Potassium Potassiate Contact Ion Pair Polymer synthesised by Metallation of a Dihydrotriazine

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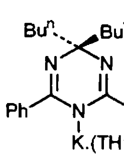
The first potassio triazine to be isolated and structurally characterised by X-ray diffraction exhibits an infinite, zig-zag, N–K propagated chain arrangement of alternating K^+ cations and $[(R_2K)^-]$ complex anions; the manner of its association sheds new light on why selected lithio alkyltriazines spontaneously dealkylate.

Knowledge of metal triazine structures is in demand as an aid to developing a greater understanding of the chemistry involved in the many technological uses of this $(CN)_3$ heterocyclic family.[1] For example, the employment of alkylamino-1,3,5-triazines as herbicides prompted structural characterisation of bis(2-ethylamino-4-isopropyl-6-methoxy-1,3,5-triazine) ('Atratone') and bis[2,4-bis(ethylamino)-6-methoxy-1,3,5-triazine] ('Simatone') monomeric $CuCl_2$ complexes, which were suggested as models for complexes possibly involved in the adsorbtion of herbicides into soil mineral matter.[2] Typically, these salts contain neutral triazine molecules, acting as complexants toward the metal cations, as opposed to *metallo*-triazine derivatives, wherein the heterocycle is present as the anion, which have been meagrely studied by comparison. While the primary aim of this study was to synthesise and crystallographically characterise a representative potassio triazine of this type, there is a surprising twist to the compound made **1** as it also turns out to be an unprecedented potassium potassiate contact ion pair species, a designation clearly discernible from an analysis of its dimensions. To our knowledge, **1** is the first potassio triazine to be isolated as a solid and studied directly, whereas, previously, they have been generated *in situ* to enable the subsequent functionalisation of the heterocyclic ring, with the potassium ultimately removed as a halide salt.[3] In addition, being the prototypal example of an associated alkali metallo triazine structure revealing the precise mechanics of how association is accomplished, it provides a basis from which the spontaneous dealkylation of certain lithio alkyltriazines can be rationalised.

Metallo triazines can be formed by cyclotrimerisation of benzonitrile with a metal alkyl reagent,[4] but in the case of **1**, metallation of the preformed 'protic' triazine **2** proved a 'cleaner' method. Made *via* its crystalline lithio derivative by a literature method,[5] **2**† and Bu^nK (5 mmol of each) were suspended in hexane (10 ml) in an argon filled Schlenk tube, mixed in a conventional ultrasonic cleaning bath, and cooled prior to the dropwise addition of THF (1 ml). On warming to room temperature an orange oil formed. Solvent was removed *in vacuo* and replaced by hexane–THF (7–3.5 ml) and the mixture was warmed, then filtered to remove fine solids. Finally, maintaining the orange filtrate at 5 °C yielded 0.72 g (32%) of the air and moisture sensitive, yellow crystalline **1** (satisfactory analyses, C, H, N and K were obtained; m.p. 108–111 °C).



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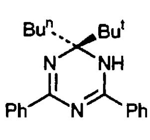

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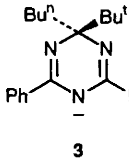

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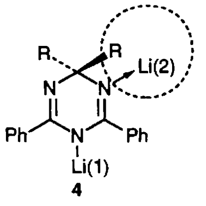

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X-ray diffraction studies‡ revealed a polymeric zig-zag chain arrangement (Fig. 1). Formally dimeric in the sense that it contains two distinct K atoms, the repeating unit is in fact composed of a K^+ cation joined to a $[(R_2K)^-]$ complex anion, as emphasised in the plan of the structure (Fig. 2). Justification for this interpretation comes from the pattern of bond lengths in the anions, as well as from consideration of the atoms involved in the K coordination spheres. The two crystallographically distinct anions display two short [C(1)–N(3), C(8)–N(2); C(24)–N(5), C(31)–N(6)], two intermediate [C(1)–N(1), C(8)–N(1); C(24)–N(4), C(31)–N(4)], and two long [C(15)–N(2), C(15)–N(3); C(38)–N(5), C(38)–N(6)] C–N ring bonds, with mean lengths of 1.289, 1.375 and 1.480 Å, respectively, which categorises them as 1,4-dihydrotriazine anions (*i.e.* with the negative charge essentially localised on the N site opposite to the saturated C centre, as depicted in **3**). Their anionic centres [N(1), N(4)] bond exclusively to K(2) [lengths: 2.806(8) and 2.869(8) Å, respectively; angle: N(1)K(2)N(4), 131.8(2)°], whose distorted tetrahedral geometry is completed by a pair of THF ligands [bond lengths: to O(2), 2.703(9); to O(3), 2.770(11) Å; angle: O(2)K(2)O(3), 80.8(4)°]. In contrast, the interactions between the cation [K(1)] and the triazine molecules involve only internal N donor atoms [N(3), N(6a)]. Mono THF solvation renders K(1) three-coordine with respect to N and O [*cf.* the four-coordination of K(2)]; consequently, K(1) forms shorter bonds to these polar atoms [to: N(3), 2.764(7) Å; N(6a), 2.769(8) Å; O(1), 2.659(8) Å] and the NKN bond angle opens wider [to

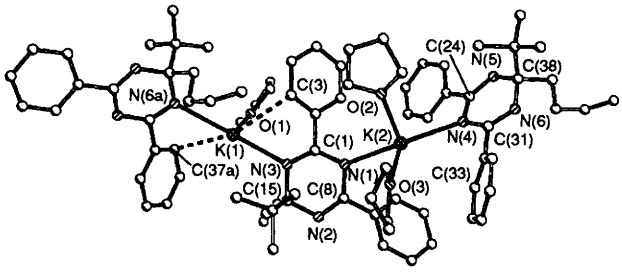


Fig. 1 Section of the polymeric structure of **1**, without hydrogen atoms and with important atoms labelled. Short C···K contacts are indicated by broken lines. Key dimensions not given in text: C(1)–N(3) 1.294(11), C(8)–N(2) 1.293(12), C(24)–N(5) 1.286(13), C(31)–N(6) 1.281(12), C(1)–N(1) 1.364(11), C(8)–N(1) 1.389(12), C(24)–N(4) 1.378(13), C(31)–N(4) 1.367(12), C(15)–N(2) 1.468(11), C(15)–N(3) 1.482(12), C(38)–N(5) 1.477(12), C(38)–N(6) 1.492(12) Å.

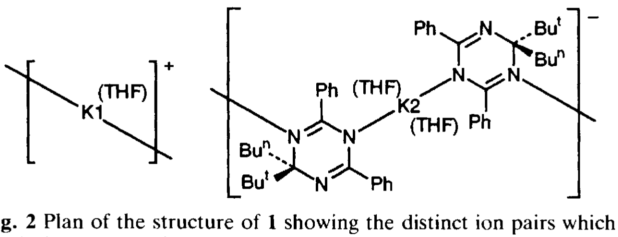
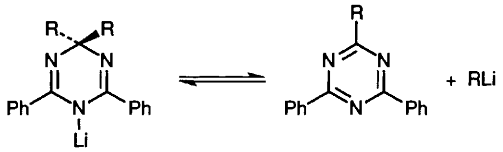


Fig. 2 Plan of the structure of **1** showing the distinct ion pairs which marks it as a potassium potassiate



147.4(2)°], but even more significantly K(1) engages in additional contacts with one *o*-C atom on each of two Ph rings, *i.e.* η^1–Ph···K$^+$ interactions. One contact [C(37a)···K(1)] is shorter than the other [C(3)···K(1)] [3.136(11) *cf.* 3.248(11) Å], but both would appear to contribute to the stability of the structure given that formal C–K bonds can be longer, though their lengths very much depend on the class of compound concerned.[6] By comparison, the closest C atom [C(33)] to K(2) lies 3.433(12) Å away.

Perhaps the most important aspect of the structure of **1** is its mechanistic implications. As discussed in depth elsewhere,[7] lithio alkyltriazines are prone to spontaneously releasing alkyllithiums to leave fully-unsaturated triazines, as outlined in equation 1. Monomeric lithio triazines stabilised by solvation can resist this elimination process. However, it proceeds in the absence of solvation, where association of the lithio triazine would be expected. With no information available on how lithio triazines might associate, the structure of **1** provides good indirect evidence. The key discovery is that the N–K propagation occurs through two distinct N atoms on the same triazine ring, rather than through the anionic N alone. Applied to the lithio congener (see **4**), Li(1) would lie opposite to the saturated C centre, the preferred situation in known monomeric solvates,[5] while Li(2) would lie adjacent to this centre. Thus Li(2) would be ideally positioned next to the *n*-butyl substituent to facilitate the elimination of *n*-butyllithium. Steric congestion is the probable trigger for this event given that the considerably larger K$^+$ cation in this site can only accommodate a solitary THF ligand.

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Footnotes

† The 'protic' dihydrotriazine is prepared in a pure form by methanolysis of the lithio triazine, subsequently crystallising as a weak methanol solvate. This methanol can be removed by extended vacuum drying.

‡ *Crystal data* for **1**: $C_{58}H_{80}K_2N_6O_3$, M = 987.5, monoclinic, a = 10.849(3), b = 18.784(6), c = 27.966(10) Å, β = 92.50(3)°, U = 5694(3) Å^3, Z = 4, D_{calc} = 1.152 g cm^{-3}, μ = 0.213 mm^{-1} (MoKα, λ = 0.71073 Å), $F(000)$ = 2128, space group $P2_1/c$. A total of 7917 reflections were measured at 160 K on a Stoe-Siemens diffractometer, to $2\theta_{max}$ = 45°, yielding 7207 unique data (R_{int} = 0.030). The structure was solved by direct methods and refined on F^2 for all data, with anisotropic displacement parameters and constrained isotropic hydrogen atoms. Final $R' = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}} = 0.370$ for all data, conventional R = 0.099 on F values of 4509 reflections with $F_o^2 > 2\sigma(F_o^2)$, goodness of fit = 1.118 for 631 refined parameters. Programs were of the SHELX family (G. M. Sheldrick, University of Göttingen). Atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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