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Synthesis of a deca-lithium cage containing an $[(RN)_2As(\mu\text{-}NR)As(NR)_2]^{4-}$ tetraanion; a homologue of group 15 trianions of the type $[E(NR)_3]^{3-}$†

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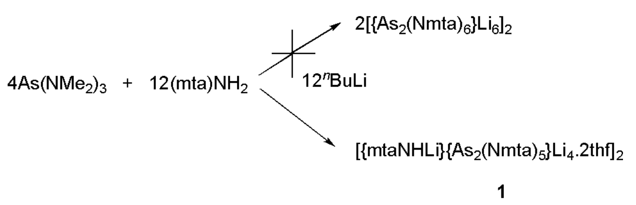
The novel, deca-lithium cage $[\{mtaNHLi\}\{As_2(Nmta)_5\}Li_4{\cdot}2thf]_2$ (1) (mtaN = 5-methylthiazolyl, $C_4H_4N_2S$) contains an imido-bridged tetraanion $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$, which represents a new type of multifunctional imido group 15 ligand framework (homologous with group 15 anions of the type $[As(NR)_3]^{3-}$).

In the past decade there has been considerable interest in group 15 and 16 anion frameworks, such as the valence-isoelectronic imido species $[E(NR)_3]^{2-}$ (E = S, Se, Te)[1] and $[E(NR)]_3^{3-}$ (E = As, Sb).[2] These species have highly varied coordination chemistries and function as multifunctional, N-centred ligands to a range of main group and transition metals.[2] Our interest in this area has focused on the applications of group 15 dimethylamido reagents, $E(NMe_2)_3$ (E = As–Bi), which provide simple access to a range of related imido anion arrangements.[2] Having established a set of broad synthetic methodologies to these ligands, our attention has turned to their elaboration, primarily by introducing additional donor atoms into the organic groups, with the aim of finding routes to readily accessible highly functionalised ligand arrangements. We present here the surprising formation of an $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ tetraanion within the novel, deca-lithium cage compound $[\{mtaNHLi\}\{As_2(Nmta)_5\}Li_5{\cdot}2thf]_2$ (**1**) (mtaN = 2-imido-5-methylthiazolyl, $C_4H_4N_2S$). This new multifunctional As(III) anion is the first homologue of the $[E(NR)_3]^{3-}$ trianions to be characterised.

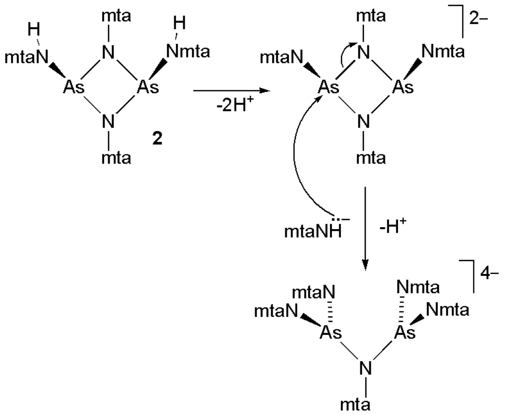
The stepwise deprotonation of 2-amino-5-methylthiazole ($mtaNH_2$) with $As(NMe_2)_3$ (1:3 equivalents), followed by reaction with ^nBuLi (3 equivalents), gives complex **1** in 22% yield (Scheme 1). This result is very different from known related reactions involving $As(NMe_2)_3$, which generate cages of the type $[\{As(NR)_3\}_2Li_6]$ (containing $[As(NR)_3]^{3-}$ trianions).[3] Initial indications of the unexpected formation of the $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ tetraanion in **1** were given by analytical and spectroscopic data on the complex. In particular, the IR spectrum contains a relatively sharp N–H stretching band at 3583 cm^{-1}, indicating that **1** contains an $mtaNH^-$ ligand. Spectroscopic investigations were limited by the low solubility of **1** in anything other than more polar solvent like DMSO (the complex being only sparingly soluble in thf once isolated). The room-temperature ^1H NMR spectrum in DMSO showed the presence of three aromatic C–H environments; the broad singlet at δ 6.67 and the quartet at δ 6.54 can be assigned to the μ-Nmta and terminal Nmta groups (respectively) of the $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ tetraanion, while the minor resonance at δ 5.83 corresponds to the $mtaNH^-$ anion (as confirmed by a ^1H NMR study of a 1:1 mixture of ^nBuLi and $mtaNH_2$ in thf). The Me resonances associated with the $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ tetraanion coincide as a doublet at δ 2.15, with the Me group of the $(mtaNH)^-$ anion being a doublet at δ 1.33. These ^1H NMR studies confirm that the $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ tetraanion survives *intact* in DMSO as the solvent. However, the room-temperature ^7Li NMR spectrum in DMSO shows only a broad singlet (δ 1.1), indicating that either further solvation the Li^+ cations of the cage occurs (with breakdown of the Li^+ framework) or that a complicated fluxional process is occurring. These spectroscopic features were, however, only fully explained once **1** had been structurally characterised.



Scheme 1

Further investigations showed that both the 1:3 and 1:2 stoichiometric reactions of $As(NMe_2)_3$ with $(mta)NH_2$ give the arsazane dimer $[(mtaNH)_2As(\mu\text{-}Nmta)]_2$ (**2**). The presence of species like **2** as intermediates in the formation of $[As(NR)_3]^{3-}$ trianions has been suggested by us recently.[3b] A possible explanation for the formation of the $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ tetraanion of **1** involves deprotonation of **2**, followed by nucleophilic addition of mtaNHLi (Scheme 2). Interestingly, this mechanism is consistent with the stoichiometry used in the formation of **1** (Scheme 1). The formation of the tetraanion in **1** can be compared to the result of the reaction of $(Me_2N)_2Sb(CH_2)_3Sb(NMe_2)_2$ with RNHLi (1:4 equivalents), which gave the μ-NR bridged dianion $[(RN)Sb(CH_2)_3(\mu\text{-}NR)Sb(NR)]^{2-}$ (rather than the expected $[(RN)_2Sb(CH_2)_3Sb(NR)_2]^{4-}$ tetraanion).[4]

Complex **1** has an elaborate cage structure in the solid state,‡ with molecules having overall C_i symmetry (Fig. 1). In addition, there are four thf molecules in the crystal lattice for each molecule of **1**. The five crystallographically-unique Li^+ cations



Scheme 2

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† Electronic supplementary information (ESI) available: synthesis and spectroscopic details for **1** and **2**. See http://www.rsc.org/suppdata/cc/b2/b202858a/

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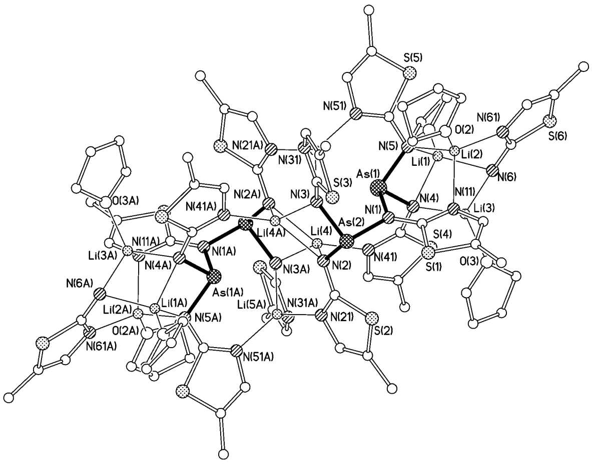

Fig. 1 Structure of the deca-lithium cage **1**·4thf. H-atoms and lattice-bound thf molecules have been omitted for clarity. Key bond lengths (Å) and angles (°): As(1)–N(1) 1.937(3), As(1)–N(4) 1.839(3), As(1)–N(5) 1.852(3), As(2)–N(1) 1.932(3), As(2)–N(2) 1.827(3), As(2)–N(3) 1.813(3), N(2)–Li(4) 2.147(7), N(2)–Li(4A) 2.283(7), N(3)–Li(5) 2.078(7), N(3)–Li(4A) 2.159(6), N(4)–Li(1) 2.060(8), N(4)–Li(3) 2.057(8), N(5)–Li(1) 2.057(8), N(5)–Li(2) 2.066(7), N(6)–Li(1) 2.078(8), N(6)–Li(3) 2.045(8), N(21,41,51)–Li(5A,4,6) range 1.990(7)–2.086(7), N(31)–Li(5) 2.143(7), N(11)–Li(2,3) mean 2.11; As(1)–N(1)–As(2) 116.33(13), C(1)–N(1)–As(1) 125.3(2), C(1)–N(1)–As(2) 118.4(2), N(1)–As(1)–N(4) 100.29(13), N(1)–As(1)–N(5) 103.11(12), N(4)–As(1)–N(5) 89.82(13), N(1)–As(2)–N(2) 101.29(12), N(1)–As(2)–N(3) 97.61(13), N(2)–As(2)–N(3) 93.46(12).

of each of the symmetry-related [{mtaNHLi}{$As_2(Nmta)_5$}-Li_4·2thf] halves of **1** are coordinated by an $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ tetraanion in the central portion of the cage, and by an $mtaNH^-$ anion at the terminus. The observed conformation of the $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ tetraanions probably has the greatest influence on the overall cage structure of **1**, and can be rationalised largely in terms of VSEPR theory. In each half of **1**, the adoption of a *trans* conformation at As(1) and As(2) within the As(μ-Nmta)As backbone presumably minimises lone-pair/lone-pair repulsion between the two As(III) centres. The roughly *trans* orientation of the lone-pairs of the terminal imido-N centres [N(2), N(3), N(4) and N(5)] with respect to the As(III) lone-pairs, has an additional advantage of avoiding steric confrontation between the terminal mtaN and the μ-Nmta group. Within each $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ tetraanion, the As–N bonds to the terminal mtaN ligands (mean 1.83 Å) are significantly shorter than those involving the μ-Nmta group (mean 1.94 Å). These bond lengths can be compared to those found in the $[\{As_2(NCy)_4\}]^{2-}$ dianion of $[\{As_2(NCy)_4\}_2Li_4]$ (terminal NCy mean 1.79, μ-NCy mean 1.92 Å).[5] Although highly distorted, the pyramidal geometries of the As(III) centres are typical of those observed in other imido As(III) anions [N–As–N in **1** range 89.8(2)–103.1(2)°].[3,5,6] The planar geometry at the μ-N centres of the tetraanions is consistent with sp^2 hybridisation [range of angles about N(1) 116.33(13)–125.3(2)°].

Given the small ionic size of Li^+, it is not surprising that of the seventeen potential (N, S and As) donor centres in the $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ ligand only the more electronegative N atoms of the mtaN groups are involved in bonding in the cage structure of **1**. All of the anionic imido-N centres of the terminal mtaN groups [associated with N(2), N(3), N(4) and N(5)] μ-bridge two Li^+ cations within the cage [N–Li range 2.056(8)–2.284(7) Å]. The different metal coordination modes exhibited by the terminal mtaN groups result from alternative use of the mta ring-N atoms in secondary, donor interactions. The same bonding pattern is found for the mta rings attached to N(2), N(4) and N(5), in which the ring-N atoms form donor bonds to single (remote) Li^+ cations [N(21,41,51)–Li(5A,4,6) 1.990(6)–2.086(6) Å]. A chelate-mode is exhibited by the remaining terminal mta group bonded to N(3) [N(31)–Li(5) 2.144(7) Å]. The ring-N centre of the μ-Nmta group of the tetraanion has a μ-bridging mode [N(11)–Li(2,3) mean 2.11 Å], with the imido-N centre [N(1)] not being involved in bonding to Li^+. A combination of thf, tetraanion and $mtaNH^-$ coordination results in all of the Li^+ cations of the cage having distorted-tetrahedral geometries, coordinated exclusively by N [Li(4), Li(5)] or by two N and two thf–O centres [Li(2), Li(3)].

The formation of the $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ tetraanion introduces the possibility of a series of related group 15 anions of general formula $[E_n(NR)_{2n+1}]^{(n+2)-}$, with the $[E(NR)_3]^{3-}$ trianions being the first homologues,[3,6] and the tetraanion of **1** being representative of a second homologue. Although phospha(III)zanes of the type $[(R_2N)_2P(\mu\text{-}NR)P(NR_2)_2]$ have been employed as neutral ligands,[7] there are no reports of $[(RN)_2E(\mu\text{-}NR)E(NR)_2]^{4-}$ tetraanions similar to that found in **1** for any group 15 element (E). To our knowledge, the group 16 dianion $[O_2S(\mu\text{-}NPh)SO_2]^{2-}$, obtained by the insertion of SO_2 into the Mg–N bonds of $[(thf)Mg(NPh)]_6$, is the closest structurally-related p block ligand species.[8] The $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ tetraanion should be highly versatile, multidentate ligand, whose arrangement and charge is similar to $EDTA^{4-}$. In the case of the $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ tetraanion, however, the S-donor sites offer an alternative soft ligand set. Studies of the coordination chemistry of the $[(mtaN)_2As(\mu\text{-}Nmta)As(Nmta)_2]^{4-}$ tetraanion are underway.

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Notes and references

‡ *Crystal data for* **1**·4thf; $C_{80}H_{112}As_4Li_{10}N_{24}O_8S_{12}$, M = 2291.74, monoclinic, space group $P2_1/c$, Z = 2, a = 13.7522(3), b = 25.1455(8), c = 15.9021(5) Å, β = 101.483(2)°, V = 5389.0(3) Å^3, μ(Mo-Kα) = 1.522 mm^{-1}, D_c = 1.412 g cm^{-3}, T = 180(2) K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 23523 reflections collected, 10181 were unique (R_{int} = 0.032). The structure was solved by direct methods and refined by full-matrix least squares on F^2.[9] Final $R1$ = 0.044 [$I > 2\sigma(I)$] and $wR2$ = 0.110 (all data). CCDC reference number 182544. See http://www.rsc.org/suppdata/cc/b2/b202858a/ for crystallographic data in CIF or other electronic format.

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