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A twenty-four membered mixed-metal macrocycle; Synthesis and structure of *cyclo*-[(3-Me-1,2-$C_6H_3O_2$)$_2$SbNa(THF)$_2$]$_6$

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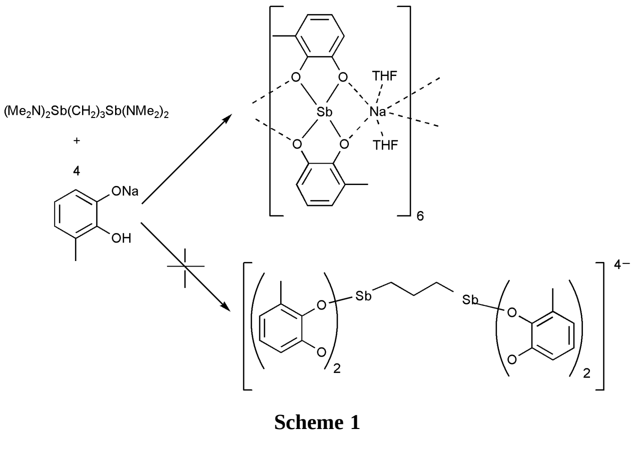
The first example of a twenty-four membered mixed p-/s-block macrocycle, *cyclo*-[(3-Me-1,2-$C_6H_3O_2$)$_2$SbNa(THF)$_2$]$_6$ 1 has been synthesised and structurally characterised from the reaction between 3-Me-1,2-C_6H_3(OH)(ONa) and (Me_2N)$_2$Sb(CH_2)$_3$Sb(NMe_2)$_2$.

The study of macrocyclic frameworks is currently an active area of research for both coordination and supramolecular chemists. Although there is a rich and varied library of organic macrocyclic compounds, literature provides relatively few examples of similar species built upon inorganic fragments. Also, in recent years there has been significant interest in the chemistry of metal-imido species and p-block anionic ligand systems.[1] Our current work,[2,3] extends these methodologies towards the reactivities of polynuclear group 14/15 dimethylamido derivatives. Thus, we recently reported the synthesis and structure of the distibine-centred polyimido anion, 1,3-[(RNLi)Sb]$_2$(μ-NR)(CH_2)$_3$·(RNHLi),[3] (R = 2-pyridyl). In this case the bridge between the group 15 centres remained intact, whereas the reaction between (Me_2N)$_2$As-CH_2As(NMe_2)$_2$ and 1,2-H_2N(C_6H_4)NHLi yields the aromatic metallacycle, benzo[1,3,2]diazaarsolyllithium·2THF, and involves the cleavage of the bridging methylene unit.[2] We now report the synthesis and structural characterisation of the first example of a twenty-four membered mixed p-/s-block metallacycle, *cyclo*-[(3-Me-1,2-$C_6H_3O_2$)$_2$SbNa(THF)$_2$]$_6$ **1**.

In an attempt to form the tetra-anionic complex [(RO)$_2$Sb(CH_2)$_3$Sb(OR)$_2$]$^{4-}$·4Na^+, from the reaction between 3-Me-1,2-C_6H_3(OH)(ONa) and (Me_2N)$_2$Sb(CH_2)$_3$Sb(NMe_2)$_2$, compound **1** was unexpectedly obtained as the only isolatable product (Scheme 1).† The low temperature X-ray structure of **1**‡ reveals that it is a 24-membered metallacycle comprising of a $Sb_6Na_6O_{24}$ core. Each antimony centre is coordinated to two catechol groups, forming a four coordinate antimony(III) anion. These anions are bridged *via* the oxygen centres of each catechol to a sodium cation, which is in turn solvated by two THF molecules leading to 6-fold coordination. Thus, the structure is built from a cyclic array of SbO_2Na units (Figs. 1 and 2).

Unexpectedly, the (CH_2)$_3$ bridge between the antimony centres has been cleaved during the reaction. Work investigating the mechanism involved is currently being undertaken. However, we can conclude from preliminary experiments that the initial presence of this bridge is crucial for the formation of this macrocyclic structure. All attempts to synthesise this compound using the more logical precursor, Sb(NMe_2)$_3$, with



Scheme 1

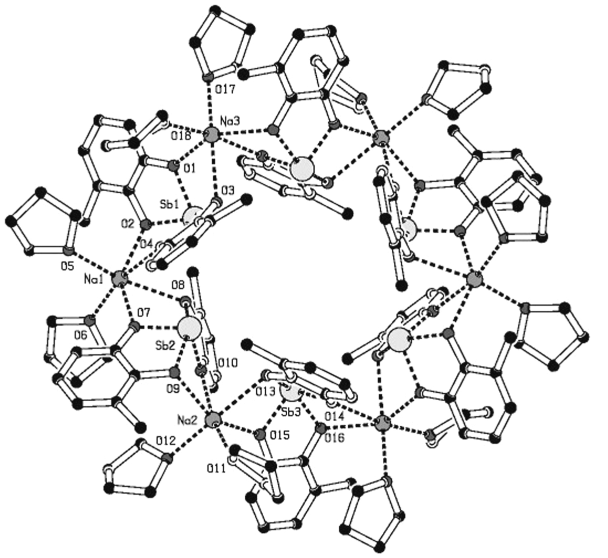


Fig. 1 Selected bond lengths (Å) and angles (°) for compound **1**. Hydrogen atoms have been omitted for clarity: O(1)–Sb(1) 2.064(11), O(2)–Sb(1) 2.131(8), O(3)–Sb(1) 2.146(9), O(4)–Sb(1) 2.027(9), O(2)–Na(1) 2.314(11), O(4)–Na(1) 2.505(12), av. cavity size Sb···Sb 8.3, O(1)–Sb(1)–O(2) 79.2(4), O(4)–Sb(1)–O(3) 78.8(4), O(1)–Sb(1)–O(3) 80.9(4), O(2)–Sb(1)–O(3) 145.2(4), O(2)–Sb(1)–O(4) 78.2(4), Sb(1)–O(4)–Na(1) 100.6(4), Sb(1)–O(2)–Na(1) 103.8(4), O(2)–Na(1)–O(4) 65.8(4), O(4)–Na(1)–O(8) 70.4(3), O(2)–Na(1)–O(5) 95.3(5), O(7)–Na(1)–O(2) 139.1(4), O(5)–Na(1)–O(8) 158.4(5), O(6)–Na(1)–O(4) 166.3(5).

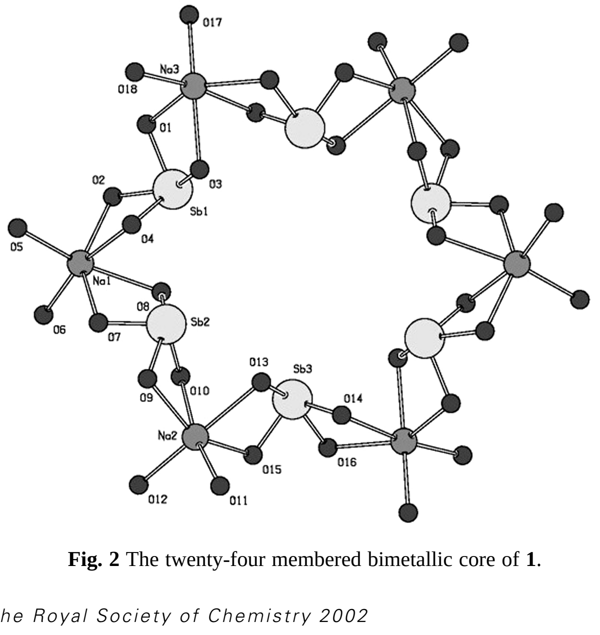


Fig. 2 The twenty-four membered bimetallic core of **1**.

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varying ratios of 3-$MeC_6H_3(OH)_2$ and 3-$MeC_6H_3(OH)(ONa)$ have failed to produce a similar outcome, which is in line with our previous observations concerning the reactivity of $(Me_2N)_2AsCH_2As(NMe_2)_2$ towards 1,2-$H_2N(C_6H_4)NHLi$.[2]

The only structurally characterised[4] twenty-four membered antimony(III) metallacycle in the literature,[4] $Sb_{12}[N\text{-}2\text{-}(MeO)C_6H_4]_{18}$ **2**, has a similar toroid core shape. This motif was also observed[5] in the core of $Sb_{12}(NPh)_{18}$ **3**, however no structural details were reported. Compound **1** is the first example of a twenty-four membered mixed p-/s-block macrocycle, there being no related literature examples. In **2** and **3** the macrocyclic ring is constructed around rhombohedral Sb_2N_2 units linked *via* single imido bridges, however, in **1** there is a Sb_6Na_6 core with double bridging of alternating antimony and sodium cations.

In **2** the inner six antimony centres are all 3.912 Å apart, whereas in **1** the distances are larger ranging from 4.16–4.51 Å. These distances are also longer than the 3.78 Å reported for the propyl bridged species, 1,3-$[(RNLi)Sb]_2(\mu\text{-}NR)(CH_2)_3\cdot(RNHLi)$.[3] The toroidal core of **1** is built around a highly skewed square pyramidal geometry about antimony and very distorted octahedral coordination of the sodium cations. The catechol O–Na distances are variable ranging from 2.299–2.531 Å, whereas the distances of the two coordinated THF molecules (driving the expected 6-fold coordination) range from 2.337–2.359 Å. Angles about Na are far from the ideal octahedral values, ranging from 65.8–166.3°, presumably as a consequence of geometrical constraints imposed by cyclisation. The presence of SbO_2Na rings leads to the a large range of angles about antimony, with O–Sb–O angles ranging from 78.2–145.2° and O–Sb bond lengths of 2.027–2.146 Å. It is also noticeable that on both 'faces' of the macrocyclic ring, three of the catechol units lie roughly perpendicular to the 'plane' facing towards the centre, whereas the remainder occupy positions around the periphery of the core.

The stability of **2** was partly assumed to be as a result of Sb···OMe interactions. This is questionable given the lack of any such interaction in compound **3**. The mechanism for the formation of **1** is not understood, in particular the key, albeit sacrificial, role of the polynuclear precursor. Common problems of macrocycle synthesis are competition between cyclisation and polymerisation, and it may be that unidentified by-products of the cleavage of the distibine precursor aid the formation and potentially template the cyclisation process in the generation of **1**.

Recently the formally trianionic 12-membered macrocycle $[\{Sb(\mu\text{-}NCy)\}_2(\mu\text{-}N)]_3(Li\cdot THF)_3(LiN{=}NH)$ containing the trianion $[\{Sb(\mu\text{-}NCy)\}_2N]_3{}^{3-}$ has been reported.[6] Unlike **1** however, the alkali metal cations are not a fundamental component of the macrocyclic ring, since they are complexed within the cavity rather than being building blocks of the ring. Compound **1** is unique in the fact that both the alkali metal cation and the antimony centres are incorporated within the macrocyclic core. Here the direct synthesis of the larger unoccupied macrocycle provides a potential route to a range of novel host compounds. The presence of a cavity (av. Sb···Sb′ cavity distance 8.3 Å, *cf.* 7.8 Å in **2**) within the core makes this a potentially useful compound for both anion and cation complexation since Lewis acid and base sites are present. Cyclic s-block amides[7] have been investigated as Lewis acids towards anion complexation, whereas a few inorganic Lewis base macrocycles, *e.g.*, $[P(NMe_2)_2N]_6$,[8] can behave as Lewis bases. It should also be noted that the series of lanthanide oxo/hydroxo complexes reported by Zheng[9] and the vanadium oxo complexes of Müller[10] exhibit related structural characteristics. We intend to further pursue the syntheses and structural characterisation of these mixed-metal macrocycles and to investigate their potential as ligands or hosts.

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Notes and references

† Synthesis of **1**: all manipulations were undertaken under an inert nitrogen atmosphere. 3-Methylcatechol (0.497g, 4 mmol) was dissolved in dry toluene and NaH (0.096g, 4 mmol) added to give a grey precipitate which was stirred, with gentle warming, for *ca.* 30 minutes. After this time $(Me_2N)_2Sb(CH_2)_3Sb(NMe_2)_2$ (0.462 g, 1 mmol) was added and the mixture stirred at 100 °C for 2 h to yield a brown precipitate. The toluene was removed *in vacuo* and the mixture dissolved in 15 cm^3 of THF to yield a dark brown solution. Reduction to *ca.* 5 cm^3 and storage at 5 °C overnight yielded a crop of colourless blocks of **1** in 20% yield (relative to NaH, 1st batch). ^1H NMR (300 MHz; DMSO-d_6; 25 °C) δ 6.28–6.41 (m, 3H, ArH), δ 3.60 (t, 4H, $-CH_2CH_2O-$), δ 2.14 (s., 3H, CH_3), δ 1.75 (m, 4H, $-CH_2CH_2O-$); ^{13}C NMR (75 MHz; DMSO– d_6; 25 °C) δ 111.3–151.2 (Ar), δ 67.0 ($-CH_2CH_2O-$), δ 25.1 (CH_2CH_2-O), δ 16.3 (CH_3). Satisfactory analyses (C, H, N) were obtained for all samples of **1**. Samples of **1** are soluble in most coordinating solvents, however appear insoluble in non-polar solvents.

‡ Crystal data for $C_{132}H_{168}Na_6O_{36}Sb_6$ **1**: $M_r = 3199.10$, triclinic, space group $P1$, $a = 15.7605(12)$, $b = 16.6786(13)$, $c = 17.2709(16)$ Å, $\alpha = 103.943(4)$, $\beta = 100.057(4)$, $\gamma = 98.356(4)°$, $U = 4254.2(6)$ Å^3, $Z = 1$, $\mu = 1.016$ mm^{-1}, crystal size 0.18 × 0.16 × 0.04 mm, $T = 150(2)$ K; refinement of 11582 unique reflections ($2\theta = 23.25°$, $R_{int} = 0.1012$) against 740 parameters gave $R_1 = 0.0856$ and $wR_2 = 0.2082$ [$I > 2\sigma(I)$] ($R_1 = 0.1997$ and $wR_2 = 0.2511$ for all data).

Data were collected on a Nonius KappaCCD area detector diffractometer, at the window of a Nonius FR591 rotating anode (λ Mo-K$_\alpha$ = 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 559 restraints, and with hydrogens included in idealised positions and refined using the Riding model. CCDC reference number 188994. See http://www.rsc.org/suppdata/cc/b2/b206228c/ for crystallographic data in CIF or other electronic format.

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