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Synthesis and structure of $[\{Sb(\mu\text{-}NCy)\}_2(\mu\text{-}N)]_3(Li{\cdot}THF)_3$-(LiN=NH), containing a macrocyclic $[\{Sb(\mu\text{-}NCy)\}_2N]_3^{3-}$ trianion

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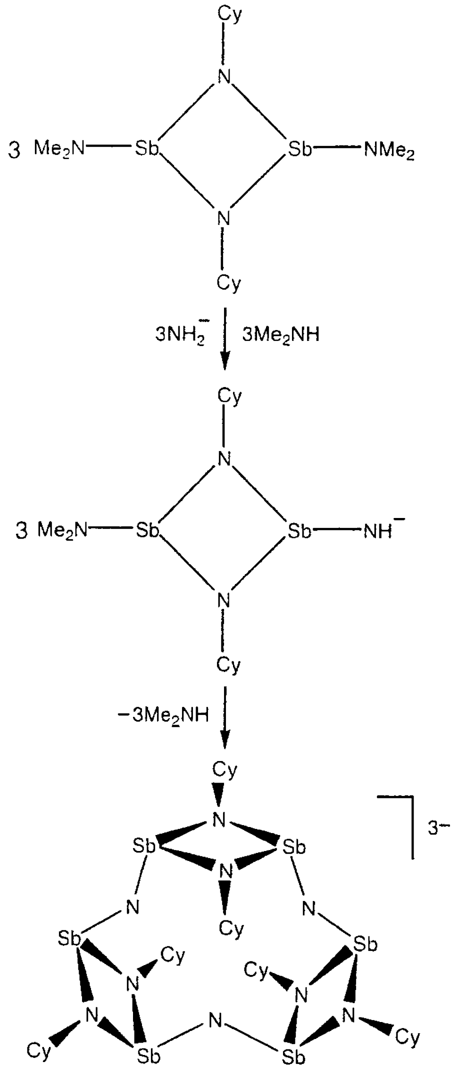
Reaction of the Sb(III) dimer $[Me_2NSb(\mu\text{-}NCy)]_2$ with $LiNH_2$ (1 : 2 equivalents, respectively) gives $[\{Sb(\mu\text{-}NCy)\}_2N]_3(Li{\cdot}THF)_3(LiN{=}NH){\cdot}0.25$(dioxane) 4, in which four Li^+ cations are coordinated within the trimeric cavity of the macrocyclic trianion $[\{Sb(\mu\text{-}NCy)\}_2N]_3^{3-}$.

We recently illustrated that the Group 15–nitrogen macrocycle $[\{P(\mu\text{-}N^tBu)\}_2(\mu\text{-}NH)]_4$ (**1**) can be prepared in good yield by the reaction of $[ClP(\mu\text{-}N^tBu)]_2$ (**2**) with $[H_2NP(\mu\text{-}N^tBu)]_2$ (**3**) in the presence Et_3N.[1] The predisposition for cyclisation in this reaction appears to result from the preferred *cis* conformations of **2** and **3**.[2] The cyclophosphazane **3** is composed of four $[P(\mu\text{-}N^tBu)]_2$ dimer units linked into a cyclic arrangement by bridging N–H groups. Significantly as regards the application of this and related species as ligands to various metals, the N–H protons of **1** are directed inwards towards the macrocyclic cavity, with all of the dimer constituents adopting *cis* conformations. We present here a key study in the development of this new class of macrocyclic Main Group ligand, providing the first glimpse of the coordination characteristics of the deprotonated framework.

Previously, we had shown that $Sb(NMe_2)_3$ reacts at low temperatures with a broad range of primary amines (RNH_2) to give symmetric dimers of the type $[Me_2NSb(\mu\text{-}NR)]_2$.[3] Condensation of the Me_2N groups of the latter with metallated primary amines (RNHM; M = alkali metal) produces the dianion frameworks $[Sb_2(NR)_4]^{2-}$, in which the Sb_2N_2 dimer units of the precursor are retained.[4] In a pilot study designed to prepare related anions of the type $[NHSb(\mu\text{-}NR)]_2^{2-}$, $LiNH_2$ (2 equivalents) was reacted with $[Me_2NSb(\mu\text{-}NCy)]_2$ (1 equivalent) in thf under argon.† In order to enhance the reactivity of the $LiNH_2$, this was prepared *in situ* from ^nBuLi and NH_3/1,4-dioxane. Surprisingly, the isolated product of this reaction is $[\{Sb(\mu\text{-}NCy)\}_2(\mu\text{-}N)]_3(Li{\cdot}thf)_3(LiN{=}NH){\cdot}0.25$(dioxane) **4**, the cyclic $[\{Sb(\mu\text{-}NCy)\}_2(\mu\text{-}N)]_3^{3-}$ trianion of which arises from the double-deprotonation of the NH_2^- anion by $[Me_2NSb(\mu\text{-}NCy)]_2$ (Scheme 1).



Scheme 1

The low-temperature X-ray structure of **4**‡ (combined with spectroscopic analysis) shows that it is a cage complex of virtual C_3-symmetry, of formula $[\{Sb(\mu\text{-}NCy)\}_2(\mu\text{-}N)]_3(Li{\cdot}thf)_3(LiN{=}NH)$ (Fig. 1). In addition, there is one quarter of a molecule of 1,4-dioxane present in the lattice for each molecule of **4**. Molecules of **4** are formed from the association of the cyclic trianion $[\{Sb(\mu\text{-}NCy)\}_2(\mu\text{-}N)]_3^{3-}$ with three Li^+ cations and a LiN=NH monomer unit. It is not possible to identify the $N{=}NH^-$ anion unambiguously on the basis of the crystallographic study alone. However, the appearance of characteristic ν(N=N) vibrations (1641 and 1622 cm^{-1}) and a weak N–H stretching band (3340 cm^{-1}) in the IR spectrum of **4**, and the presence of a singlet proton resonance (at δ 6.44) in the ^1H NMR spectrum of the complex strongly supports the $N{=}NH^-$ anion. In addition, two resonances are found in the ^{14}N NMR spectrum of **4**; the very broad resonance at δ −585 ($W_{1/2}$ = 10 kHz) can be assigned to the sp^3 μ-N and μ-NCy centres of the macrocycle, while the sharper resonance at δ −67.6 is characteristic of sp^2 hybridised N (relative to $MeNO_2/d_6$-benzene). The latter resonance is absent in the ^{14}N spectrum of the dimer $[Me_2NSb(\mu\text{-}N^tBu)]_2$. Unfortunately, the N–H resonance in the ^1H NMR spectrum of **4** proved to be too broad to enable a successful ^1H, ^{15}N-HMQC study. Lastly, the associated N=N bond length [N(1H)–N(2H)

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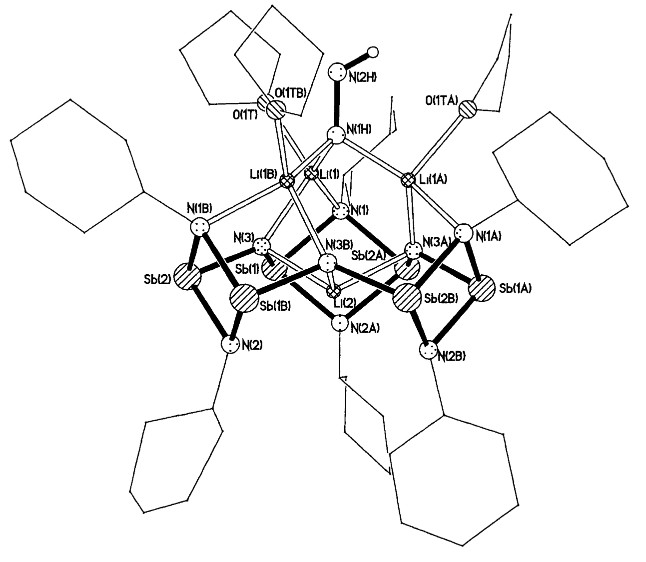

Fig. 1 Structure of $[\{Sb(\mu\text{-}NCy)\}_2N]_3(Li{\cdot}thf)_3(LiN{=}NH)$ **4**. H-atoms and the lattice dioxane molecule have been omitted for clarity. Key bond lengths (Å) and angles (°): Sb(1)–N(1) 2.094(4), Sb(1)–N(2) 2.066(5), Sb(1)–N(3) 1.998(4), Sb(2)–N(1) 2.100(4), Sb(2A)–N(2A) 2.086(5), Sb(2A)–N(3A) 1.988(4), N(3) ··· N(3A) 3.48, Li(2)–N(3) 2.181(8), Li(1)–N(3) 2.06(1), Li(1)–N(1) 2.12(1), Li(1)–O(1T) 2.10(1), Li(1)–N(1H) 1.89(1), N(1H)–N(2H) 1.38(2); Sb(1)–N(3)–Sb(2B) 117.3(2), N(2)–Sb(1)–N(3) 94.8(2), N(1)–Sb(1)–N(3) 89.3(2), N(1)–Sb(1)–N(2) 81.3(2), N(1)–Sb(2)–N(2) 80.7(2), N(3A)–Sb(2)–N(1) 93.5(2), N(3A)–Sb(2)–N(2) 95.1(2), Sb(1)–N(1)–Sb(2) 98.3(2), Sb(1)–N(2)–Sb(2) 99.6(2).

1.38(2) Å] in the X-ray structure of **4** is also consistent with related metal-bonded N=NR ligands.[5,6] Obvious alternatives of $N{=}N^{2-}$, O_2^{2-} or O_2^- can be excluded on the basis of their paramagnetic nature and/or the spectroscopic data.[7] The mechanism by which the $N{=}NH^-$ anion is formed is not fully understood at this stage. Since the synthesis of **4** was performed in an argon atmosphere, molecular N_2 can be excluded as a source of the $N{=}NH^-$ anion. Model *ab initio* calculations reveal that the decomposition of $2LiNH_2$ into LiN=NH, LiH and H_2 is not a viable pathway thermodynamically. There is a possible role for Sb in this oxiadation process and, indeed, Sb metal is apparently formed as a byproduct in the reaction producing **4**.

The constituent $[Sb(\mu\text{-}NCy)]_2$ dimer units of the $[\{Sb(\mu\text{-}NCy)\}_2(\mu\text{-}N)]_3^{3-}$ trianion of **4** are planar within experimental error, with the Sb–N(Cy) bond lengths within these units (mean 2.09Å) being significantly longer than the Sb–μ-N bonds linking them into a trimeric ring (mean 1.99Å). The pattern and magnitude of these bond lengths is broadly similar to that found in the related neutral macrocycles $[\{Sb(\mu\text{-}NR)\}_2(\mu\text{-}NR)]_6$ (R = 2-MeOC$_6$H$_4$, Ph).[8] Also similar are the dimer-bridging Sb–(μ-N)–Sb angles in **4** [Sb(1)–N(3)–Sb(2B) 117.3(2)°; *cf.* 120.2(6)° for R = 2-MeOC$_6$H$_3$[8a]], which are consistent with sp^2 hybridisation at the anionic μ-N centres. One obvious difference is the *cis* (rather than *trans*) conformation of the dimer units in **4**. In the hexamers $[\{Sb(\mu\text{-}NR)\}_2(\mu\text{-}NR)]_6$ a *trans* conformation is adopted for the dimer units on steric grounds, since otherwise the bridging R groups would have to be directed (*endo*) towards the core of the macrocycle. The reasons for the formation of a trimeric macrocycle in the case of the $[\{Sb(\mu\text{-}NCy)_3\}_2(\mu\text{-}N)]_3^{3-}$ trianion, as opposed to a tetrameric arrangement similar to $[\{P(\mu\text{-}N^tBu)\}_2(\mu\text{-}NH)]_4$ (**3**), are uncertain. However, the coordination of Li$^+$ cations during the formation of **4** (*i.e.*, a templating effect), the greater degree of p-character in the Sb–N bonds compared to analogous P–N systems (promoting more acute exocyclic N–Sb–N bond angles), and the differing steric effects of the organic substituents are likely to be the major influences.

The coordination of the macrocyclic $[\{Sb(\mu\text{-}NCy)\}_2(\mu\text{-}N)]_3^{3-}$ trianion to three symmetry-related Li$^+$ ions [Li(1,1A,1B)] on one side of the anion and one unique Li$^+$ ion [Li(2)] on the other results in a large deviation (*ca.* 16°) of the $[Sb(\mu\text{-}NCy)]_2$ ring planes away from perpendicular to the macrocyclic plane. The adoption of this 'cone' conformation in **4** is reminiscent of that commonly found for coordinated and uncoordinated calixarenes.[9] The unique Li$^+$ ion [Li(2)] is coordinated solely by the three anionic μ-N centres of the macrocycle [Li(2)–N(3) 2.181(8) Å], and is displaced by *ca.* 0.85 Å below the plane formed by the three anionic N centres. The three, symmetry-related Li$^+$ ions [Li(1,1A,1B)] are each coordinated by one of the anionic μ-N atoms [Li(1)–N(1) 2.12(1) Å] of the macrocycle, by one of the neutral μ-NCy N centres of the $[Sb(\mu\text{-}NCy)]_2$ rings [Li(1)–N(3) 2.06(1) Å], and by a thf ligand. These three Li$^+$ ions are capped by the μ$_3$-bridging $N{=}NH^-$ anion [Li(1)–N(1H) 1.89(1) Å], whose N=N bond is aligned along the C_3 axis of the cage.

In conclusion, the study presented here indicates that, despite the apparently sterically congested nature of macrocyclic ligands of this type, cone-distortion of the Group 15–N frameworks can indeed allow effective coordination of metal cations within the cavities of the deprotonated species. Both the anionic μ-N and formally neutral μ-NR functionalities are available to bond to these metal centres.

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Notes and references

† Synthesis of **4**. To a solution of CyNH$_2$ (0.34 ml, 3.0 mmol) in thf (10 ml) at room temperature was added Sb(NMe$_2$)$_3$ (2.0 ml, 2.0 mol dm^{-3} in toluene, 3.0 mmol) under argon. The mixture was heated to reflux briefly to afford a light yellow solution of $[Me_2NSb(\mu\text{-}NCy)]_2$. A suspension of LiNH$_2$ was prepared by adding ^{n}BuLi (2.0 ml, 1.5 mol dm^{-3} in hexanes, 3.0 mmol) to a solution of NH$_3$ (6.0 ml, 0.5 mol dm^{-3} in 1,4-dioxane) in thf (10 ml). This suspension was added to the $[Me_2NSb(\mu\text{-}NCy)]_2$ solution at room temperature, producing a bright yellow solution. A small quantity of black decomposition product (probably Sb metal) was filtered off (P3, Celite). Removal of the solvent from the filtrate under vacuum gave **4** as a yellow powder (yield 0.68 g, 82% based on Sb). Decomp. *ca.* 160 °C. Crystalline blocks of **4** can be readily obtained by recrystallisation of the powder from thf (*ca.* 2.0 ml) at room temperature (yield *ca.* 15%). Analytical and spectroscopic data confirm that samples of the complex obtained as a powder are of high purity. IR (Nujol, NaCl), ν/cm^{-1} = 3340 (w, N–H str.), 1641, 1622 (m., N=N str.), other major bands at 1259(m), 1192(m), 1073(vs), 1026(m), 980(m), 909(w), 889(w) 794(m), 722(w), 676(m). ^{1}H NMR (400.16 MHz, d$_6$-benzene, +25 °C), δ = 6.44 (br s, 1H, N–H), 3.62 (m, 12H, –C*H*$_2$–O thf), 3.40 (s, 8H, dioxane), 2.47–0.8 (overlapping m, 66H, Cy), 1.47 (m, 8H, –C*H*$_2$–CH$_2$–O thf). ^{7}Li NMR (155.51 MHz, d$_6$-benzene, relative to PhLi/d$_6$-benzene), δ = 0.53 ($W_{1/2}$ = 300 Hz). ^{14}N NMR (28.90 MHz, d$_6$-benzene, +25 °C, relative to MeNO$_2$/d$_6$-benzene), δ = −585 (s, μ-N and μ-NCy), −67.6 (s, N=NH). Elemental analysis, calcd. for **4** C 35.7, H 5.5, N 9.2; found C 36.0, H 5.7, N 8.2%.

‡ Crystal data for **4**; $C_{49}H_{93}Li_4N_{11}O_{3.5}Sb_6$, M = 1650.6, triclinic, space group $P\bar{3}$, $Z = 2$, $a = b$ = 16.7042(5), c = 13.1999(5) Å, V = 3189.72(18) Å^3, μ(Mo–Kα) = 2.550 mm^{-1}, T = 230(2) K. Data were collected on a Nonius Kappa CCD diffractometer. Of a total of 10759 reflections collected, 3747 were independent (R_{int} = 0.037). The structure was solved by direct methods and refined by full-matrix least squares on F^2.[10] Final $R1$ = 0.038 [$I > 2\sigma(I)$] and $wR2$ = 0.105 (all data). The symmetry-related Cy groups connected to N(2,2A,2B) are disordered over two 50 : 50 sites at one of the C centres. The dioxane molecule in the lattice is disordered about the crystallographic −3 axis. CCDC reference number 165000. See http://www.rsc.org/suppdata/dt/b1/b110984g/ for crystallographic data in CIF or other electronic format.

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