)	0.0462 (4396)	0.0959 (7039)	0.0363 (2968)	0.0343 (4859)
goodness of fit	1.168	1.135	1.093	1.142	1.090	1.079
Max. electron density [e/Å^3]	0.49	0.54	0.54	0.86	0.18	0.39

Table 2. Selected bond lengths [Å] and angles [°] for **2**[a]

K(1)–N(2)	2.760 (3)	K(1)–N(6a)	2.788(3)
K(1)–N(9)	2.805 (4)	K(1)–C(7)	3.206(4)
K(1)–C(37a)	3.314(3)	K(2)–N(4)	2.762(3)
K(2)–N(1)	2.803(3)	K(2)–N(8)	2.813(7)
K(2)–N(7)	2.888(5)	K(2)–C(26)	3.280(4)
N(1)–C(1)	1.358(4)	N(1)–C(8)	1.375(4)
N(2)–C(1)	1.294(4)	N(2)–C(15)	1.483(4)
N(3)–C(8)	1.283(4)	N(3)–C(15)	1.463(4)
N(4)–C(31)	1.356(4)	N(4)–C(24)	1.379(4)
N(5)–C(24)	1.288(4)	N(5)–C(38)	1.475(5)
N(6)–C(31)	1.299(4)	N(6)–C(38)	1.485(4)
N(2)–K(1)–N(6a)	148.40(9)	N(2)–K(1)–N(9)	101.55(10)
N(6a)–K(1)–N(9)	106.68(10)	N(4)–K(2)–N(1)	141.02(9)
N(4)–K(2)–N(8)	96.23(14)	N(1)–K(2)–N(8)	108.4(2)
N(4)–K(2)–N(7)	97.09(12)	N(1)–K(2)–N(7)	116.00(11)
N(8)–K(2)–N(7)	80.6(2)	C(1)–N(1)–K(2)	113.7(2)
C(8)–N(1)–K(2)	121.2(2)	C(1)–N(2)–C(15)	117.0(3)
C(1)–N(2)–K(1)	112.7(2)	C(15)–N(2)–K(1)	124.3(2)
C(8)–N(3)–C(15)	117.9(3)	N(2)–C(1)–N(1)	128.9(3)
N(3)–C(8)–N(1)	128.5(3)	N(3)–C(15)–N(2)	115.3(3)
C(31)–N(4)–C(24)	113.1(3)	C(31)–N(4)–K(2)	125.6(2)
C(24)–N(4)–K(2)	112.1(2)	C(24)–N(5)–C(38)	116.7(3)
C(31)–N(6)–C(38)	116.7(3)	C(31)–N(6)–K(1b)	119.0(2)
C(38)–N(6)–K(1b)	118.7(2)	N(5)–C(24)–N(4)	128.6(3)
N(6)–C(31)–N(4)	128.3(3)	N(5)–C(38)–N(6)	116.0(3)

[a] Symmetry transformation used to generate equivalent atoms: a: $x, -y + 3/2, z - 1/2$; b: $x, -y + 3/2, z + 1/2$.

protective argon blanket either in a double-manifold argon/vacuum line or in an argon-filled recirculating glove box.

^{1}H-NMR spectra were recorded at room temperature on a Bruker AMX 400 spectrometer. C, H, and N analysis was performed by use of a Perkin-Elmer 240 elemental analyser, and metal analysis was carried out by atomic absorption spectroscopy by use of a PU 9100 Philips spectrometer.

2: Potassium potassate **1** was made as described previously[6]. Freshly prepared solid **1** (2.47 g, 5 mmol) was dissolved in a hexane/pyridine (5 ml:5 ml) mixture to give a yellow solution. No crystallisation occurred on maintaining the solution at ambient temperature for three days. Solvents were removed in vacuo and replaced by a toluene/pyridine (10 ml:2 ml) mixture to give another solution which deposited a yellow powder after one day. Further addition of pyridine (1 ml) effected redissolution. Subsequent cooling to 3 °C for one day yielded pale yellow rectangular crystals, which were dried in vacuo, and identified as **2**: yield 1.60 g, 64%. – M.p. 109–111 °C. – ^{1}H NMR (400 MHz, [D$_5$]pyridine, 25 °C, TMS): δ = 0.76 (t, 3 H, CH$_3$-*n*Bu), 1.40 (m, 2 H, γCH$_2$-*n*Bu), 1.61 (s, 9 H, *t*Bu), 1.91 (m, 2 H, βCH$_2$-*n*Bu), 2.19 (m, 2 H, αCH$_2$-*n*Bu), 7.31 (t, 3 H, βPyr), 7.42 (t, 2 H, *p*Ph), 7.49 (t, 4 H, *m*Ph), 7.70 (t, 1.5 H, γPyr), 8.74 (m, 3 H, αPyr), 8.94 (d, 4 H, *o*Ph). – $C_{30.5}H_{35.5}N_{4.5}K$ (503.5): calcd. C 72.6, H 12.5, N 7.5, K 7.8; found C 71.7, H 12.0, N 7.3, K 7.3%.

3: 1,4-dioxane (3 ml) was added to a suspension of **1** (2.47 g, 5 mmol) in hexane (5 ml) to produce a yellow solution, which failed to yield a solid over six days. Solvents were replaced by toluene (5 ml) to give a solution that deposited poor quality crystals on standing at room temperature. The crystals were redissolved by the addition of more dioxane (1 ml), but again only poor quality crystals were forthcoming. Finally, solvents were replaced by a hexane/dioxane (5 ml:3 ml) mixture and the yellow solution left at ambient temperature for five days, at which time a crop of X-ray quality yellow crystals were obtained: yield 1.00 g 43.7%. – M.p. 112–114 °C. – ^{1}H NMR (400 MHz, [D$_5$]pyridine, 25 °C, TMS): δ = 0.75 (t, 3 H, CH$_3$-*n*Bu), 1.40 (m, 2 H, γCH$_2$-*n*Bu), 1.58 (s, 9 H, *t*Bu), 1.72 (t, 4 H, THF), 1.88 (m, 2 H, βCH$_2$-*n*Bu), 2.16 (m, 2 H, αCH$_2$-*n*Bu), 3.72 (t, 4 H, THF), 7.41 (t, 2 H, *p*Ph), 7.48 (t, 4 H, *m*Ph), 8.92 (d, 4 H, *o*Ph). – $C_{27}H_{36}N_3OK$ (441): calcd. C 70.8, H 9.2, N 8.0, K 8.6; found C 68.5, H 8.9, N 7.9, K 8.3.

4: DMSO (0.65 ml, 9.2 mmol) was added dropwise to a slightly warm solution of **1** (1.23 g, 2.5 mmol) in toluene (5 ml). Cooling of the resulting yellow/green solution led to the formation of an oily lower layer, which deposited a small quantity of crystals. These were redissolved to a homogeneous solution by addition of more THF (1 ml) with gentle warming. Maintaining the solution at

Table 3. Selected bond lengths [Å] and angles [°] for **3**[a]

K(1)–O(1)	2.695(2)	K(1)–N(5)	2.755(2)
K(1)–N(2)	2.782(2)	K(1)–C(26)	3.109(2)
K(1)–C(7)	3.151(2)	K(2)–O(2)	2.651(3)
K(2)–N(4)	2.730(2)	K(2)–N(7)	2.749(2)
K(2)–C(53)	3.242(3)	K(2)–C(37)	3.243(2)
K(3)–O(3)	2.660(2)	K(3)–N(1b)	2.769(2)
K(3)–N(8)	2.793(2)	N(1)–C(1)	1.364(3)
N(1)–C(8)	1.373(3)	N(2)–C(1)	1.298(3)
N(2)–C(15)	1.477(3)	N(3)–C(8)	1.289(3)
N(3)–C(15)	1.476(3)	N(4)–C(24)	1.365(3)
N(4)–C(31)	1.372(3)	N(5)–C(24)	1.299(3)
N(5)–C(38)	1.482(3)	N(6)–C(31)	1.288(3)
N(6)–C(38)	1.473(3)	N(7)–C(47)	1.361(3)
N(7)–C(54)	1.370(3)	N(8)–C(47)	1.302(3)
N(8)–C(61)	1.474(3)	N(9)–C(54)	1.295(3)
N(9)–C(61)	1.475(3)		
O(1)–K(1)–N(5)	108.21(6)	O(1)–K(1)–N(2)	98.46(6)
N(5)–K(1)–N(2)	150.09(6)	O(2)–K(2)–N(4)	107.56(8)
O(2)–K(2)–N(7)	107.80(7)	N(4)–K(2)–N(7)	133.16(6)
O(3)–K(3)–N(1b)	115.65(6)	O(3)–K(3)–N(8)	101.36(6)
N(1b)–K(3)–N(8)	138.81(6)	C(1)–N(1)–C(8)	111.7(2)
C(1)–N(1)–K(3a)	115.70(15)	C(8)–N(1)–K(3a)	117.75(13)
C(1)–N(2)–C(15)	116.0(2)	C(1)–N(2)–K(1)	110.74(14)
C(15)–N(2)–K(1)	123.15(13)	C(8)–N(3)–C(15)	116.1(2)
N(2)–C(1)–N(1)	128.4(2)	N(3)–C(8)–N(1)	128.6(2)
N(3)–C(15)–N(2)	114.3(2)	C(24)–N(4)–C(31)	112.2(2)
C(24)–N(4)–K(2)	128.00(14)	C(31)–N(4)–K(2)	104.31(13)
C(24)–N(5)–C(38)	116.3(2)	C(24)–N(5)–K(1)	117.04(14)
C(38)–N(5)–K(1)	124.32(12)	C(31)–N(6)–C(38)	117.2(2)
N(5)–C(24)–N(4)	128.7(2)	N(6)–C(31)–N(4)	128.4(2)
N(6)–C(38)–N(5)	114.7(2)	C(47)–N(7)–C(54)	112.6(2)
C(47)–N(7)–K(2)	112.39(13)	C(54)–N(7)–K(2)	124.85(14)
C(47)–N(8)–C(61)	116.2(2)	C(47)–N(8)–K(3)	126.07(15)
C(61)–N(8)–K(3)	115.90(12)	C(54)–N(9)–C(61)	116.6(2)
N(8)–C(47)–N(7)	128.5(2)	N(9)–C(54)–N(7)	128.4(2)
N(8)–C(61)–N(9)	115.7(2)		

[a] Symmetry transformations used to generate equivalent atoms: a: $x + 1, -y + 1, z + 1/2$; b: $x - 1, -y + 1, z - 1/2$.

−5 °C for one day yielded rhomboidal crystals of the product: yield 0.20 g, 14.8%. – M.p. 130–132 °C. – ^{1}H NMR (400 MHz, [D$_5$]pyridine, 25 °C, TMS): δ = 0.75 (t, 3H, CH$_3$-*n*Bu), 1.40 (m, 2H, γCH$_2$-*n*Bu), 1.59 (s, 9H, *t*Bu), 1.89 (m, 2H, βCH$_2$-*n*Bu), 2.15 (m, 2H, αCH$_2$-*n*Bu), 2.50 (s, 12H, DMSO), 7.39 (t, 2H, *p*Ph), 7.47 (t, 4H, *m*Ph), 9.03 (d, 4H, *o*Ph). – $C_{27}H_{40}N_3S_2O_2K$ (541): calcd. C 59.8, H 7.5, N 7.8, K 7.2; found C 59.8, H 5.5, N 7.7, K 6.9.

5: A mixture of the lithium dihydrotriazinide **8** (made as described previously[8]) and sodium *tert*-butoxide was treated with THF (5 ml) and stirred for thirty minutes. Refrigeration (to −30 °C) of the resulting greenish yellow solution afforded a slight precipitate which was redissolved on addition of hexane (5 ml). On controlled cooling by standing the solution in a water bath at ambient temperature yellow needle crystals of the product were obtained: yield 1.84 g, 62.9%. – M.p. 84 °C (decomp.). – ^{1}H NMR (400 MHz, [D$_5$]pyridine, 25 °C, TMS): δ = 0.77 (t, 3H, CH$_3$-*n*Bu), 1.41 (m, 2H, γCH$_2$-*n*Bu), 1.58 (s, 9H, *t*Bu), 1.76 (t, 12H, THF), 1.84 (m, 2H, βCH$_2$-*n*Bu), 2.16 (m, 2H, αCH$_2$-*n*Bu), 3.74 (t, 12H, THF), 7.43 (m, 6H, *m*/*p*Ph), 8.82 (d, 4H, *o*Ph). – $C_{35}H_{52}N_3O_3Na$ (585): calcd. C 71.7, H 9.0, N 7.2, Na 3.9; found C 67.4, H 8.8, N 7.3, Na 3.0.

6: The lithium dihydrotriazinide **8** (25.0 g, 43.9 mmol) was dissolved in a methanol/THF [10 ml (246.9 mmol):10 ml] mixture and refluxed gently for five hours. Solvents were then replaced by toluene (15 ml), and the light yellow mixture filtered to remove precipitated LiOMe. The filtrate volume was reduced until cloudy, at which time a few drops of THF were added to re-establish homogeneity. Colourless crystals were obtained on leaving the solution standing at ambient temperature for one day. These crystals were washed with hexane and dried for a number of hours in vacuo to remove any weak solvate molecules: yield 10.83 g, 71.0%. – M.p. 122–124 °C. – ^{1}H NMR (400 MHz, [D$_5$]pyridine, 25 °C, TMS): δ = 0.70 (t, 3H, CH$_3$-*n*Bu), 1.29 (m, 11H, *t*Bu/γCH$_2$-*n*Bu), 1.61 (m, 2H, βCH$_2$-*n*Bu), 1.75 (t, 1H, αCH-*n*Bu), 2.06 (t, 1H, αCH′-*n*Bu), 7.53 (m, 6H, *m*/*p*Ph, Ph′), 8.39 (d, 2H, *o*Ph), 8.86 (d, 2H, *o*Ph′). – $C_{23}H_{29}N_3$ (347): calcd. C 79.5, H 8.4, N 12.1; found C 77.9, H 8.1, N 11.6%.

7: A mixture of the lithium dihydrotriazinide **8** and MgBr$_2$. OEt$_2$ (2.85 g, 5 mmol: 0.65 g, 2.5 mmol) was treated with THF (5 ml) and heated gently for two hours. The resulting yellow solution was pumped to dryness in vacuo then toluene (5 ml) was introduced, and the solution was filtered to remove fine solids. Left cooling at 20 °C for one week, the solution afforded a small crop of lightly-yellow coloured crystals, identified as the lithium bromide solvate **7**: yield 0.20 g, 7.8%. – M.p. 99–102 °C. – ^{1}H NMR (400 MHz, [D$_5$]pyridine, 25 °C, TMS): 0.68 (t, 3H, CH$_3$-*n*Bu), 1.27 (m, 11H, *t*Bu/γCH$_2$-*n*Bu), 1.65 (m, 10H, βCH$_2$-*n*Bu/THF), 1.82 (t, 1H, αCH-*n*Bu), 2.05 (t, 1H, αCH′-*n*Bu), 3.67 (t, 8H, THF), 7.51 (m, 6H, *m*/*p*Ph, Ph′), 8.42 (d, 2H, *o*Ph′), 8.83 (d, 2H, *o*Ph). – $C_{32}H_{45}N_3O_2BrLi$ (589.8): calcd. C 65.1, H 7.7, N 7.1, Li 1.2; found C 2.6, H 7.6, N 7.2, Li 0.9.

Table 4. Sum of bond angles [°] for dihydro-*s*-triazinide N centres within the potassium potassate series

Potassium potassate	"Neutral" donor atoms	"Anions"
1	N(3) 356.6	N(1) 348.2
	N(6) 357.5	N(4) 351.5
2	N(2) 354.0	N(1) 347.1
	N(6) 354.4	N(4) 350.8
3	N(2) 349.9	N(1) 345.2
	N(5) 357.7	N(4) 344.5
	N(8) 358.2	N(7) 349.8

Table 5. Selected bond lengths [Å] and angles [°] for **4**[a]

K–O(1)	2.565(2)	K–O(2a)	2.688(2)
K–O(2)	2.702(2)	K–N(1)	2.762(2)
K–C(14)	3.324(3)	N(1)–C(8)	1.367(3)
N(1)–C(1)	1.372(3)	N(2)–C(1)	1.298(3)
N(2)–C(15)	1.485(3)	N(3)–C(8)	1.293(3)
N(3)–C(15)	1.475(3)	O(1)–S(1)	1.520(2)
O(2)–S(2)	1.503(2)		
O(1)–K–O (2a)	146.03(7)	O(1)–K–O(2)	100.40(7)
O(2a)–K–O(2)	87.64(6)	O(1)–K–N(1)	105.75(6)
O(2a)–K–N(1)	101.36(6)	O(2)–K–N(1)	112.31(6)
C(8)–N(1)–C(1)	112.5(2)	C(8)–N(1)–K	109.18(13)
C(1)–N(1)–K	119.91(14)	C(1)–N(2)–C(15)	116.1(2)
C(8)–N(3)–C(15)	116.3(2)	N(2)–C(1)–N(1)	128.3(2)
N(3)–C(8)–N(1)	128.8(2)	N(3)–C(15)–N(2)	115.3(2)
S(1)–O(1)–K	152.3(2)	S(2)–O(2)–K(a)	129.41(10)
S(2)–O(2)–K	133.01(11)	K(a)–O(2)–K	92.36(6)

[a] Symmetry transformations used to generate equivalent atoms: a: $-x + 1, -y, -z + 1$.

X-ray Crystallography: Crystals of compounds **2–7** were examined on a Siemens SMART CCD area detector diffractometer at 160 K, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensities were integrated from series of exposures taken to cover more than a hemisphere of reciprocal space in each

Table 6. Selected bond lengths [Å] and angles [°] for **5**

Na(1)–O(1)	2.314(4)	Na(1)–O(2)	2.268(4)
Na(1)–O(3)	2.308(4)	Na(1)–N(1)	2.356(4)
N(1)–C(8)	1.367(5)	N(1)–C(1)	1.374(5)
N(2)–C(1)	1.287(5)	N(2)–C(15)	1.477(5)
N(3)–C(8)	1.286(5)	N(3)–C(15)	1.475(5)
Na(2)–O(4)	2.295(4)	Na(2)–O(5)	2.315(4)
Na(2)–O(6)	2.268(4)	Na(2)–N(4)	2.336(4)
N(4)–C(43)	1.365(5)	N(4)–C(36)	1.378(5)
N(5)–C(36)	1.292(5)	N(5)–C(50)	1.474(5)
N(6)–C(43)	1.298(5)	N(6)–C(50)	1.483(5)
O(2)–Na(1)–O(3)	106.18(15)	O(2)–Na(1)–O(1)	100.89(14)
O(3)–Na(1)–O(1)	89.18(14)	O(2)–Na(1)–N(1)	121.19(14)
O(3)–Na(1)–N(1)	121.39(14)	O(1)–Na(1)–N(1)	111.54(13)
C(8)–N(1)–C(1)	112.0(3)	C(8)–N(1)–Na(1)	126.5(3)
C(1)–N(1)–Na(1)	113.7(3)	C(1)–N(2)–C(15)	116.5(3)
C(8)–N(3)–C(15)	116.2(3)	N(2)–C(1)–N(1)	128.6(4)
N(3)–C(8)–N(1)	129.3(4)	N(3)–C(15)–N(2)	115.7(3)
O(6)–Na(2)–O(4)	99.8(2)	O(6)–Na(2)–O(5)	95.6(2)
O(4)–Na(2)–O(5)	99.0(2)	O(6)–Na(2)–N(4)	122.8(2)
O(4)–Na(2)–N(4)	118.88(15)	O(5)–Na(2)–N(4)	115.94(14)
C(43)–N(4)–C(36)	112.5(3)	C(43)–N(4)–Na(2)	116.2(3)
C(36)–N(4)–Na(2)	115.2(2)	C(36)–N(5)–C(50)	116.6(3)
C(43)–N(6)–C(50)	117.0(3)	N(5)–C(36)–N(4)	128.4(4)
N(6)–C(43)–N(4)	127.9(4)	N(5)–C(50)–N(6)	114.7(3)

case, each exposure giving a 0.3° range in Ω[23]. Cell parameters were refined from observed Ω angles for all strong reflections in the data set. Semi-empirical absorption corrections, based on the high degree of data redundancy, were applied only for compound 7, with transmission factors 0.701–0.866[24]. The structures were solved by direct methods and refined on F^2 for all measured data[24], with weighting $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were assigned anisotropic displacement parameters and isotropic H atoms were constrained with riding models. An isotropic extinction coefficient x was refined (to zero for some structures), whereby F_c is divided by $(1 + xF_c^2\lambda^3/\sin 2\Theta)^{1/4}$. The refined enantiopole parameter for the non-centrosymmetric structure of **3** was −0.03(2), indicating the correct assignment of absolute structure[25]. Two-fold disorder was resolved and refined for some alkyl substituents and DMSO and THF ligands, with geometrical and displacement parameter restraints. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223) 336-033, e-mail: teched@chemcrys.cam.ac.uk) on quoting the deposition number CCDC-100054.

Table 7. Selected bond lengths [Å] and angles [°] for **7**[a]

N(1)–C(1)	1.308(3)	N(1)–C(8)	1.401(3)
N(2)–C(1)	1.337(3)	N(2)–C(15)	1.483(3)
N(3)–C(8)	1.279(3)	N(3)–C(15)	1.464(3)
Li–Br	2.529(4)	Li–Br(a)	2.494(4)
Li–O(2)	1.900(4)	Li–O(1)	1.941(4)
C(1)–N(1)–C(8)	114.2(2)	C(1)–N(2)–C(15)	122.1(2)
C(8)–N(3)–C(15)	118.7(2)	N(1)–C(1)–N(2)	123.1(2)
N(3)–C(8)–N(1)	128.0(2)	N(3)–C(15)–N(2)	109.7(2)
Li(a)–Br–Li	78.51(14)	O(2)–Li–O(1)	101.8(2)
O(2)–Li–Br(a)	120.8(2)	O(1)–Li–Br(a)	105.5(2)
O(2)–Li–Br	106.0(2)	O(1)–Li–Br	122.9(2)
Br(a)–Li–Br	101.49(14)		

[a] Symmetry transformations used to generate equivalent atoms: a: $-x + y, -y, -z$.

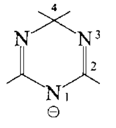
Table 8. Selected bond lengths [Å] and angles [°] for **6**

N(1)–C(1)	1.308(2)	N(1)–C(8)	1.393(2)
N(2)–C(1)	1.341(2)	N(2)–C(15)	1.475(2)
N(3)–C(8)	1.286(2)	N(3)–C(15)	1.461(2)
C(1)–N(1)–C(8)	114.67(10)	C(1)–N(2)–C(15)	121.89(11)
C(8)–N(3)–C(15)	118.88(10)	N(1)–C(1)–N(2)	123.34(11)
N(3)–C(8)–N(1)	127.66(12)	N(3)–C(15)–N(2)	110.06(10)

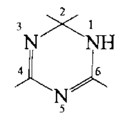
Table 9. Mean lengths [Å] of corresponding C–N bonds within the substituted C_3N_3 rings of compounds **1**–**7**

Compound	Bonds[a]		
	1–2 (4–5)	2–3 (5–6)	3–4 (6–1)
1	1.375	1.289	1.480
2	1.367	1.292	1.477
3	1.368	1.296	1.476
4	1.370	1.296	1.480
5	1.372	1.291	1.478
6	1.475 (1.393)	1.461 (1.308)	1.286 (1.475)
7	1.483 (1.401)	1.464 (1.308)	1.279 (1.337)

[a] Key to numbering:



for 1-5



for 6 and 7

Residuals are defined as $R_w = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$ for all data, conventional $R = \Sigma||F_o| - |F_c||/\Sigma F_o|$ on F values of reflections having $F_o^2 > 2\sigma(F_o^2)$. The goodness of fit is calculated on all F^2 values.

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