Synthesis and Structure of $[Sb_2Li_2\{N(C_6H_{11})\}_4]_2$; a Cage Complex containing a Core of Two Interlocked 'Broken' Cubes

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The imido cage complex $[Sb_2Li_2\{N(C_6H_{11})\}_4]_2$, synthesised by the condensation reaction of dimeric $[Sb(NMe_2)\{\mu\text{-}N(C_6H_{11})\}]_2$ with $[LiNH(C_6H_{11})]_n$ (1 : 1 monomer equiv.) consists of an $Sb_4Li_4N_8$ polyhedral core which can be viewed as being constructed from two interlocked 'broken' cubes.

Recently we showed that the reactions of $SbCl_x(NMe_2)_{3-x}$ (x = 0–2) with various organic acids, containing O and N centres, gave two possible outcomes depending on the reaction solvent employed and on the particular organic acid and Sb reagent used.[1,2] Surprisingly, we found that the reactions of $SbCl_x(NMe_2)_{3-x}$ (x = 1 and 2) with organic acids in Et_2O gave dimeric complexes in which Me_2NH, produced as a gaseous byproduct, acts as a Lewis base donor to Sb.[1] In contrast, the reactions of $Sb(NMe_2)_3$ with 1 equivalent of a primary amine (RNH_2) in toluene lead to dimeric complexes, $[Sb(NMe_2)(\mu\text{-}NR)]_2$, in which no Me_2NH ligation of Sb occurs.[2] Significantly, these complexes are themselves potential metallating reagents since they contain dimeric Sb_2N_2 cores in which two reactive Me_2N groups are retained. We have also shown recently that 'mixed-metallation' reactions of $Sb(NMe_2)_3$ can be used to prepare heterometallic complexes.[3] The polynuclear Sb–amido anion complex $Li[Sb_3\{N(C_6H_{11})\}_4(NMe_2)_2]$ is produced by the metallation reaction of $Sb(NMe_2)_3$ with $Li^+[Sb\{NH(C_6H_{11})\}_4]^-$ (2 : 1 equiv.) and the cage complex $[Sb(LiNCH_2CH_2Ph)_3(thf)]_2$ is the product of the reaction of $Sb(NMe_2)_3$ with $[LiNHCH_2CH_2Ph]_n$ (1 : 3 monomer equiv.).[3]

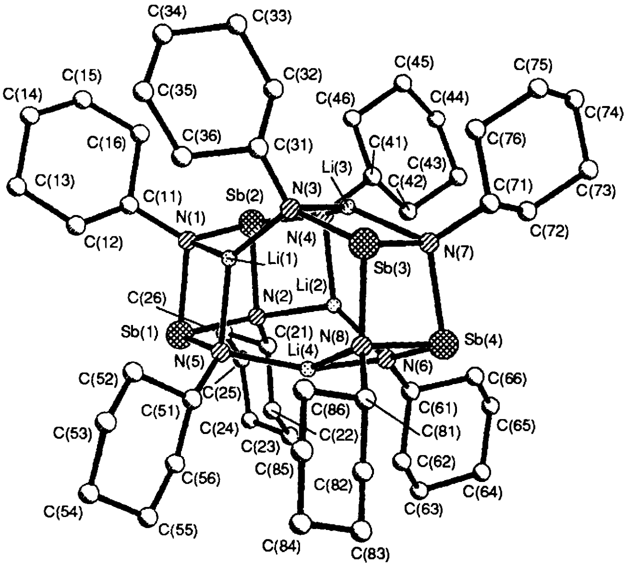

Fig. 1 Molecular structure of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sb(1)–N(1) 2.401(9), Sb(1)–N(2) 2.08(1), Sb(1)–N(5) 1.99(1), Sb(2)–N(1) 2.104(9), Sb(2)–N(2) 2.119(9), Sb(2)–N(4) 2.00(1), Sb(3)–N(3) 2.01(1), Sb(3)–N(7) 2.123(9), Sb(3)–N(8) 2.108(9), Sb(4)–N(6) 1.98(1), Sb(4)–N(7) 2.116(9), Sb(4)–N(8) 2.102(9), Li(1)–N(1) 2.14(2), Li(2)–N(2) 2.07(2), Li(3)–N(7) 2.14(2), Li(4)–N(8) 2.10(2), Li(1)–N(3) 2.00(2), Li(1)–N(5) 2.03(2), Li(2)–N(4) 2.02(2), Li(2)–N(6) 1.99(2), Li(3)–N(3) 2.00(3), Li(3)–N(4) 1.96(3), Li(4)–N(5) 1.94(2), Li(4)–N(6) 2.02(2), range Li···C 2.53(2)–2.63(2). Within Sb_2N_2 rings, av. N–Sb–N 79.6, av. Sb–N–Sb 98.6; within SbN_2Li rings, av. N–Sb–N 90.8, av. N–Li–N 90.4, av. Sb–N–Li 89.5; geometry about Li, N–Li–N 88.0(8)–135.6(1), sum of angles av. 353.8.

We report here that the reactive dimeric complexes $[Sb(NMe_2)(\mu\text{-}NR)]_2$ can be used in mixed-metallation reactions to prepare heterometallic complexes in a targeted way. Thus, the reaction between $[Sb(NMe_2)\{\mu\text{-}N(C_6H_{11})\}]_2$ and $[LiNH(C_6H_{11})]_n$ (1 : 1 monomer equiv.) gives $[Sb_2Li_2\{N(C_6H_{11})\}_4]_2$ **1** in which the rational assembly of an $Sb_4N_8Li_4$ cage of two interlocked broken cubes is achieved.†

An X-ray crystallographic study of **1**‡ shows it to be a polyhedral cage complex $[Sb_2Li_2\{N(C_6H_{11})\}_4]_2$ (Fig. 1), which can be regarded as being constructed from two interlocked 'broken-cube' fragments $Sb_2\{N(C_6H_{11})\}_2Li_2\{N(C_6H_{11})\}_2$ (Fig. 2). Although a similar core arrangement has been observed in the structures of the octameric aluminium complexes $[AlH(NPr^i)]_8$[4] and $[AlMe(NMe)]_8$[5] and heteroatom cage complexes containing a variety of main group metals are comparatively common,[6] the structure of **1** is unprecedented for the metallo-organic complexes of Group 15 and is a rare example of an imido complex containing an early main group metal.[7]

The stepwise assembly of **1** from its precursors, $[Sb(NMe_2)\{\mu\text{-}N(C_6H_{11})\}]_2$ and $[LiNH(C_6H_{11})]_n$, is evidenced in the overall structure of the cage and in the pattern of bond lengths and angles found within it. Thus, the core is built around two almost identical terminal $Sb_2\{\mu\text{-}N(C_6H_{11})\}_2$ dimeric rings whose geometries, although now slightly puckered, are similar to that of the dimeric precursor {av. values: Sb–N 2.108 Å, N–Sb–N 79.7°, Sb–N–Sb 98.6°; *cf.* corresponding values in $[Sb(NMe_2)(\mu\text{-}2\text{-}N(4\text{-}Mepy))]_2$ of av. 2.060 Å, 73.6(2) and 106.4(2)°, respectively}.[3] The reaction of two monomers of $(C_6H_{11})NHLi$ with the $[Sb(NMe_2)\{\mu\text{-}N(C_6H_{11})\}]_2$ dimers produces almost identical broken-cube halves of **1**, in each of which the two incorporated $(C_6H_{11})NLi$ units form approximately square $Sb\{\mu\text{-}N(C_6H_{11})\}_2Li$ sides (Sb–N–Sb, Sb–N–Li and Li–N–Li close to 90°, Sb–N and Li–N 2.00–2.11 Å). Presumably, the geometric constraints imposed by the rhombic Sb_2N_2 rings are responsible for the inability for each $Sb_2\{N(C_6H_{11})\}_2Li_2\{N(C_6H_{11})\}_2$ half of **1** (the anticipated structure of the product) to close into separate cubes. Instead, the association of two broken cubes, by the formation of Li–N bonds, appears to be preferred. This situation can be compared to that in the mixed Na–Li complex $Li_4Na_2[N{=}C(Ph)Bu^t]$[8] which, in the absence of such constraints, forms a typical 'triple-stack' structure.[9]

The Li–N bonds in the central Li_4N_4 portion of the core of **1** are surprisingly uniform (av. 2.00 Å) and are shorter than those made with the μ-N bridges of the terminal Sb_2N_2 rings (av. Li–N 2.11 Å). The four Li^+ cations, which are each bound to three $\mu_3\text{-}N(C_6H_{11})$ atoms, have very similar extremely

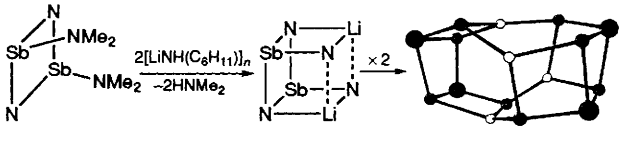

Fig. 2 Schematic representation of the construction of the core of **1** from two interlocked broken cubes. The cyclohexyl groups have been omitted for clarity.

irregular planar geometries [range N–Li–N 88.0(8)–135.6(1)°, sum of N–Li–N av. 353.8°]. In addition, α-C(–H)···Li interactions occur with adjacent C_6H_{11} groups which (in effect) reinforce the association of the broken-cube halves of the core {2.53(2)–2.63(2) Å; *cf.* 2.60–2.70 Å in $[LiN(CH_2Ph)_2]_3$}[10]

We are investigating the use of **1**, as a source of the novel $[Sb_2\{N(C_6H_{11})\}_4]^{2-}$ dianion, in the syntheses of a range of mixed Sb–main group and transition metal complexes.

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Footnotes

† A solution of $NH_2(C_6H_{11})$ (0.29 ml, 2.5 mmol) in toluene (10 ml) was added at 0 °C to a solution of $Sb(NMe_2)_3$ (0.64 g, 2.5 mmol) in toluene (10 ml). The mixture was warmed to reflux and stirred (1 h) to give a yellow solution. To this was added a suspension of $[LiNH(C_6H_{11})]_n$ (0.26 g, 2.5 mmol) in toluene (20 ml) at 0 °C. The resulting mixture was stirred at 60 °C (0.5 h) to yield an intense yellow solution. Reduction of this to *ca.* 8 ml yielded a pale yellow precipitate which was gently warmed into solution. Storage at room temperature for 24 h yielded crystalline blocks of **1** in 25% yield (first batch): softens to yellow semi-solid at 175 °C, decomp. 220 °C; IR (Nujol), no distinctive bands; ^1H NMR (250 MHz; C_6D_6; 25 °C), collection of poorly resolved overlapping multiplets δ 0.5–4.0 (C_6H_{11} groups). Satisfactory analyses (C, H, N) were obtained for all samples of **1**.

‡ *Crystal data* for **1**: $C_{48}H_{88}Li_4N_8Sb_4$, $M = 1292.02$, tetragonal, space group $P4_1$, $a = 12.179(1)$, $b = 12.179(1)$, $c = 36.743(7)$ Å, $U = 5450.0(12)$ Å^3, $Z = 4$, $D_c = 1.565$ Mg m^{-3}, $F(000) = 2592$, $\lambda = 0.71073$ Å, $T = 153(2)$ K, μ(Mo-Kα) = 2.000 mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated rapidly-cooled crystal (T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615) of dimensions 0.41 × 0.40 × 0.34 mm by the θ/ω method ($7.04 \leqslant 2\theta \leqslant 45.04°$). Of a total of 4005 collected reflections, 3625 were unique. The structure was solved by direct methods (SHELX TL PLUS) and refined by full-matrix least squares on F^2 (SHELXL93; G. M. Sheldrick, Göttingen, 1993) to $R1$ 0.0312 and $wR2$ 0.1000 $[F > 4\sigma(F)]$ and $R1$ 0.0330 and $wR2$ 0.1096 (all data) $[Rz = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o\}^{\frac{1}{2}}]$. Largest peak and hole in the final difference map 1.079 and −1.084 eÅ^{-3}. The Flack parameter was refined to 0.04(5), indicating that the absolute configuration has been determined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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