DALTON
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A novel chiral distibine-centred polyimido anion

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Received 30th August 2000, Accepted 30th August 2000
First published as an Advance Article on the web 15th September 2000

Reaction of $(Me_2N)_2Sb(CH_2)_3Sb(NMe_2)_2$ with 4 equivalents of 2-NHLiPy (Py = pyridyl) generates the novel distibine-centred dianion complex 1,3-$[(RNLi)Sb]_2$-(μ-NR)$(CH_2)_3$·(RNHLi)·3THF (1), incorporating the co-complexation of primary lithium amide; the X-ray crystal structure of 1 reveals a bimetallic imido-/amido-bridged cage structure of interlocking 6-membered rings, crystallising as a single enantiomer.

Recent investigations into the reactivities of p-block metal dimethylamido derivatives, $M(NMe_2)_x$ [$x = 2$ (M = Sn, Te), $x = 3$ (M = As, Sb, Bi)], with organic acids and primary alkali metal amides have highlighted a novel and versatile route towards a host of polyimidoanion species.[1–8] Of particular interest have been the structural motifs adopted by mixed antimony/lithium polyimidoanions, *e.g.* $[Sb_3(NCy)_4(NMe_2)_2]$-Li, $[Sb_2(NCy)_4]_2Li_4$ and $[(PhCH_2CH_2NLi)_3Sb{\cdot}THF]_2$.[5,6] With these results in mind we decided to turn our attention towards polynuclear stibine systems. Bidentate ligands such as $Ph_2Sb(CH_2)_3SbPh_2$ have received considerable attention in terms of their Lewis base coordination chemistry with a range of transition metal centres.[9] However, the organometallic chemistry at the stibine centres is still relatively unexplored. It is well-known that the phenyl groups of such systems may be cleaved with dry HCl, to yield $Cl_2Sb(CH_2)_3SbCl_2$.[10] Thus, by simple transmetallation it is possible to introduce organo-functional groups to the metal centres. We therefore decided to synthesise the Me_2N– derivatives of polynuclear stibine systems, *e.g.*, $(Me_2N)_2Sb(CH_2)_3Sb(NMe_2)_2$. This was achieved by reaction of the tetrachloride with $LiNMe_2$ in dry ether.

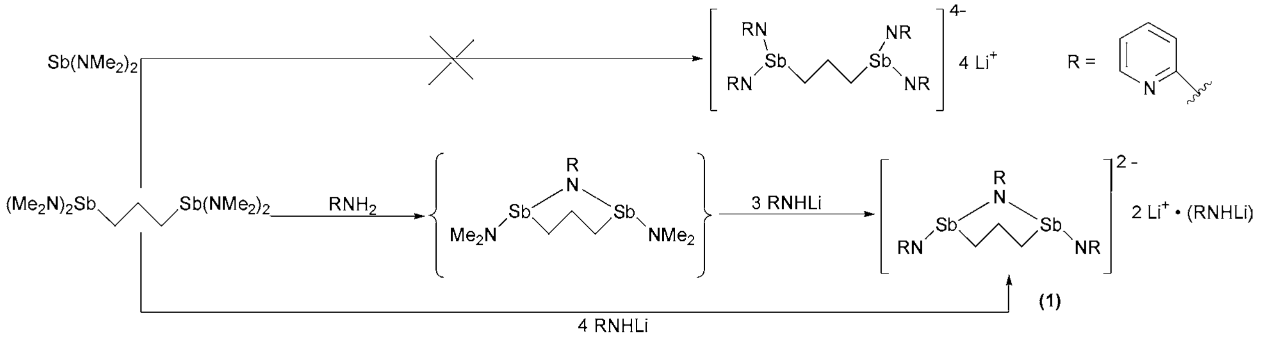
In an attempt to synthesise a formally tetraanionic imido complex, $(RNLi)_2Sb(CH_2)_3Sb(RNLi)_2$, $(Me_2N)_2Sb(CH_2)_3Sb(NMe_2)_2$ was reacted with four molar equivalents of RNHLi (R = 2-Py). However, unexpectedly, the only compound isolated was identified as 1,3-$[(RNLi)Sb]_2$(μ-NR)$(CH_2)_3$·(RNHLi)·3THF (**1**), the first example of a distibine-centred polyimido anion (Scheme 1).†

The X-ray crystal structure of **1** ‡ was elucidated and revealed that **1** consists of two stibine centres linked *via* a $(CH_2)_3$ bridge, with a pendant imido-lithium group attached to each Sb centre (see Fig. 1 and 2). Instead of generation of a tetraanionic derivative (see Scheme 1), an imido group bridges the Sb centres forming a 6-membered ring. Repetition of the experiment yielded the same product, ruling out any possibility of incomplete lithiation of the 2-aminopyridine. The complex can also be synthesised systematically by reaction of one equivalent of amine followed by addition of 3 equivalents of primary lithium amide. In addition a co-complexed molecule of 2-NHLiPy is present in the unit cell. The N–H proton could not be located within the crystal structure or by ^{1}H NMR, however its presence was established in the infrared spectrum.†

The two stibine centres are bridged *via* a $(CH_2)_3$ backbone [av. Sb–C 2.17(3) Å] and an imido group. The double deprotonation of the 2-aminopyridine is analogous to the previously reported reaction of $Sb(NMe_2)_3$ with primary amines, in these cases generating imido bridged dimers, $[Me_2NSb(\mu\text{-}NR)]_2$,[4] with comparable bond lengths, *e.g.* in $[Me_2NSb\{\mu\text{-}N(C_6H_2(OMe)_3\text{-}3,4,5)\}]_2$ Sb-μ-N 2.05(1) Å compared to av. Sb-μ-N 2.08(2) Å in **1**. The angle about the bridging imido nitrogen is, however, much larger [Sb–N–Sb 130.8(7)° in **1**, *cf.* Sb–N–Sb 104.2(2)° in the dimer] reflecting the presence of a 6-membered ring over the 4-membered ring in the dimers. The bridging nitrogen is in a roughly trigonal planar environment [angles about N ranging from 111.0(10) to 130.8(7)°]. All three of the lithium atoms are solvated by one THF molecule. Two of the three lithium centres (Li1 and Li3) possess a four coordinate tetrahedral geometry [angles about Li ranging from 100.7(14)° to 120.4(13)°], while Li2 adopts a trigonal planar environment [range 114.5(17)° to 128.9(18)°].

Within the structure of **1** two of the pyridyl nitrogen atoms (N2 and N8) chelate to two of the three lithium centres (Li1 and Li3) to yield 6-membered rings. However, bearing in mind the coordinatively unsaturated nature of Li2, it is surprising that one of the other pyridyl groups (*i.e.*, N6) does not rotate and allow a four-fold coordination to be achieved. The pyridyl N–Li distances [av. 2.13(5) Å] are longer than those between the imido nitrogens and lithium [av. 2.00(7) Å].

The formation of **1** may be considered to result from the co-complexation of a primary lithium amide fragment, 2-LiHNPy, and the di-anionic imido antimony species, $[PyNSb(CH_2)_3(\mu\text{-}PyN)SbNPy]^{2-}{\cdot}2Li^+$. Similar behaviour has been observed



Scheme 1

DOI: 10.1039/b007031i

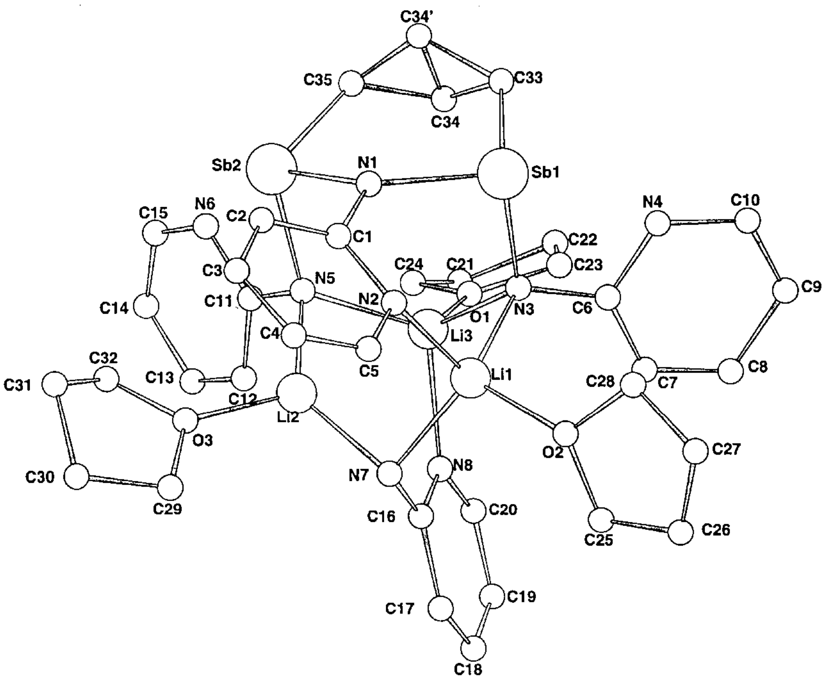


Fig. 1 The crystal structure and atomic numbering scheme for **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sb(1)–C(33) 2.175(15), Sb(1)–N(1) 2.051(11), Sb(1)–N(3) 2.062(11), Sb(2)–C(35) 2.168(19), Sb(2)–N(1) 2.106(11), Sb(2)–N(5) 2.050(12), Li(1)–O(2) 2.00(2), Li(1)–N(3) 2.08(4), Li(1)–N(7) 2.00(3), Li(1)–N(2) 2.12(3), Li(2)–O(3) 1.87(4), Li(2)–N(5) 2.02(3), Li(2)–N(7) 1.93(3), Li(3)–O(1) 2.12(3), Li(3)–N(3) 2.01(3), Li(3)–N(5) 2.00(3), Li(3)–N(8) 2.14(4), C(1)–N(1) 1.408(19), C(6)–N(3) 1.378(19), C(11)–N(5) 1.336(18), C(16)–N(7) 1.309(19); C(33)–Sb(1)–N(3) 97.2(6), C(33)–Sb(1)–N(1) 95.0(6), N(1)–Sb(1)–N(3) 94.2(5), C(35)–Sb(2)–N(5) 101.2(8), C(35)–Sb(2)–N(1) 93.4(6), N(1)–Sb(2)–N(5) 91.1(5), O(2)–Li(1)–N(7) 107.6(14), O(2)–Li(1)–N(3) 113.0(14), N(7)–Li(1)–N(3) 120.4(13), O(2)–Li(1)–N(2) 105.6(13), N(7)–Li(1)–N(2) 104.2(14), N(3)–Li(1)–N(2) 104.8(12), O(3)–Li(2)–N(7) 114.5(17), O(3)–Li(2)–N(5) 116.5(15), N(7)–Li(2)–N(5) 128.9(18), N(5)–Li(3)–N(3) 118.1(16), N(5)–Li(3)–O(1) 109.8(13), N(3)–Li(3)–O(1) 108.1(15), N(5)–Li(3)–N(8) 111.8(15), N(3)–Li(3)–N(8) 107.0(13), O(1)–Li(3)–N(8) 100.7(14), Sb(1)–N(1)–Sb(2) 130.8(7), Sb(1)–N(1)–C(1) 114.5(9), Sb(2)–N(1)–C(1) 111.0(10), C(16)–N(7)–Li(2) 110.5(15), C(16)–N(7)–Li(1) 111.8(12), Li(2)–N(7)–Li(1) 94.5(13), C(11)–N(5)–Li(3) 115.7(13), C(11)–N(5)–Li(2) 113.7(14), Li(3)–N(5)–Li(2) 84.7(13), C(11)–N(5)–Sb(2) 104.4(10), Li(3)–N(5)–Sb(2) 121.8(11), Li(2)–N(5)–Sb(2) 116.2(12), C(6)–N(3)–Li(3) 121.3(13), C(6)–N(3)–Sb(1) 107.0(10), Li(3)–N(3)–Sb(1) 122.8(11), C(6)–N(3)–Li(1) 113.3(11), Li(3)–N(3)–Li(1) 88.6(12), Sb(1)–N(3)–Li(1) 99.3(8).

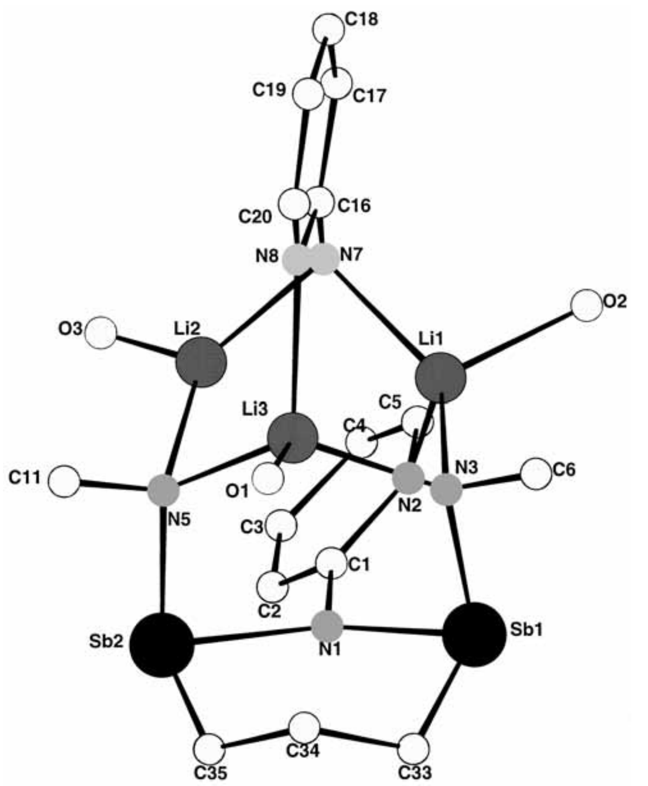


Fig. 2 The core structure of **1**. Hydrogen atoms and non-essential carbon atoms are omitted for clarity.

for the co-complexation between $[(CyNLi)_3Sb]_2$ and KO^tBu, resulting in the termetallic complex, $[(CyNLi)_3Sb]_2(^tBuOK)_3$.[3]

Molecule **1** preferentially crystallises as a single enantiomer. The chirality is a consequence of the presence of the three coordinate lithium centre (Li2) since in solution we would expect the pyridyl group containing N2 to be rapidly oscillating between solvating Li1 and Li2 (*i.e.*, leading to a racemic mixture of both enantiomers).

This work clearly demonstrates the synthetic strategy allowing access to polyimido anion complexes based around polynuclear stibine frameworks. We are currently investigating the imido chemistry of higher nuclearity stibine and stannane moieties with a view to elucidating their structural motifs and coordination chemistry as a class of polydentate metal-based ligands bearing polyfunctional sites.

Acknowledgements

We would like to thank the EPSRC for a project studentship (J. S. J.) and for funding crystallographic facilities.

Notes and references

† 2-Aminopyridine (0.376 g, 4 mmol) was dissolved in 20 ml of hot (dry) toluene. The solution was cooled to 0 °C, ^nBuLi was added (2.5 ml, 4 mmol, 1.6 M in hexanes) and the mixture stirred at room temperature for 4 hours. Subsequently $(Me_2N)_2Sb(CH_2)_3Sb(NMe_2)_2$ (0.462 g, 1 mmol was added to the white suspension and the mixture was heated to reflux overnight to yield a yellow solution. This was reduced to dryness *in vacuo*, and addition of 3 ml THF led to a pale yellow precipitate which dissolved upon gentle warming. Storage at 10 °C overnight resulted in colourless plate-like crystals of **1** in 55% yield (first batch): IR ν/cm^{-1} (Nujol mull), 3315 (N–H); ^1H NMR (300 MHz; C_6D_6; 25 °C), collection of poorly resolved overlapping multiplets δ 6.1–7.9 (pyridyl groups, 16H), 3.55 (t, 12H, O–CH_2), 1.79 (qnt, 2H, $-CH_2CH_2CH_2-$), 1.51 (t 4H, $-CH_2CH_2CH_2-$), 1.31 (m, 12H, O-CH_2CH_2); Satisfactory analyses (C, H, N) were obtained for all samples of **1**.

‡ Crystal data: for $C_{35}H_{47}Li_3N_8O_3Sb_2$ (**1**), $M_r = 892.13$, orthorhombic, space group $P2_12_12_1$, $a = 12.857(3)$, $b = 13.962(3)$, $c = 26.230(5)$ Å,

$\alpha = \beta = \gamma = 90°$, $U = 4708.6(16)$ Å^3, $Z = 4$, $\mu = 1.184$ mm^{-1}, crystal size 0.13 × 0.10 × 0.03 mm, $T = 150$ K; refinement of 8422 unique reflections ($2.92 \leq \theta \leq 26.96°$, $R_{\text{int}} = 0.1856$) against 471 parameters gave $R_1 = 0.0783$ and $wR_2 = 0.1682$ [$I > 2\sigma(I)$] ($R_1 = 0.2253$ and $wR_2 = 0.2206$ for all data).

Data were collected on a Nonius KappaCCD area detector diffractometer, at the window of a Nonius FR591 rotating anode [λ(Mo-Kα) = 0.71073 Å]. Corrections were applied to account for absorption effects by means of comparing multiple and equivalent reflections. Solutions were obtained *via* direct methods and refined by full-matrix least squares on F_o^2, with hydrogens included in idealised positions and refined using the riding model. The absolute structure was confirmed by refinement of the Flack parameter. CCDC reference number 186/2166. See http://www.rsc.org/suppdata/dt/b0/b007031i/ for crystallographic files in .cif format.

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