DALTON COMMUNICATION

Synthesis and structure of $[\{As_2(NCy)_4\}_2Li_4]$, containing an imido As(III) dianion

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Reaction of $[As(NMe_2)_3]$ with $CyNH_2$ (1 : 1 equivalents), followed by the addition of [CyNHLi] (1 equivalent) gives the heterobimetallic cage complex $[\{As_2(NCy)_4\}_2Li_4]$, the first example of a complex containing an imido As(III) anion; the missing link in a series of Group 15 anions of the type $[\{E_2(NCy)_4\}]^{2-}$ (E = Bi, Sb and P).

In previous work we showed that a series of imido Bi and Sb anions could be prepared utilising dimethyl amido derivatives.[1] The complexes $[\{Bi_2(N^tBu)_4\}Li_2{\cdot}2thf]$[2] and $[\{Sb_2(NCy)_4\}_2Li_4]$[3] are obtained from the *in situ* reactions of $[E(NMe_2)_3]$ (E = Sb, Bi) with primary amines $[RNH_2$; R = ^tBu, Cy (cyclohexyl)], followed by the reaction of the resulting $[(Me_2N)E(\mu\text{-}NR)]_2$ dimers with [RNHLi]. Whereas $[\{Sb_2(NCy)_4\}_2Li_4]$ has an elaborate cage structure consisting of two interlocked broken $[Sb_2N_4Li_2]$ cubanes in the solid state,[3] such aggregation is precluded in the case of $[\{Bi_2(N^tBu)_4\}Li_2{\cdot}2thf]$ by the solvation of the Li^+ cations by thf (the complex remaining as a discrete cubane).[2] Recently it has also been shown that a P analogue of these systems $[\{P_2(N^tBu)_4\}Li_2{\cdot}2thf]$, isostructural with the previous Bi complex, can be obtained by deprotonation of $[(^tBuNH)P(\mu\text{-}N^tBu)]_2$ with ^nBuLi in thf.[4] Transmetallation of the Sb complex with metal salts provides a versatile strategy to heterobimetallic complexes containing $[E_2(NR)_4]^{2-}$ ligands.[5] In view of the current interest in these species as ligand systems and in the light of the recent application of related alkali metal/Sb(III) phosphinidene cages as sources of photoemissive materials,[6] we have initiated studies of the corresponding As systems as potential precursors to GaAs.

We present here the synthesis and structure of $[\{As_2(NCy)_4\}_2Li_4]$ **1**, containing an $[As_2(NR)_4]^{2-}$ anion; the missing link in the series of Group 15 containing $[E_2(NR)_4]^{2-}$ ligands and the first such polyimido anion of As(III) to be reported. Complex **1** is prepared by the reaction of $[As(NMe_2)_3]$ with $[CyNH_2]$ (1 : 1 equivalent) followed by the addition of [CyNHLi] (1 equivalent) in toluene [eqn. (1)].†

$$4[As(NMe_2)_3] \xrightarrow[(ii)\ +4CyNHLi]{(i)\ +4CyNH_2} [\{As_2(NCy)_4\}_2Li_4] + 12Me_2NH \quad (1)$$

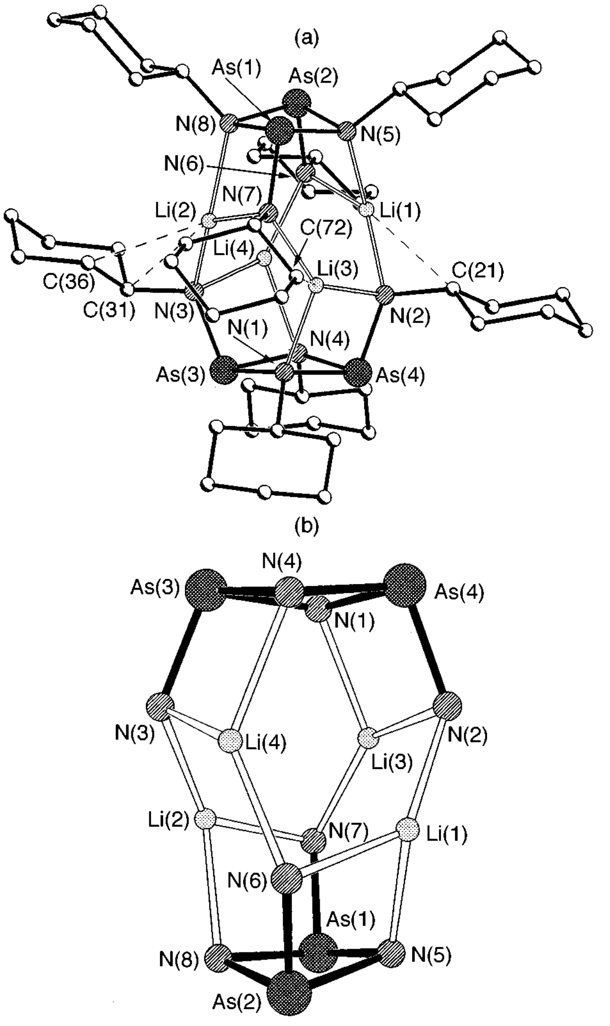

Fig. 1 (a) Structure of **1**. H atoms have been omitted for clarity. Key bond lengths (Å) and angles (°): As(1)–N(5) 1.916(4), As(1)–N(7) 1.790(3), As(1)–N(8) 1.929(4), As(2)–N(5) 1.932(4), As(2)–N(6) 1.789(4), As(2)–N(8) 1.915(4), As(3)–N(1) 1.917(4), As(3)–N(3) 1.792(4), As(3)–N(4) 1.943(4), As(4)–N(1) 1.922(4), As(4)–N(2) 1.797(4), As(4)–N(4) 1.914(4), N(1)–Li(3) 2.10(1), N(2)–Li(1) 1.941(9), N(2)–Li(3) 2.039(9), N(3)–Li(2) 1.966(9), N(3)–Li(4) 2.043(9), N(4)–Li(4) 2.130(9), N(5)–Li(1) 2.08(1), N(6)–Li(1) 2.008(9), N(6)–Li(4) 2.012(9), N(7)–Li(3) 1.979(9), N(7)–Li(2) 2.037(9), N(8)–Li(2) 2.132(9), C(21) ··· Li(1) 2.614(9), C(31) ··· Li(2) 2.79(1), C(36) ··· Li(2) 2.78(1), C(72) ··· Li(3) 2.774(9); As–(μ-N)–As mean 96.2, (μ-N)–As–(μ-N) mean 82.5, *exo*-(μ-N)–As–N mean 100.2, (μ-N)–Li–N mean within SbN_2Li rings 85.1, sum of N–Li–N angles about Li 348.7; (b) core of **1**.

The low-temperature X-ray structure determination of **1**‡ shows that it possesses a cage structure constructed from the association of two interlocked 'broken' $[As_2(NCy)_4Li_2]$ cubanes (Fig. 1). The roughly tetrahedral arrangement of the Li^+ cations at the centre of the cage and the pattern of the coordination of the Li^+ cations by the μ-N [Li–N range 2.08(1)–2.132(9) Å] and terminal CyN groups [Li–N range 1.941(9)–2.043(9) Å] of the $[As_2(NCy)_4]^{2-}$ anions are very similar to that occurring in the Sb analogue [μ-N–Li range 2.07(2)–2.14(2), terminal N–Li range 1.96(3)–2.03(2) Å].[3] This similarity with the Li_4N_4 substructure of **1** occurs despite the presence of significantly shorter As–N bonds in the $[As_2(NCy)_4]^{2-}$ anion (μ-N–As average 1.92 Å, terminal As–N average 1.79 Å[7]), which at first sight may be anticipated to result in a markedly smaller ligand bite. However, the overall compression in the $[As(\mu\text{-}NCy)]_2$ ring units of **1** compared to the $[Sb(\mu\text{-}NCy)]_2$ units of the Sb counterpart is largely offset by the greater exocyclic N–As–N angles in **1** [average μ-N–As–N (terminal) 100.2°; *cf.* average 90.8° in the Sb complex[3]], so that the bite of the terminal CyN groups is almost identical in **1** and its Sb analogue [N(2,6)···N(3,7) average 4.20 Å in **1**; *cf.* average 4.27 Å in the Sb complex]. The only noticeable concession to the presence of a more compact dianion ligand in **1** is the more acute N–Li–N angles made with the chelating μ-N and terminal-N centres (average 85.1°; *cf.* 90.4° in the Sb analogue[3]). There is also some effect on the pattern of peripheral agostic C(–H)···Li interactions with the Cy groups. In the Sb analogue the α-C–H of each of the pendant CyN groups are orientated towards and involved with adjacent Li^+ cations (effectively reinforcing the association of the cubane units).[3] However, a far less regular pattern of C(–H)···Li interactions is present in **1**, involving both the α and β carbons of Cy groups.

Despite the differences in the steric demands of the ^{t}Bu and Cy groups present in the structurally characterised complexes $[\{E_2(N^tBu)_4\}Li_2\cdot 2thf]$ (E = P,[4] Bi[2]) and $[\{E_2(NCy)_4\}_2Li_4]$ (E = As, Sb[3]), and the presence of different Group 15 elements and Lewis base solvation, it is now possible to obtain some general structural trends from this series. In particular the N–E–N (range 79.6–82.8°) and E–N–E (range 96.2–98.6°) angles in the $[E(\mu\text{-}NR)]_2$ ring units of the $[E_2(NR)_4]^{2-}$ dianions in all of these species are surprisingly similar. One of the most significant differences in the geometry of the dianions occurs in the exocyclic N–E–N angles which exhibit an overall reduction going from P (average 99.4°) to Bi (average 87.9°), consistent with the idea of increased s-character in the lone pair and increased p-character in the E–N bonds as Group 15 is descended. This effect offsets the increase in E–N bond lengths so that coordination of the Li^+ cations can be achieved without major structural modification of the $[E_2(NR)_4Li_2]$ units. Dimerisation of the cubane substituents of **1** and the Sb analogue is made possible by puckering of the E_2N_2 ring units (the N centres being an average of 18.4° out of the plane in **1** and an average of 21.2° in the Sb complex). This expands the ligand bite and allows inter-cubane Li–N bonding to be established.

The use of $[As(NMe_2)_3]$ as a precursor should allow other imido anions of As(III) to be prepared {*e.g.*, $[As(NR)_3]^{3-}$} and the coordination chemistry of these species to be explored. Of potential technological relevance is the synthesis of As(III)/Group 13 (Ga, In) heterometallics.

Notes and references

† Synthesis of **1**: $[As(NMe_2)_3]$ (6.0 mmol, 2.4 ml, 2.5 mol dm^{-3} solution in toluene) was added to a solution of $CyNH_2$ (6.0 mmol, 0.70 ml) in toluene (20 ml) at 25 °C. The mixture was brought to reflux briefly and a pale yellow solution was formed. This was added to a suspension of [CyNHLi] (6.0 mmol, made by the *in situ* reaction of $CyNH_2$ with ^{n}BuLi) in hexanes. The solid dissolved immediately and a bright yellow solution was produced after heating to reflux. The solvent was reduced to *ca.* 6 ml and a colourless solid precipitated. This was warmed back into solution and storage at 5 °C for 24 h gave crystals of **1**; yield 0.37 g (22%). Decomp. *ca.* 75 °C to red semi-solid, darkens and becomes black at *ca.* 200 °C. IR (Nujol), ν_{max}/cm^{-1}: 1225.4s, 1143.3m, 1056.2vs (br), 973.3s, 921.5m, 890.4s, 845.7s, 766.6s. ^1H NMR (+25 °C, 400 MHz, d_6-benzene): 3.46 (2H, α-C–H Cy), 3.27 (2H, α-C–H Cy), 2.7–1.0 (40H, overlapping multiplets, CH_2 Cy) (*ca.* 0.33 molecules of toluene were also present per molecule of **1**, CH_3 at 2.13). ^7Li NMR (100.6 MHz, d_8-toluene, relative to LiCl–D_2O, 50 mg per 0.5 mol dm^{-3}): δ 1.25 (s, line width 23 Hz, +25 °C) [Found: C, 54.8; H, 8.2; N, 10.1. Calc.: C, 52.2; H, 8.0; N, 10.1% (the high %C is a result of minor amounts of toluene, up to *ca.* 0.33 per molecule of **1** as confirmed by ^1H NMR].

‡ Crystal data for **1**: $C_{48}H_{88}As_4Li_4N_8$, $M = 1104.70$, triclinic, space group $P\bar{1}$, $a = 10.415(5)$, $b = 11.809(8)$, $c = 23.502(13)$ Å, $\alpha = 97.75(4)$, $\beta = 100.35(4)$, $\gamma = 103.30(4)°$, $U = 2720(3)$ Å^3, $Z = 2$, $D_c = 1.349$ Mg m^{-3}, $\lambda = 0.71073$ Å, $T = 180(2)$ K, $\mu(\text{Mo-K}\alpha) = 2.475$ mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer. Of a total of 11222 data collected ($3.50 \le \theta \le 24.01°$) 8458 were independent ($R_{int} = 0.0988$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1[F > 4\sigma(F)] = 0.040$ and $wR2 = 0.122$ (all data); largest peak and hole in the final difference map 0.713 and −0.820 e Å^{-3}. CCDC reference number 186/1261.

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