DALTON
FULL PAPER

Co-ordination of heavier alkali metals by polyimido antimony(III) ligands; syntheses and structures of $[\{Sb_2(NC_6H_{11})_4\}_2M_4]$ (M = Li or Na), $Li[\{(Me_2N)Sb(\mu\text{-}NC_6H_{11})_2\}_2Sb]$ and $M[\{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})_2\}_2Sb]\cdot 2thf$ (M = K or Rb)

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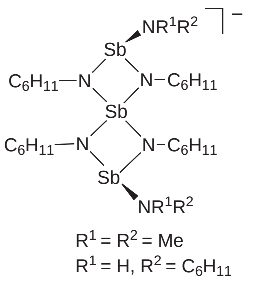
The *in situ* reactions of MCH_2Ph (M = Na, K or Rb) with $C_6H_{11}NH_2$ in toluene followed by the addition of the appropriate stoichiometric quantity of $Sb(NMe_2)_3$ gave the new heterobimetallic antimony(III)/alkali metal complexes $[\{Sb_2(NC_6H_{11})_4\}_2Na_4]$ and $M[\{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})_2\}_2Sb]\cdot 2thf$ (M = K or Rb). Comparison of the crystal structures of these species with those of the lithium complexes $[\{Sb_2(NC_6H_{11})_4\}_2Li_4]$ and $Li[\{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})_2\}_2Sb]$ reveals that the geometries of these heterobimetallic cages are fundamentally dictated by the rigidity of the $[Sb_2(NC_6H_{11})_4]^{2-}$ and $[\{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})_2\}_2Sb]^-$ anions.

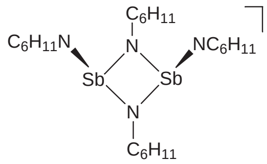
Recently we have shown that the antimony(III) polyimido and phosphinidine anions $[\{(Me_2N)Sb(\mu\text{-}NR)_2\}_2Sb]^-$ **I**,[1b] $[Sb_2(NR)_4]^{2-}$ **II** ($R = C_6H_{11}$),[1a] and $[Sb(ER)_3]^{3-}$ **III** [E = N, $R = C_6H_{11}$,[1a] Bu^t or 2,4-$(MeO)_2C_6H_3$;[1g] E = P, $R = C_6H_{11}$[1e]] can be prepared by the stepwise metallation reactions of dimethylamidoantimony(III) reagents and primary amido and phosphido lithium complexes.[1] The resulting heterometallic Sb^{III}/Li cage compounds are versatile precursors for further cage assembly, the polyimidoantimony(III) anions remaining *intact* in transmetallation and co-complexation reactions with various main-group and transition-metal sources.[2] For example, the transmetallation reaction of $[\{Sb(NC_6H_{11})_3\}_2Li_6]$ with $Pb(C_5H_5)_2\cdot$tmen [tmen = $(MeNCH_2)_2$] gives the polyhedral Sb^{III}/Pb^{II} cage $[\{Sb(NC_6H_{11})_3\}_2Pb_3]$,[2a] whereas the reaction of $[\{Sb(NC_6H_{11})_3\}_2Li_6]$ with KOBu^t results in the co-complex $[\{Sb(NC_6H_{11})_3\}_2Li_6]\cdot 3KOBu^t$.[2c] The accommodation of metal ions of very different sizes by the $[Sb(NR)_3]^{3-}$ ligand owes much to the flexibility of the antimony bridgehead, whose N–Sb–N bond angles can adjust in order to satisfy the co-ordination requirements of the metal ion incorporated.[2d] This situation is in marked contrast to analogous silicon(IV) ligand systems, $[RSi(NR)_3]^{3-}$, where the angles at the silicon bridgehead are constrained by the more rigid sp^3 hybridisation and by the absence of a lone pair.[3]

In order to provide a broader assessment of the co-ordination behaviour of the other antimony(III) polyimide ligands [the monoanion (type **I**) and dianion (type **II**)] and to examine the extents to which modification in their Sb–N cores may occur with the varied ionic radii of the co-ordinated metals, we present here a structural study of the co-ordination of the heavier alkali metals with these ligands. The new complexes $[\{Sb_2(NC_6H_{11})_4\}_2Na_4]$ **2**, containing the $[Sb_2(NC_6H_{11})_4]^{2-}$ dianion, and $M[\{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})_2\}_2Sb]\cdot 2thf$ (M = K **4** or Rb **5**), containing the $[\{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})_2\}_2Sb]^-$ monoanion, have been structurally characterised. Comparison of these complexes with the lithium analogues $[\{Sb_2(NC_6H_{11})_4\}_2Li_4]$ **1**[1a] and $Li[\{(Me_2N)Sb(\mu\text{-}NR_2)\}_2Sb]$ **3**,[1b] whose structures have been communicated previously, gives new insights into the formation and stability of these species and of the geometric flexibility of their monoanion and dianion ligands.

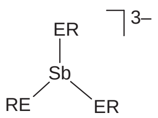


$R^1 = R^2 = Me$
$R^1 = H$, $R^2 = C_6H_{11}$

I



II



$R = C_6H_{11}$, Bu^t, 2,4-$(MeO)_2C_6H_3$; E = N
$R = C_6H_{11}$; E = P

III

Results and Discussion

The preparation of the lithium complex **1** was achieved by the *in situ* reaction of the antimony(III) dimer $[\{(Me_2N)Sb(\mu\text{-}NC_6H_{11})\}_2]$ [prepared from the 1:1 reaction of $C_6H_{11}NH_2$ with $Sb(NMe_2)_3$] with $(LiNHC_6H_{11})_n$ (1:1 monomer equivalents, respectively) in toluene (Scheme 1).[1a] Yields of up to 80% of this species can be obtained in large-scale preparations, thus providing a readily accessible starting material for the investigation of the co-ordination chemistry of the $[Sb_2(NC_6H_{11})_4]^{2-}$ anion. The new complex **2** was prepared by the one-pot reaction of a mixture of $C_6H_{11}NH_2$ with $NaCH_2Ph$ in toluene (2:1 equivalents) with $Sb(NMe_2)_3$ (1 equivalent) in *ca.* 50% yield. The reaction is assumed to occur in a similar way to that producing **1**, by the initial formation of $[\{(Me_2N)Sb(\mu\text{-}NC_6H_{11})\}_2]$ which then reacts with $NaNHC_6H_{11}$. Attempts to prepare **2** by the exchange reaction of **1** with NaOBu^t proved unsuccessful owing, we assume, to competing incorporation of

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$$2\,\mathrm{Sb(NMe_2)_3} + 2\mathrm{C_6H_{11}NH_2} \xrightarrow{-4\mathrm{Me_2NH}} [\{\mathrm{(Me_2N)Sb(\mu\text{-}NC_6H_{11})}\}_2] \xrightarrow{2\mathrm{LiNHC_6H_{11}}} \tfrac{1}{2}[\{\mathrm{Sb_2(NC_6H_{11})_4}\}_2\mathrm{Li_4}] + 2\mathrm{Me_2NH}$$

1

$$2\,\mathrm{Sb(NMe_2)_3} + 4\mathrm{C_6H_{11}NH_2} + 2\mathrm{NaCH_2Ph} \longrightarrow \tfrac{1}{2}[\{\mathrm{Sb_2(NC_6H_{11})_4}\}_2\mathrm{Na_4}] + 2\mathrm{C_6H_5Me} + 6\mathrm{Me_2NH}$$

2

$$\mathrm{Li^+[Sb(NHC_6H_{11})_4]^-} + 2\,\mathrm{Sb(NMe_2)_3} \longrightarrow \mathrm{Li}[\{\mathrm{(Me_2N)Sb(\mu\text{-}NC_6H_{11})_2}\}_2\mathrm{Sb}] + 4\mathrm{Me_2NH}$$

3

$$3\,\mathrm{Sb(NMe_2)_3} + 6\mathrm{C_6H_{11}NH_2} + \mathrm{MCH_2Ph} \xrightarrow{\mathrm{thf}} \mathrm{M}[\{\mathrm{(C_6H_{11}NH)Sb(\mu\text{-}C_6H_{11})_2}\}_2\mathrm{Sb}]\cdot 2\mathrm{thf} + \mathrm{C_6H_5Me} + 9\mathrm{Me_2NH}$$

M = K **4**, Rb **5**

Scheme 1

the metal alkoxide into the cage of **1**[2c] (only a highly soluble, impure material could be isolated by removal of the solvent in this case).

The preparation of the lithium monoanion complex **3** was performed by the reaction of the primary amido antimony(III) intermediate $\mathrm{Li^+[Sb(NHC_6H_{11})_4]}$ [prepared *in situ* from $\mathrm{SbCl_3}$ and $\mathrm{LiNHC_6H_{11}}$ (1 : 4 equivalents)] with $\mathrm{Sb(NMe_2)_3}$ (1 : 2 equivalents, respectively).[1b] The crystallisation of **3** from toluene is very temperamental and as a result of its high solubility the yield of crystalline material is usually low (up to 32%). However, yields of up to *ca.* 60% can be obtained by precipitation of the complex with hexane. Unlike the stepwise process used in the preparation of **3**, the preparations of the new monoanion complexes **4** and **5** were achieved directly by the simple *in situ* reactions of $\mathrm{Sb(NMe_2)_3}$ (3 equivalents) with a mixture of $\mathrm{C_6H_{11}NH_2}$ (6 equivalents) and $\mathrm{MCH_2Ph}$ (M = K or Rb) (1 equivalent). This route provides the cleanest and without doubt the best route to the related $[\{\mathrm{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})_2}\}_2\mathrm{Sb}]^-$ monanion. Although it is not clear how the spiro Sb–N framework of the monoanion comes about from this reaction, Norman and co-workers[4] have recently shown that the reaction of $\mathrm{SbCl_3}$ with LiNHR (1 : 3 equivalents) gives the imido-antimony(III) dimer $[\{\mathrm{(RNH)Sb(\mu\text{-}NR)}\}_2]$ (R = 2,6-$\mathrm{Me_2C_6H_3}$). The related complex $[\{\mathrm{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})}\}_2]$, generated from the reaction of $[\{\mathrm{(Me_2N)Sb(\mu\text{-}NC_6H_{11})}\}_2]$ with excess of $\mathrm{C_6H_{11}H_2}$, is a likely intermediate in the formation of the $[\{\mathrm{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})_2}\}_2\mathrm{Sb}]^-$, which can be conceived to occur by the equilibration reaction of $[\{\mathrm{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})}\}_2]$ with the known dianion $[\mathrm{Sb_2(NC_6H_{11})_4}]^{2-}$ (Scheme 2). However, it should be noted that repeated attempts to prepare various neutral dimers similar to $[\{\mathrm{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})}\}_2]$, by the reactions of $[\{\mathrm{(Me_2N)Sb(\mu\text{-}NR)}\}_2]$ (R = 2-$\mathrm{MeOC_6H_4}$) with $\mathrm{R'NH_2}$, have so far failed, owing to the apparently low reactivity of the terminal $\mathrm{Me_2N}$ groups with primary amines (only the unchanged species $[\{\mathrm{(Me_2N)Sb(\mu\text{-}NR)}\}_2]$ being isolated).

The initial characterisation of all of the complexes **1**–**5** was made using a combination of ^{1}H NMR spectroscopy and elemental analyses (C, H and N). The presence of $\mathrm{C_6H_{11}}$ groups, whose $\mathrm{CH_2}$ protons appear as a set of broad overlapping multiplets in the region δ 0.5–2.5, in these complexes makes their definitive characterisation difficult on the strength of basic techniques. In particular, for the monoanion complexes **4** and **5** only very weak and broad N–H stretching bands are observed in their IR spectra and no N–H proton could be identified unequivocally in their room-temperature ^{1}H NMR spectra, despite the presence of terminal $\mathrm{C_6H_{11}NH}$ groups (as later revealed by X-ray structural determinations). The structural characterisation of these complexes was therefore of primary importance, especially in respect of the assessment of potential structural variation induced in the cage frameworks by the incorporation of alkali-metal cations of vastly different ionic radii.

$$[\{\mathrm{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})}\}_2] + \tfrac{1}{4}[\{\mathrm{Sb_2(NC_6H_{11})_4}\}_2\mathrm{M_4}] \xrightarrow{\mathrm{thf}} \mathrm{M}[\{\mathrm{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})_2}\}_2\mathrm{Sb}]\cdot 2\mathrm{thf}$$

Scheme 2

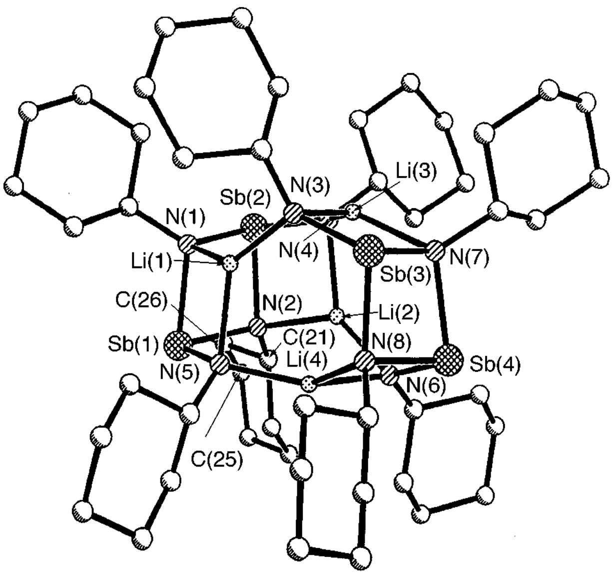

Fig. 1 Structure of $[\{\mathrm{Sb_2(NC_6H_{11})_4}\}_2\mathrm{Li_4}]$ **1**

The structures of complexes **1**–**5** were determined using low-temperature X-ray crystallography. Those of **1** and **3** have previously been communicated and will only be discussed here by way of comparison with the new complexes **2**, **4** and **5**. Table 1 lists key bond lengths and angles for **2**. For comparison, data for **4** and **5** are given collectively in Table 2.

The comparison of the structures of complexes **1**–**5** allows the assessment of the way in which the $[\mathrm{Sb_2(NC_6H_{11})_4}]^{2-}$ dianion and $[\{\mathrm{(RNH)Sb(\mu\text{-}NR)_2}\}_2\mathrm{Sb}]^-$ monoanion can adjust to accommodate different alkali-metal cations. The structure of $[\{\mathrm{Sb_2(NC_6H_{11})_4}\}_2\mathrm{Li_4}]$ **1** (Fig. 1) is that of a molecular cage which can be regarded as being formed by the association of two $[\{\mathrm{Sb_2(NC_6H_{11})_4}\}\mathrm{Li_2}]$ cubane halves.[1c] This formulation is supported by the dissociation of the complex into its cubane fragments in arene solutions and by the observation of discrete cubane units for the related bismuth complex $[\{\mathrm{Bi_2(NBu^t)_4}\}_2\mathrm{(Li{\cdot}thf)_2}]$, in which solvation of the $\mathrm{Li^+}$ cations intercepts the formation of the larger dimeric cage arrangement.[1c] The overall structure of **1** is similar to that of $[\mathrm{AlH(NPr^i)}]_8$[5] and $[\mathrm{AlMe(NMe)}]_8$.[6,7] The $[\mathrm{Sb_2(NC_6H_{11})_4}]^{2-}$ dianions co-ordinate the $\mathrm{Li^+}$ cations of the core using their μ-$\mathrm{NC_6H_{11}}$ [2.00(2)–2.14(2) Å] and pendant $\mathrm{NC_6H_{11}}$ groups [1.94(2)–2.03(2) Å], resulting in similar, highly irregular planar geometries for the lithium centres [range N–Li–N 88.0(8)–135.6(1)°, sum of N–Li–N average 353.8°]. The Li–N bonds throughout the core of **1** are typical of amidolithium complexes.[8] In addition, α-C–H interactions occur with adjacent $\mathrm{C_6H_{11}}$ groups which (in effect) reinforce the association of the cubane halves of the core {2.53(2)–2.63(2) Å; *cf.* 2.60–2.70 Å in $[\mathrm{LiN(CH_2Ph)_2}]_3$[9]}.

The structure of the sodium complex $[\{\mathrm{Sb_2(NC_6H_{11})_4}\}_2\mathrm{Na_4}]$ **2** has similar features to those observed in **1**. There are two independent chemically identical molecules of **2** in the asymmetric unit which differ marginally in their bond lengths and angles (one of which is shown in Fig. 2). Despite the similarity with **1** in terms of its composition, the accommodation of the larger alkali-metal cations by the $[\mathrm{Sb_2(NC_6H_{11})_4}]^{2-}$ dianions in **2** has a profound effect on the geometry of the cage. The most obvious result is the adoption of a planar, rhombic $\mathrm{Na_4}$ arrangement at the centre of the cage (with alternating Na ··· Na ··· Na angles of average 93.5 and average 86.4° and with the mean deviation from the $\mathrm{Na_4}$ plane of 0.05 Å), rather than the tetrahedral pattern that is present in **1**. As a consequence of the greater ionic radius of $\mathrm{Na^+}$ and of the correspondingly longer

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

Molecule 1				Molecule 2			
Sb(1)–N(2)	2.14(2)	Na(1)–N(1)	2.95(3)	Sb(5)–N(15)	2.14(2)	Na(5)–N(14)	3.23(3)
Sb(1)–N(7)	2.12(2)	Na(1)–N(1)	3.18(3)	Sb(5)–N(16)	2.15(2)	Na(5)–N(15)	2.90(3)
Sb(2)–N(2)	2.09(2)	Na(2)–N(6)	2.30(2)	Sb(6)–N(15)	2.13(2)	Na(6)–N(12)	2.29(2)
Sb(2)–N(7)	2.12(2)	Na(2)–N(2)	2.31(2)	Sb(6)–N(16)	2.12(2)	Na(6)–N(11)	2.25(3)
Sb(1)–N(5)	1.95(2)	Na(2)–N(8)	2.97(3)	Sb(5)–N(9)	1.99(2)	Na(6)–N(15)	2.96(3)
Sb(2)–N(6)	1.99(2)	Na(2)–N(2)	2.74(3)	Sb(6)–N(11)	2.00(2)	Na(6)–N(10)	3.23(3)
Sb(3)–N(1)	2.11(2)	Na(3)–N(4)	2.26(2)	Sb(7)–N(14)	2.11(2)	Na(7)–N(11)	2.32(2)
Sb(3)–N(8)	2.17(2)	Na(3)–N(5)	2.33(3)	Sb(7)–N(10)	2.12(2)	Na(7)–N(13)	2.36(2)
Sb(4)–N(1)	2.10(2)	Na(3)–N(1)	2.92(3)	Sb(8)–N(14)	2.09(2)	Na(7)–N(10)	2.77(3)
Sb(4)–N(8)	2.13(2)	Na(3)–N(7)	2.89(3)	Sb(8)–N(10)	2.10(2)	Na(7)–N(16)	2.80(2)
Sb(4)–N(4)	1.97(2)	Na(4)–N(6)	2.37(2)	Sb(7)–N(13)	1.96(2)	Na(8)–N(9)	2.37(2)
Sb(8)–N(3)	2.00(2)	Na(4)–N(4)	2.36(2)	Sb(8)–N(12)	1.99(2)	Na(8)–N(13)	2.37(2)
Na(1)–N(5)	2.28(3)	Na(4)–N(7)	2.90(2)	Na(5)–N(9)	2.24(3)	Na(8)–N(14)	2.65(3)
Na(1)–N(3)	2.25(2)	Na(4)–N(8)	2.78(3)	Na(5)–N(12)	2.30(3)	Na(8)–N(16)	2.98(2)
		Na···Na	3.16*			Na···Na	3.16*
Sb–(μ-N)–Sb	94.8*	N(5,6)–Na–N(3,4)	154(1)–164(1)	Sb–(μ-N)–Sb	94.8*	N(11,9)–N–N(12,13)	151(1)–169.3(9)
(μ-N)–Sb–(μ-N)	77.0*	N(2,7)–Na–N(1,8)	126.0(8)–131.1(7)	(μ-N)–Sb–(μ-N)	77.7*	N(15,16)–Na–N(10,14)	129.3(7)–135.3(7)
(μ-N)–Sb–N	99.4*	Na···Na···Na	85.5(5)–94.2(5)	(μ-N)–Sb–N	99.6*	Na···Na···Na	86.7(4)–93.8(4)
SbNNSb dihedral	140.3*			SbNNSb dihedral	141.2*		

* Average

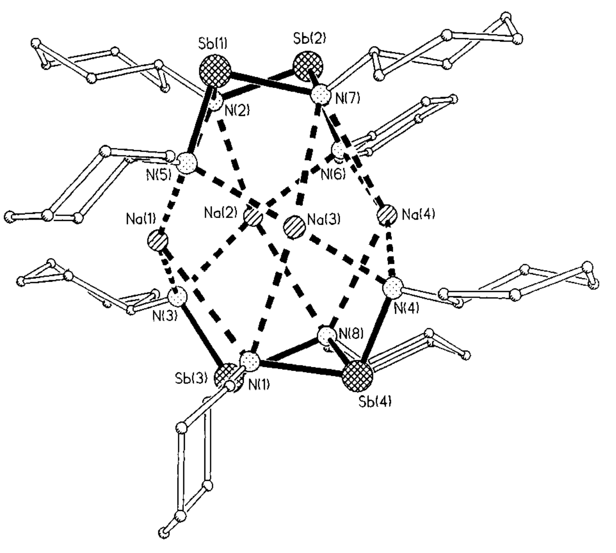

Fig. 2 Structure of $[\{Sb_2(NC_6H_{11})_4\}_2Na_4]$ **2**

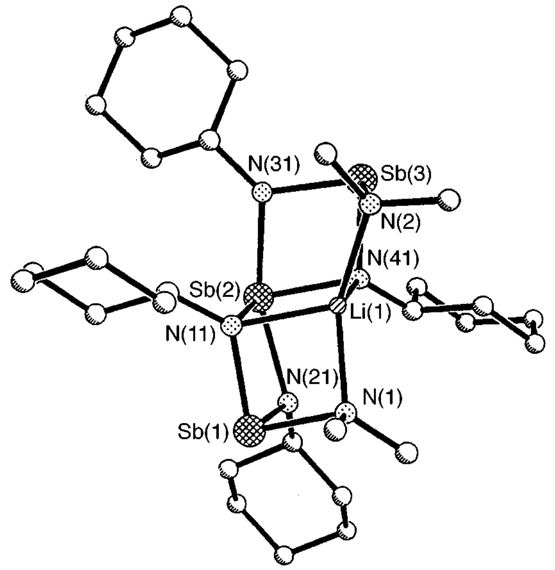

Fig. 3 Structure of $Li[\{(Me_2N)Sb(\mu\text{-}NC_6H_{11})_2\}_2Sb]$ **3**

alkali metal–nitrogen bonds, the $[\{Sb_2(NC_6H_{11})_4\}Na_2]$ halves of the molecule no longer resemble cubane fragments. The strain induced by the complexation of the larger cations results in greater puckering in the $[Sb(\mu\text{-}NC_6H_{11})]_2$ rings of the $[Sb_2(NC_6H_{11})_4]^{2-}$ dianions, which are splayed open in order to engage the Na^+ cations using their $\mu\text{-}NC_6H_{11}$ and pendant NC_6H_{11} groups. The major advantage of this more open arrangement is that the Na^+ cations ultimately obtain a greater co-ordination number than is observed for the Li^+ cations of **1**, with each being bonded to a $\mu\text{-}NC_6H_{11}$ and pendant NC_6H_{11} group of the $[Sb_2(NC_6H_{11})_4]^{2-}$ dianions in the molecule. The metal core arrangement and the mode of co-ordination of the metal centres by the $\mu\text{-}NC_6H_{11}$ and pendant NC_6H_{11} groups in **2** are similar to those in the copper(I) complex $[\{Sb_2(NC_6H_{11})_4\}_2Cu_4]$, where a central square-planar Cu_4 core is stabilised by two $[Sb_2(NC_6H_{11})_4]^{2-}$ dianions.[2a,b] However, this similarity does not stem from similar ionic sizes [*i.e.* Cu^+ 0.91 Å; *cf.* Na^+ 1.10 Å and Li^+ (four-co-ordinated) 0.73 Å],[10] but rather from the preference for approximately linear co-ordination of the copper(I) centres by the pendant NC_6H_{11} groups of the dianion (N–Cu–N average 168.7°; *cf.* N–Na–N average 159.6°) and from the formation of weak Cu···Cu interactions (average 2.57 Å; *cf.* 2.56 Å in copper metal[10]). The possibility of Na···Na bonding can be discounted in **2**.[8]

The molecular arrangement of complex **2** can be understood in terms of the compromise between the bonding demands of the $[Sb_2(NC_6H_{11})_4]^{2-}$ dianions and the co-ordination requirements of the Na^+ cations. The more rigid bonding demands of the $[Sb_2(NC_6H_{11})_4]^{2-}$ dianion units clearly dominate this balance, as can be seen from the similarity of the bond lengths and angles observed in the $[Sb_2(NC_6H_{11})_4]^{2-}$ dianions of **1** and **2** and from the large rearrangement in the imidoalkali metal core geometries. The Na^+ cations of **2** have extremely irregular, squared-based pyramidal co-ordination geometries. Although the Na–N bonds made with the pendant NC_6H_{11} groups of the $[Sb_2(NC_6H_{11})_4]^{2-}$ dianions fall in the expected range [2.24(3)–2.37(2) Å] found in amidosodium complexes,[8b,11] the bonds made with the $\mu\text{-}NC_6H_{11}$ groups are unusually long and highly irregular [2.65(3)–3.19(2) Å]. These are best described as weak co-ordinative interactions.

The molecular structures of $Li[\{(Me_2N)Sb(\mu\text{-}NC_6H_{11})_2\}_2Sb]$ **3**[1b] (Fig. 3), $K[\{(C_6H_{11}NH)Sb(\mu\text{-}NC_6H_{11})_2\}_2Sb]\cdot 2thf$ **4** and

Table 2 Selected bond lengths (Å) and angles (°) for complexes **4** (M = K) and **5** (M = Rb)*

	4	**5**		**4**	**5**
Sb(1)–N(1A)	2.219(6)	2.224(6)	Sb(2)–N(1C)	2.092(7)	2.088(7)
Sb(1)–N(1B)	2.091(5)	2.086(6)	N(1B)–M	2.916(6)	3.019(7)
Sb(2)–N(1A)	2.000(6)	1.991(6)	N(1C)–M	2.941(6)	3.060(7)
Sb(2)–N(1B)	2.047(6)	2.039(6)	O–M	2.788(8)	3.023(8)
N(1A)–Sb(1)–N(1B)	73.5(2)	73.0(2)	Sb(1)–N(1B)–Sb(2)	102.7(2)	103.1(3)
N(1A)–Sb(1)–N(1B^I)	88.2(2)	89.0(2)	O–M–O	82.3(4)	86.4(4)
N(1A)–Sb(1)–N(1A^I)	151.5(2)	151.8(4)	N(1B)–M–N(1B^I)	66.9(2)	63.5(2)
N(1B)–Sb(1)–N(1B^I)	100.5(3)	101.0(4)	N(1C)–M–N(1C^I)	160.4(3)	154.0(3)
N(1A)–Sb(2)–N(1B)	79.3(2)	79.1(2)	N(1C)–M–N(1B)	64.1(2)	61.6(2)
N(1A)–Sb(2)–N(1C)	94.1(3)	94.4(3)	N(1C)–M–N(1B^I)	98.8(2)	95.3(2)
N(1B)–Sb(2)–N(1C)	97.4(3)	98.0(3)	O(1D)–M–N(1C)	96.5(2)	93.2(2)
Sb(1)–N(1A)–Sb(2)	99.9(2)	100.0(2)	O(1D)–M–N(1C^I)	98.3(2)	105.8(2)
			O(1D)–M–N(1B^I)	108.6(2)	106.9(2)

* Symmetry transformation used to generate equivalent atoms: I $-x + 1, y, -z + \frac{1}{2}$.

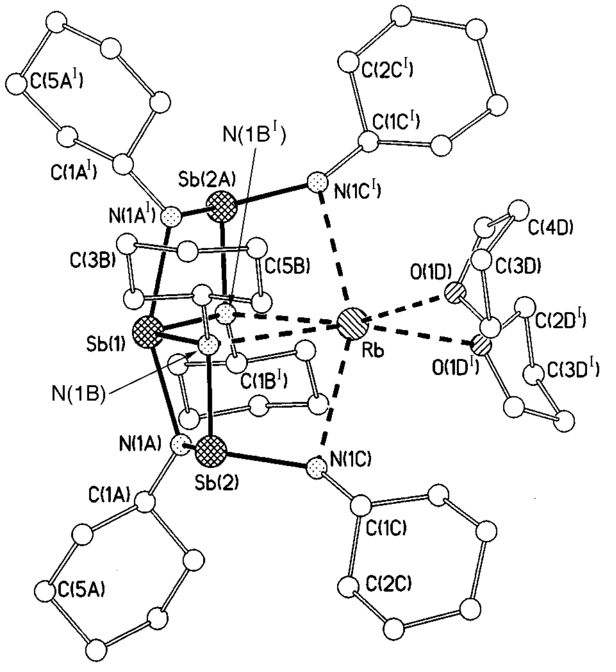

Fig. 4 Structure of Rb[{(C_6H_{11}NH)Sb(μ-NC_6H_{11})$_2$}$_2$Sb]·2thf, illustrating the structural pattern found in the isomorphous complexes (M = K **4** or Rb **5**)

Rb[{(C_6H_{11}NH)Sb(μ-NC_6H_{11})$_2$}$_2$Sb]·2thf **5** (Fig. 4) all contain similar imidoantimony(III) monoanion ligands which consist of two fused Sb_2N_2 rings sharing a central four-co-ordinate (10e) square-based pyramidal antimony centre. The alkali-metal cations are co-ordinated in a similar way in all of these species, by the terminal amide ligands of the antimony(III) monoanions and by two of the μ-NC_6H_{11} imido groups within the [Sb_3N_4] cores. The Li^+ cation of **3** adopts a highly distorted tetrahedral geometry (N–Li–N range 87.4–143.6°), while the additional co-ordination of the K^+ and Rb^+ cations by two thf molecules in **4** and **5** (each of which is disordered over two 1 : 1 sites) results in distorted octahedral geometries for these ions [N(1C)–K–N(1C^I) 160.4(3), N(1B)–K–N(1B^I) 66.9(2), O–K–O 82.3(4)° in **4**; N(1C)–Rb–N(1C^I) 154.0(3), N(1B)–Rb–N(1B^I) 63.5(2), O–Rb–O 86.4(4)° in **5**].

Despite the obvious differences in the steric demands of the terminal NMe_2 and NHC_6H_{11} substituents present in complexes **3**, **4** and **5** and the differing co-ordination numbers and ionic radii of the alkali-metal cations in these species, the geometries of their imidoantimony(III) anions are extremely similar. The pattern of (short, medium and long) Sb–N bond lengths and N–Sb–N angles within these units largely reflects the electronic and bonding demands of the antimony(III) centres. The longest Sb–N bonds occur at the axial positions of the four-co-ordinate (10e) antimony(III) centres [Sb(2)–N(21,31) average 2.23 Å in **3**;[1b] Sb(1)–N(1A) 2.219(6) and 2.224(6) Å in **4** and **5** respectively], with Sb–N bonds of intermediate lengths being found at the equatorial positions [Sb(2)–N(11,41) average 2.12 Å;[1b] Sb(1)–N(1B) 2.091(5) and 2.086(6) Å in **4** and **5** respectively], and with the shortest Sb–N bonds occurring at the terminal, three-co-ordinate (8e) antimony(III) centres [Sb–μ-NC_6H_{11} average 2.02 Å in all the complexes]. The more asymmetrical structure of the [{(Me_2N)Sb(μ-NC_6H_{11})$_2$}$_2$Sb]$^-$ anion of **3** presumably results from strain induced by the accommodation of the smaller Li^+ cation into the cage arrangement and from the presence of stronger alkali metal–nitrogen bonds which can compete more effectively for the electron density on the NC_6H_{11} groups. In this connection, the only major difference in the geometries of the imidoantimony(III) anions of **3**–**5** is in the N–Sb–N angle between the equatorial NC_6H_{11} groups of the central four-co-ordinate Sb atom [N(11)–Sb(2)–N(41) 92.5(2)° in **3**; *cf.* N(1B)–Sb(1)–N(1B^I) 100.5(3) and 101.0(4)° in **4** and **5** respectively]. In K[{(C_6H_{11}NH)Sb(μ-NC_6H_{11})$_2$}$_2$Sb]·2toluene,[2a] in which the K^+ cation is only loosely solvated by toluene C–H···K^+ interactions, not only is the [{(C_6H_{11}NH)Sb(μ-NC_6H_{11})$_2$}$_2$Sb]$^-$ anion almost identical in terms of its bond lengths and angles to that present in **4**, but a similar N–Sb–N angle between the equatorial NC_6H_{11} groups of the four-co-ordinate antimony centre [100.8(2)°] is observed. The expansion of this angle is directly related to the increased size of the co-ordinated alkali-metal cations (Li^+ 0.73, K^+ 1.33, Rb^+ 1.48 Å[10]) which are chelated by the equatorial NC_6H_{11} groups, and presumably this results in a reduction in strain within the more symmetrical antimony(III) anion arrangements found in the heavier alkali-metal complexes.

Conclusion

The structural investigation presented here provides a more detailed understanding of the co-ordination behaviour, flexibility and bonding demands of imidoantimony(III) monoanions, of the type [{(R^1R^2N)Sb(μ-NC_6H_{11})$_2$}$_2$Sb]$^-$ (R^1, R^2 = Me; R^1 = H, R^2 = C_6H_{11}), and of the imidoantimony(III) dianion ligand, [Sb_2(NC_6H_{11})$_4$]$^{2-}$. Comparison of the Li^+ complex [{Sb_2(NC_6H_{11})$_4$}$_2$$Li_4$] **1** with the Na^+ analogue [{Sb_2(NC_6H_{11})$_4$}$_2$$Na_4$] **2** and Li[{($Me_2$N)Sb(μ-NR)$_2$}$_2$Sb] **3** with M[{($C_6H_{11}$NH)Sb(μ-NR)$_2$}$_2$Sb]·2thf (M = K **4** or Rb **5**) illustrates that the structures of these heterobimetallic antimony(III)/alkali metal cages depend on a subtle balance between the bonding demands of the antimony and alkali-metal centres. The greatest deformations in the antimony anion geometries occur in the Li^+ complexes, where the alkali metal–nitrogen bonding is strongest. However, overall the more rigid requirements of Sb^{III} dominate

Table 3 Crystal data for complexes **2**, **4** and **5**

	2	**4**	**5**
Chemical formula	$C_{48}H_{88}N_8Na_4Sb_4$	$C_{44}H_{82}KN_6O_2Sb_3$	$C_{44}H_{82}N_6O_2RbSb_3$
M	1356.22	1131.51	1177.88
Crystal size/mm	0.30 × 0.10 × 0.08	0.16 × 0.20 × 0.40	0.20 × 0.32 × 0.40
T/K	150(2)	223(2)	223(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$C2/c$	$C2/c$
a/Å	24.560(4)	23.616(3)	22.733(4)
b/Å	18.46(1)	11.067(1)	11.298(1)
c/Å	25.187(5)	20.777(2)	21.075(4)
β/°	91.28(2)	104.233(7)	103.52(2)
U/Å^3	11 413(7)	5263(1)	5263(2)
Z	8	4	4
D_c/g cm^{-3}	1.579	1.428	1.487
μ/mm^{-1}	1.942	1.645	2.485
θ Range/°	2.54–20.00	1.78–25.00	1.84–25.00
F(000)	5440	2304	2376
Reflections collected	11 085	9491	5570
Independent reflections (R_{int})	10 631 (0.021)	4637 (0.040)	4630 (0.067)
$R1$, $wR2$ [$F > \sigma(F)$]*	0.076, 0.173	0.048, 0.115	0.051, 0.097
(all data)	0.254, 0.252	0.085, 0.139	0.111, 0.121
Peak and hole/e Å^{-3}	1.129, −1.211	0.888, −0.491	0.889, −0.717

* $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2[\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$.

the essentially ionic alkali metal–nitrogen frameworks in these species, as is illustrated by the predominant rigidity of the Sb–N cores. Larger metal ions can be accommodated by the $[Sb_2(NC_6H_{11})_4]^{2-}$ dianion by maximising the M–N bonding with the μ-N and terminal N groups and by deformation about the N · · · N axis of the Sb_2N_2 ring. In the monoanions the complexation of ions with greater ionic radii is achieved almost entirely by expanding the chelating N–Sb–N angle at the central Sb.

Experimental

General preparative techniques

All the reactions were undertaken under dry, O_2-free argon using a vacuum line and standard inert-atmosphere techniques.[12] Tetahydrofuran, Et_2O and toluene were dried by distillation over sodium–benzophenone and hexane was distilled over Na. Cyclohexylamine was dried using molecular sieves (13X). Complexes **1**–**5** were isolated and characterised with the aid of a N_2-filled glove-box (Miller-Howe, fitted with a Belle internal circulation system). Melting points were determined using a conventional apparatus and sealing samples in capillaries under N_2. Elemental analyses (C, H and N) were performed by first sealing samples in air-tight aluminium boats (1–2 mg) prior to analysis using a Perkin-Elmer 240 Elemental Analyser. Proton NMR spectra were recorded on a Bruker WH 250 MHz spectrometer, using the NMR solvents as internal reference standards. The syntheses of $[\{Sb_2(NC_6H_{11})_4\}_2Li_4]$ **1** and $Li[\{(Me_2N)Sb(\mu\text{-}NC_6H_{11})_2\}_2Sb]$ **3** have been communicated previously [see refs. 1(*a*) and 1(*b*)]. The compounds MCH_2Ph (M = Na, K, or Rb) were prepared by the reactions of $MOBu^t$ with $LiBu^n$ in toluene (by deprotonation of C_6H_5Me with the MBu^n initially formed), the reagents being isolated as orange-red amorphous materials in quantitative yields.

Syntheses

Complex 2. A solution of $C_6H_{11}NH_2$ (1.72 cm^3, 15 mmol) in toluene (10 cm^3) was added at −78 °C to a suspension of $NaCH_2Ph$ (0.98 g, 7.5 mmol) in toluene (10 cm^3). The mixture was warmed to room temperature and stirred (5 min) to give a slightly cloudy, brown solution. A standardised solution of $Sb(NMe_2)_3$ (3.75 cm^3, 7.5 mmol, 2.0 mol dm^{-3} in thf) was added to the cooled solution at −78 °C. The resulting solution was stirred (20 min) and allowed to warm to room temperature. Filtration (porosity 3, Celite) gave a brown solution. Reduction of the filtrate under vacuum to *ca.* 10 cm^3 gave a pale green precipitate which was heated into solution. Storage at room temperature (24 h) gave light yellow crystalline rods of **2**; 1.2 g (50%); decomp. 130 °C; ^{1}H NMR (+25 °C, 250 MHz, C_6D_6) δ 0.8–2.5 (overlapping multiplet, C_6H_{11} groups) (Found: C, 42.4; H, 6.6; N, 7.9. Calc. for $[\{[Sb_2(NC_6H_{11})_4]Na_2\}_n]$: C, 43.5; H, 6.5; N, 8.2%).

Complex 4. A solution of $C_6H_{11}NH_2$ (1.72 cm^3, 15 mmol) in toluene (10 cm^3) was added at −78 °C to a suspension of KCH_2Ph (0.33 g, 2.5 mmol) in toluene (10 cm^3). The mixture was warmed to room temperature and stirred (5 min) to give a red-brown solution. A standardised solution of $Sb(NMe_2)_3$ (3.75 cm^3, 7.5 mmol, 2.0 mol dm^{-3} in thf) was added to the cooled solution at −78 °C. The resulting solution was stirred (20 min) and allowed to warm to room temperature. Filtration (porosity 3, Celite) gave a red solution. The toluene was removed under vacuum and Et_2O (10 cm^3) added. Addition of thf gave initial precipitation of a colourless solid which redissolved upon addition of further thf (*ca.* 2 cm^3). Crystals of **4** were grown by storage (12 h) of this solution at −15 °C; 1.55 g (54%); decomp. 130 °C; IR (Nujol) >3000vw (br) cm^{-1} (N–H str.); ^{1}H NMR (+25 °C, 250 MHz, C_6D_6), δ 0.8–2.5 (overlapping multiplet, C_6H_{11} groups) (Found: C, 46.2; H, 7.1; N, 7.4. Calc. for $\{K[Sb_3(NC_6H_{11})_4(NHC_6H_{11})_2]\cdot 2thf\}_n$: C, 44.3; H, 7.7; N, 7.7%).

Complex 5. A solution of $C_6H_{11}NH_2$ (1.72 cm^3, 15 mmol) in toluene (10 cm^3) was added at −78 °C to a suspension of KCH_2Ph (0.42 g, 2.5 mmol) in toluene (10 cm^3). The mixture was warmed to room temperature and stirred (5 min) to give a deep red solution. A standardised solution of $Sb(NMe_2)_3$ (3.75 cm^3, 7.5 mmol, 2.0 mol dm^{-3} in thf) was added to the cooled solution at −78 °C. The resulting solution was stirred (20 min) and allowed to warm to room temperature. Filtration (porosity 3, Celite) gave a dark brown-red solution. The toluene was removed under vacuum and Et_2O (10 cm^3) added. Addition of thf gave initial precipitation of a colourless solid which redissolved upon addition of further thf (*ca.* 2 cm^3). Crystals of complex **5** were grown at room temperature (12 h); 1.73 g (59%); decomp. 130 °C; IR (Nujol) >3000vw (br) cm^{-1} (N–H str.); ^{1}H NMR (+25 °C, 250 MHz, C_6D_6) δ 0.8–2.5 (overlapping multiplet, C_6H_{11} groups) (Found: C, 44.4; H, 7.1; N, 7.4. Calc. for $\{Rb[Sb_3(NC_6H_{11})_4(NHC_6H_{11})_2]\cdot 2thf\}_n$: C, 44.8; H, 7.1; N, 7.1%).

X-Ray crystallography

Crystals were mounted directly from solution under argon using a perfluorocarbon oil which protects them from atmospheric O_2 and moisture.[13] The oil freezes at reduced temperatures and holds the crystal static in the X-ray beam. Data for complexes **1**, **2** and **3** were collected on a Stoe-Siemens AED four-circle diffractometer and for **4** and **5** on a Siemens P4 diffractometer. The structures of all the complexes were solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL[14]). In the isomorphous crystals of **4** and **5** the alkali metal-co-ordinated thf ligands and one cyclohexyl ring are all disordered over two sites of approximately 0.5 occupancy. Details of the structure refinements for **2**, **4** and **5** are shown in Table 3.

CCDC reference number 186/902.

See http://www.rsc.org/suppdata/dt/1998/1389/ for crystallographic files in .cif format.

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