Synthesis and structure of [{(Bu^{t}O)$_2$Sb$_3$(μ-NCy)$_3$(μ$_3$-NCy)}K·η^6-C$_6$H$_5$Me]; a sandwich complex containing a unique Sb^{III} *nido* cage anion (Cy = cyclohexyl, C$_6$H$_{11}$)

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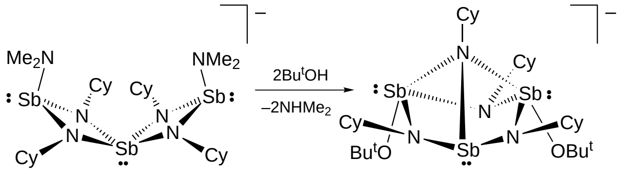
Reaction of the terminal NMe$_2$ groups of the *spiro* antimony(III) imido anion [{(Me$_2$N)Sb(μ-NCy)}$_2$Sb]$^-$ with Bu^{t}OH results in major rearrangement in the Sb–N framework as witnessed in the structure of the sandwich complex [{(Bu^{t}O)$_2$Sb$_3$(μ-NCy)$_3$(μ$_3$-NCy)}K·η^6-C$_6$H$_5$Me] 1, containing the novel *nido* cage anion [(Bu^{t}O)$_2$Sb$_3$(μ-NCy)$_3$(μ$_3$-NCy)]$^-$.

We have recently investigated the structures and coordination chemistry of imido and phosphinidene anions of p block metals (group 13–15).[1–3] These species are readily prepared by the reactions of primary amido or phosphido lithium complexes, [REHLi] (E = N, P), with dimethylamido metal reagents or neutral metal imido cages and function as relatively robust ligands for a range of main group and transition metal ions.[4] For example, the transmetallation reaction of [{Sb(NCy)$_3$}$_2$Li$_6$] (Cy = cyclohexyl) with [PbCp$_2$] gives the cage [Pb$_3${Sb(NCy)$_3$}$_2$], in which the [Sb(NCy)$_3$]$^{3-}$ trianions of the alkali metal precursor are transferred intact to Pb^{II}.[4a] Reactions of this type therefore provide a general strategy for the assembly of heterometallic cage compounds containing diverse mixed-metal stoichiometries. A current interest in this area concerns the factors controlling the formation and stability of these new ligand systems.[5] To this end we report here the investigation of the effects of ligand substitution on the SbN framework of one such anion arrangement, the *spiro* monoanion [{(Me$_2$N)Sb(μ-NR)$_2$}$_2$Sb]$^-$.[3b]

The reaction of [{(Me$_2$N)Sb(μ-NR)$_2$}$_2$Sb]K with [Bu^{t}OH] (1 : 2 equiv.) gives [{(Bu^{t}O)$_2$Sb$_3$(μ-NCy)$_3$(μ$_3$-NCy)}K·η^6-C$_6$H$_5$Me] **1**, for which spectroscopic and analytical analysis suggests that simple ligand exchange of the terminal NMe$_2$ groups of the precursor has occurred.† However, subsequent X-ray structural investigation of **1** reveals that ligand substitution is accompanied by isomerism of the initial *spiro* structure of the anion in to a *nido* cage arrangement (Scheme 1). It is interesting to note that the *spiro* structure of the precursor is preserved upon substitution with NHR groups.[4a] It therefore appears that this rearrangement is a consequence of the increased Lewis acidity of the O-attached Sb centres, with the *nido* structure of the anion of **1** maximising their coordination numbers. The same effect can also be seen to underlie the coordination of NHMe$_2$ to Sb^{III} in [(Me$_2$NH)ClSb(μ-NBu^t)]$_2$ (during the reaction of [(Me$_2$N)$_2$ClSb] with NH$_2$Bu^t)[6] and the aggregation of [Cl$_3$SbNMe]$_4$ in to a cubane (as opposed to a dimer) structure.[7] However, the formation of **1** provides, to our knowledge, the first intramolecular example of the structure-directing influence of the electronegativity of substituents on cage geometry within such a p-block metal system.



Scheme 1

The low-temperature X-ray structure of **1**‡ shows it to be the ion-contacted complex [{(Bu^{t}O)$_2$Sb$_3$(μ-NCy)$_3$(μ$_3$-NCy)}K·η^6-C$_6$H$_5$Me], in which the K$^+$ cation is coordinated at the open Sb$_3$N$_3$ face of the *nido* [(Bu^{t}O)$_2$Sb$_3$(μ-NCy)$_3$(μ$_3$-NCy)]$^-$ anion and by a π-bonded toluene molecule (Fig. 1). The [(Bu^{t}O)$_2$Sb$_3$(μ-NCy)$_3$(μ$_3$-NCy)]$^-$ anion of **1** is composed of three Sb^{III} centres which are linked together in the equator by three μ-NCy groups and capped by a μ$_3$-NCy group. In addition, Sb(1)

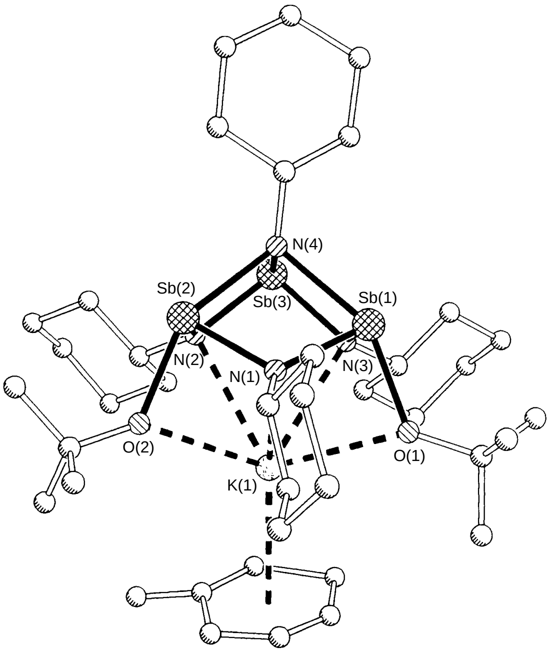


Fig. 1 Structure of **1**. H atoms have been omitted for clarity. Only major core components of the Bu^t group [on O(2)] and of the toluene molecule are shown. Key bond lengths (Å) and angles (°): Sb(1)–N(1) 2.064(5), Sb(1)–N(3) 2.090(5), Sb(1)–N(4) 2.335(5), Sb(1)–O(1) 2.113(4), Sb(2)–N(1) 2.061(5), Sb(2)–N(2) 2.077(5), Sb(2)–N(4) 2.311(4), Sb(2)–O(2) 2.122(4), Sb(3)–N(2) 2.027(5), Sb(3)–N(3) 2.025(5), Sb(3)–N(4) 2.033(5), K(1)–N(1) 2.718(5), K(1)–N(2) 2.991(5), K(1)–N(3) 2.953(5), K(1)–O(1) 2.942(4), K(1)–O(2) 2.865(4), K(1)···C 3.20–3.47, arene(centroid)···K 3.03; N(1)–Sb(1)–N(3) 98.9(2), N(1,3)–Sb(1)–N(4) av. 74.3, O(1)–Sb(1)–N(4) 147.6(2), N(1,3)–Sb(1)–O(1) av. 85.0, N(1)–Sb(2)–N(2) 100.5(2), N(1,2)–Sb(2)–N(4) av. 75.0, O(2)–Sb(2)–N(4) 146.0(2), N(1,2)–Sb(2)–O(2) 83.5(2), N(2)–Sb(2)–N(3) 92.5(2), N(2,3)–Sb(3)–N(4) av. 81.6, Sb(1)–N(4)–Sb(2) 95.3(2), Sb(1)–N(4)–Sb(3) 98.2(2), Sb(2)–N(4)–Sb(3) 97.9(2), N(1)–K(1)–N(2) 67.6(1), N(1)–K(1)–N(3) 67.5(1), N(1)–K(1)–O(1) 60.0(1), N(1)–K(1)–O(2) 59.8(1), O(1)–K(1)–N(3) 107.6(1), O(2)–K(1)–N(2) 107.9(1), O(1)–K(1)–O(2) 118.7(1).

and Sb(2) are bonded to terminal OBu^t groups [Sb(1,2)–O av. 2.12 Å], resulting in 10e pseudo-trigonal bipyramidal geometries for these centres and with Sb(3) adopting an 8e pyramidal geometry. Although the majority of the Sb–N bond lengths in **1** fall in a narrow range [2.027(5)–2.090(5) Å], longer Sb–N bonds occur between the μ_3-NCy group and the four-coordinate Sb centres [Sb(1)–N(4) 2.335(5), Sb(2)–N(4) 2.311(4) Å]. These correspond to the use of orbitals by Sb(1) and Sb(2) at an axial position of their pseudo-trigonal bipyramidal environments. The overall arrangement of the imido antimony(III) anion fragment of **1** is similar to that occurring in the neutral, isoelectronic complex $[Cl_2Sb_2Se(\mu\text{-}NBu^t)_3(\mu_3\text{-}NBu^t)]$, formed by the desilylation reaction of $[Se\{NBu^t(SiMe_3)\}_2]$ with $SeCl_2$.[8]

The bonding of the imido antimony(III) anion of **1** to the K^+ cation is very asymmetrical. The shortest contact between the imido antimony(III) anion and the K centre occurs with N(1) [2.718(5) Å] and is typical of those found in a range of amido potassium compounds.[9] However, far weaker interactions occur between the K^+ cation and the remaining N centres of the Sb_3N_3 face of the anion [N(2)–K(1) 2.991(5), N(3)–K(1) 2.953(5) Å]. In addition, the O atoms of the pendant OBu^t groups only weakly coordinate the K^+ cation {O(1)–K(1) 2.942(4), O(2)–K(1) 2.865(4) Å; *cf.* 2.788(8) Å for the thf O–K bonds in $[\{(RNH)Sb(\mu\text{-}NR)_2\}_2Sb]K\cdot 2thf$[10]}. This arrangement leaves the K^+ cation open to further coordination by the η^6-toluene ligand. Similar ion–dipole interactions of aromatic ligands with K^+ are well known in a variety of complexes, with typical centroid···K^+ distances lying in the range 3.18–3.59 Å.[11] The shortness of the arene···K interactions in **1** [centroid···K(1) 3.03 Å, K···C 3.20–3.47 Å] is a further reflection of the overall weakness of the interaction of the imido antimony(III) anion with the K^+ cation and of its sterically uncongested environment.

Clearly there are considerable differences between the electron-precise bonding present in the *nido* $[(Bu^tO)_2Sb_3(\mu\text{-}NCy)_3(\mu_3\text{-}NCy)]^-$ anion of **1** and structurally similar electron deficient borane ligands such as *nido*-2,3- and 2,4-$[R_2C_2B_4H_4]^{2-}$.[12] However, their geometric similarity and the fact that the $[Sb(\mu\text{-}NCy)]_3$ face (although localised) is isoelectronic with the open C_2B_3 face of the latter suggests that the *nido* $[(Bu^tO)_2Sb_3(\mu\text{-}NCy)_3(\mu_3\text{-}NCy)]^-$ anion may perform an analogous structural role as a building block in metal complexes.[13] In this regard, the structure of **1** which can be viewed as a mixed-ligand sandwich complex of K^+, provides an initial indication of this behaviour.

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Footnotes and References

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† *Synthesis* of **1**: to a solution of $[\{(Me_2N)Sb(\mu\text{-}NCy)_2\}_2Sb]Li$ (0.77 g, 0.91 mmol) in toluene (10 ml) was added Bu^tOK (0.10 g, 0.91 mmol). Stirring the solution at room temp. gave a change from yellow to orange. To this was added Bu^tOH (0.18 ml, 1.82 mmol) and the mixture was brought briefly to reflux and stirred at room temp. (24 h). The solvent was removed under vacuum and the colourless solid produced was dissolved in hexane (5 ml) and toluene (2 ml). Storage at −18 °C (48 h) gave colourless crystals of **1**. The low yield of crystalline **1** (0.22 g, 23%) is due to its high solubility; mp 130 °C; ^1H NMR (250 MHz, C_8D_6, 25 °C), δ 7.0 (m, 5 H, aryl C–H, toluene), 2.40 (m, 4 H, C^α-H, μ-NCy), 2.11 (s, 3 H, Me, toluene), *ca.* 1.9–0.9 (overlapping m, 40 H, CH_2, Cy), 1.49 (s, 18 H, Bu^t). Found: C, 43.1; H, 6.6; N, 5.3. Calc. for $[C_{32}H_{62}KN_4O_2Sb_3.C_7H_8]^n$: C, 45.4; H, 6.8; N, 5.4%.

¶ *Crystal data* for **1**: $C_{39}H_{70}KN_4O_2Sb_3$, M = 1031.34, monoclinic, space group $P2_1/c$, a = 18.749(1), b = 13.113(1), c = 18.848(2) Å, β = 103.831(7)°, U = 4499.5(7) Å^3, Z = 4, D_c = 1.522 Mg m^{-3}, λ = 0.710 73 Å, T = 203(2) K, μ(Mo-Kα) = 1.915 mm^{-1}, F(000) = 2080. Data were collected on a Siemens P4 diffractometer using an oil-coated rapidly cooled crystal[14] of dimensions 0.60 × 0.50 × 0.40 mm by the θ–2ω method ($1.91 \leqslant \theta \leqslant 25.00°$). Of a total of 9158 collected reflections, 7727 were independent (R_{int} = 0.0512). The structure was solved by direct methods; all non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were placed in idealised geometry riding on the relevant carbon atoms. The structure has a disordered Bu^t group [on O(2)] (*ca.* 60 : 40); the ring atoms of each disordered toluene component were fixed in a regular hexagonal geometry (C–C 1.39 Å). In the crystal the ion-contacted units of **1** are arranged in centrosymmetric pairs held together by π stacking interactions of the aryl rings with centroid offset distance of 1.27 Å (mean) and centroid···centroid distance 3.80 Å (mean). 421 parameters were refined on F^2 to final conventional R_1 = 0.043 [$F > 4\sigma(F)$] and wR_2 = 0.120 (all data) [$R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = F_o^2 + (2F_c^2/3)]$, x = 0.0636, y = 5.28, $P = (F_o^2 + 2F_c^2)/3$;[15] largest peak and hole in the final difference map, 0.999 and −0.897 e Å^{-3}. CCDC 182/699.

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