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Reactions of *cyclo*-(t-Bu_4Sb_4) with alkali metals; syntheses and crystal structures of [$M(L)_n$(t-Bu_4Sb_3)] ($M = Na, K; n = 1, 2$) and [K(L)(t-Bu_3Sb_2)] ($L = (Me_2NCH_2CH_2)_2NMe$)

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Abstract

Reduction of *cyclo*-(t-Bu_4Sb_4) (**1**) with sodium or potassium in boiling tetrahydrofuran leads to the anions [t-Bu_4Sb_3]$^-$ and [t-Bu_3Sb_2]$^-$. Crystallization with pentamethyldiethylenetriamine (L) gives [$M(L)_n$(t-Bu_4Sb_3)] ($n = 1$, M = Na (**2**), K (**3**); $n = 2$, M = K (**4**)) and [K(L)(t-Bu_3Sb_2)] (**5**). Crystal structure analyses reveal coordination of the anionic antimony ligands on the alkali metal ions for **2**, **3**, and **5**. In contrast, no Sb–K interactions were observed in the structure of **4**.

Keywords: *cyclo*-(t-Bu_4Sb_4); Crystal structures; Alkali metals

1. Introduction

Recently, we reported the formation of an ionic triantimonide, [$K(L)_2$][t-Bu_4Sb_3] (**4**) by reaction of *cyclo*-(t-Bu_4Sb_4) (**1**) with potassium and excess pentamethyldiethylenetriamine (L) [1]. The crystal structure determination showed that the potassium cation is coordinated by two of the tridentate amine ligands L and there are no close contacts between the cation and the [t-Bu_4Sb_3]$^-$ ion, which is not only an interesting antimony reagent but also a potential ligand in main group and transition metal complexes.

In order to develop the chemistry of this anion, we have studied the reactions of **1** with Na or K, varying the reaction time and the concentration of the amine ligand L. We report here on the syntheses and structures of [M(L)(t-Bu_4Sb_3)] (M = Na (**2**), K (**3**)), two complexes of the triantimonide ligand and on [K(L)(t-Bu_3Sb_2)] (**5**), a potassium complex of a novel diantimonide ligand. In contrast to **4**, all the new complexes exhibit coordination of the antimonides on the alkali metal centres.

Complex **2** is also remarkable as the first sodium organoantimonide [2,3] characterized by single crystal X-ray diffraction. Structures of complexes with Sb–Na interactions but without Sb–C bonds have been reported for [{$(CyP)_4Sb$}$Na \cdot Me_2NH \cdot$tmeda] [4] and [$Sb_7Na_3 \cdot 3$tmeda$\cdot 3$thf] [5] (tmeda = tetramethylethylenediamine). Alkali metal organoantimonides with reported crystal structures are the potassium compounds, **4** [1] and [$K(thf)_{1/4}$(*cyclo*-(Et_4C_4Sb))] [6], and the lithium derivatives, [Li(12-crown-4)$_2$][$SbPh_2$]$\cdot$1/3thf [7], [Li(dme){$Sb(SiMe_3)_2$}] [8] (dme = 1,2-dimethoxyethane), and [Li(12-crown-4)$_2$][Sb_3Ph_4]$\cdot$thf [7] (thf = tetrahydrofuran). The latter complex, as well as [Rb(18-crown-6)(Ph_4P_2N)] [9], and [Li(L)(R_4P_3)] (R = t-Bu, i-Pr; L = 2thf, tmeda) [10] are related to the triantimonides **2**–**4**. Analogues of the diantimonide **5** are [Li(thf)(t-Bu_3As_2)] [11], [K(L)(t-Bu_2HP_2)] [12], and [$Li(OEt_2)(Ph_3PN)$] [13].

2. Results and discussions

The reactions of **1** with alkali metals and pentamethyldiethylenetriamine (L) depend on the reaction time and on the concentration of L. When **1** is reacted in thf under reflux with excess sodium for 4 h or with

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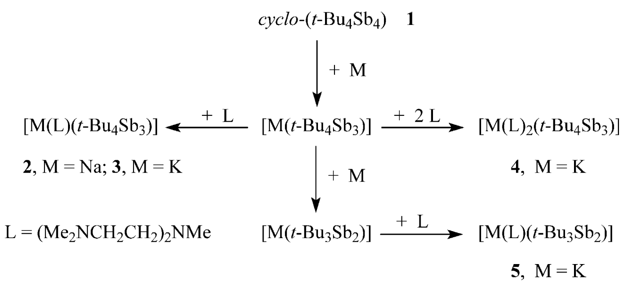
potassium for 1 h, red solutions containing $[t\text{-Bu}_4\text{Sb}_3]^-$ form. Addition of the triamine in molar ratios, [L]–[**1**] = 1.5 and crystallization leads to the formation of the complexes $[\text{M(L)}(t\text{-Bu}_4\text{Sb}_3)]$ (M = Na (**2**), K (**3**)). With [L]–[**1**] = 3 the salt $[\text{K(L)}_2][t\text{-Bu}_4\text{Sb}_3]$ (**4**) is obtained [1]. Prolongation of the reaction results in the decomposition of $[t\text{-Bu}_4\text{Sb}_3]^-$ with formation of the diantimonide $[t\text{-Bu}_3\text{Sb}_2]^-$. Crystallization after addition of the triamine ligand gives $[\text{K(L)}(t\text{-Bu}_3\text{Sb}_2)]$ (**5**). An overview of the observed reactions is given in Scheme 1.

The progress of the reaction of **1** with potassium in boiling thf was monitored by ^{1}H-NMR spectra of samples taken from the reaction mixture after 10 min, 1 h, 1.5 h, and 2 h, which were worked up with addition of the triamine ligand, removal of the thf, and dissolution in C_6D_6. The spectra are shown in Fig. 1. There is one singlet signal for the $[t\text{-Bu}_4\text{Sb}_3]^-$ moiety (Fig. 1b), as expected for the symmetric configuration $[(t\text{-Bu})_2\text{Sb–Sb–Sb}(t\text{-Bu})_2]^-$, which was confirmed by crystal structure determinations of **2**–**4**. The diantimonide gives rise to two singlets in the 2:1 ratio of intensities (Fig. 2d). This pattern is characteristic for the $[(t\text{-Bu})_2\text{Sb–Sb}(t\text{-Bu})]^-$ configuration in a symmetric environment, as found in the crystal structure. The structures of **2**, **3**, and **5** were also confirmed by observation of the expected signals in the ^{13}C-NMR spectra.

Other intermediates of the reaction of **1** with alkali metals were not observed spectroscopically. It is probable however that in the first step of the reduction the radical anion $\mathbf{1}^-$ should form. Migration of the *tert*-butyl groups and elimination of antimony can lead to $[t\text{-Bu}_4\text{Sb}_3]^-$. Precipitation of Sb was in fact observed during the reaction. The second step, the transformation of $[t\text{-Bu}_4\text{Sb}_3]^-$ to $[t\text{-Bu}_3\text{Sb}_2]^-$ requires the elimination of a *t*-BuSb unit, which, after tetramerization, should give the initial product **1** and react with the alkali metals. It is remarkable that $[t\text{-Bu}_3\text{Sb}_2]^-$ is not formed, when solutions of **2**–**4** in C_6D_6 are exposed to ambient temperature. Instead decomposition with formation of $t\text{-Bu}_3\text{Sb}$ and **1** is observed.

The isolation of solid samples of **2**, **3**, **5** is achieved by addition of pentamethyldiethylenetriamine to the reaction mixture after the appropriate reaction time followed by cooling, filtration, and removal of the solvent. Single crystals of $\mathbf{2}\cdot C_6H_6$, $\mathbf{3}\cdot 0.5C_6H_6$, or **5** were obtained by recrystallization from benzene. Compounds **2**–**5** are red or brown–red solids which are extremely sensitive towards traces of moisture or air. In sealed tubes **2**, **3**, and **5** are stable up to 70 or 80 °C, whereas **4** decomposes at room temperature. The solubility of **2**–**5** in petroleum ether is low; in thf, benzene, toluene or other organic solvents they are readily soluble (Table 1).



Scheme 1.

For the characterization of $\mathbf{2}\cdot C_6H_6$, $\mathbf{3}\cdot 0.5C_6H_6$, and **5** single crystal X-ray structure analyses were performed.

The structure of $\mathbf{2}\cdot C_6H_6$ (Fig. 2) contains the $[(t\text{-Bu})_2\text{Sb–Sb–Sb}(t\text{-Bu})_2]^-$ ion, coordinated through the terminal antimony atoms as a bidentate chelating ligand to the sodium ion, which bears the tridentate amine as an additional ligand. The coordination geometry around the sodium centre is distorted trigonal bipyramidal with Sb(1) and N(2) in axial and Sb(3), N(1), and N(3) in equatorial positions. The central antimony atom of the $[(t\text{-Bu})_2\text{Sb–Sb–Sb}(t\text{-Bu})_2]^-$ ion is disordered over two positions with an occupancy of 0.78 (Sb(2b)) and 0.22 (Sb(2a)), respectively. The Sb_3Na heterocycles are slightly folded; the Na–Sb(1)–Sb(3)/Sb(1)–Sb(2b)–Sb(3) dihedral angle is 176.1° and the Na–Sb(1)–Sb(3)/Sb(1)–Sb(2a)–Sb(3) dihedral angle is 171.4°. The Sb–Na bond lengths in $\mathbf{2}\cdot C_6H_6$ (330.4(2) and 322.5(2) pm) range between the sums of covalent (294.0 pm) and van der Waals radii [14] (450.0 pm) of Sb and Na, closer to the former. They compare well with the corresponding values found in $[\{(\text{CyP})_4\text{Sb}\}\text{Na}\cdot\text{Me}_2\text{NH}\cdot\text{tmeda}]$ [4] (322.9(4) pm) and $[\text{Sb}_7\text{Na}_3\cdot 3\text{tmeda}\cdot 3\text{thf}]$ [5] (319.6(9) pm), which also contain coordinative bonds between antimonides and sodium cations. The coordination of the $[(t\text{-Bu})_2\text{Sb–Sb–Sb}(t\text{-Bu})_2]^-$ ion to Na^+ in $\mathbf{2}\cdot C_6H_6$ leads to small changes of the geometry of the ligand. This is shown by comparison with the structure of **4**, where the $[(t\text{-Bu})_2\text{Sb–Sb–Sb}(t\text{-Bu})_2]^-$ unit is not included in the coordination sphere of the cation. The Sb–Sb bond lengths ($\mathbf{2}\cdot C_6H_6$, 274.97; **4**, 276.47 pm), the Sb–Sb–Sb bond angles ($\mathbf{2}\cdot C_6H_6$, 90.6; **4**, 87.6°) are similar, the SbC_2 and Sb_2C bond angles range between 97 and 106° in $\mathbf{2}\cdot C_6H_6$ and between 101 and 105° in **4**. The conformation of $[(t\text{-Bu})_2\text{Sb–Sb–Sb}(t\text{-Bu})_2]^-$ is described using the dihedral angles $\Phi = \text{Sb–Sb–Sb–lp}$, where lp denotes the assumed direction of the lone pair of electrons at the terminal antimony atoms. In $\mathbf{2}\cdot C_6H_6$ the conformation is close to *syn–syn* ($\Phi_1 = 11.44$, $\Phi_2 = 17.06°$) with almost perfect orientation of the lone pairs of electrons to the Na centres. The conformation of the 'naked' anion in **4** is similar ($\Phi_1 = 7.23$, $\Phi_2 = 24.04°$). It is surprising that the $[(t\text{-Bu})_2\text{Sb–Sb–Sb}(t\text{-Bu})_2]^-$ ligand in $\mathbf{2}\cdot C_6H_6$ is not coordinated through the central antimony atom. Apparently the chelating coordination through the terminal donor atoms is more effective. Other examples of this type of coordination are the complexes $[\text{Li(L)}(\text{R}_4\text{P}_3)]$ (R = *t*-Bu, *i*-Pr; L = 2thf, tmeda) [10].

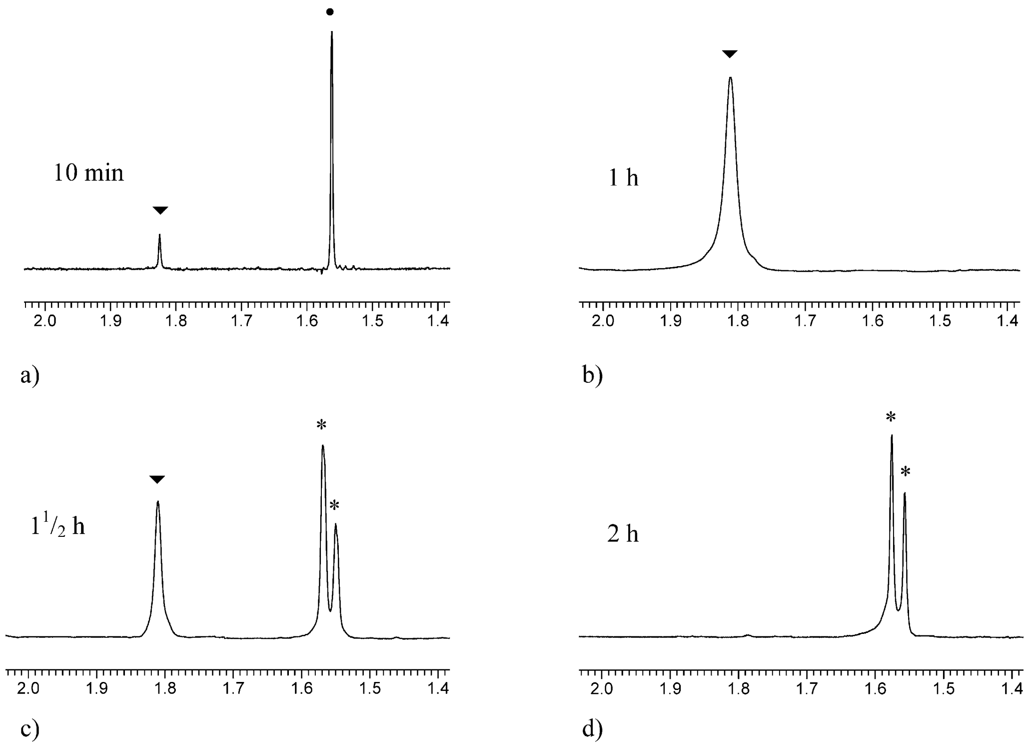


Fig. 1. ^{1}H-NMR (C_6D_6) spectra of samples taken from the reaction mixture of **1** with K. ●, *cyclo*-(t-BuSb)$_4$; ▼, [t-Bu$_4$Sb$_3$]$^-$; *, [t-Bu$_3$Sb$_2$]$^-$.

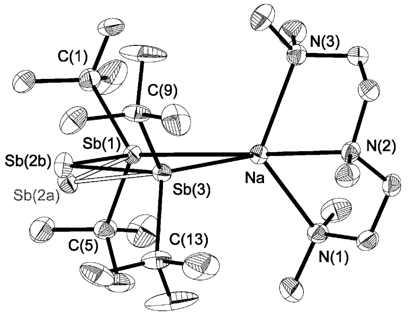


Fig. 2. ORTEP-like representation of **2**·C_6H_6 (H atoms omitted) at 30% probability showing the atomic numbering scheme. Bond lenghts (pm) and angles (°): Sb(1)–Na 330.4(2), Sb(3)–Na 322.5(2), Sb(1)–Sb(2a) 272.0(8), Sb(1)–Sb(2b) 277.6(2), Sb(2a)–Sb(3) 274.1(8), Sb(2b)–Sb(3) 276.2(2), Sb–C 221.5(6)–224.1(6), Na–N 245.0(5)–249.5(5), Na–Sb(1)–Sb(2a) 96.44(18), Na–Sb(1)–Sb(2b) 97.18(6), Sb(2a)–Sb(1)–C 96.9(2)–107.7(2), Sb(2b)–Sb(1)–C 100.5(2)–103.84(17), Sb(2a)–Sb(3)–C 97.3(2)–106.6(2), Sb(2b)–Sb(3)–C 99.3(2)–104.2(2), C(1)–Sb(1)–C(5) 102.7(3), C(9)–Sb(3)–C(13) 104.2(2), Sb(1)–Sb(2a)–Sb(3) 91.4(2), Sb(1)–Sb(2b)–Sb(3) 89.80(7), Na–Sb(1)–C 120.92(17)–126.8(2), Na–Sb(3)–C 117.0(2)–128.45(18), Sb(1)–Na–Sb(3) 73.54(4), N–Na–N 74.97(17)–75.79(17), C(1)–Sb(1)–Sb(2b)–Sb(3) 132.7, C(5)–Sb(1)–Sb(2b)–Sb(3) 121.26, C(9)–Sb(3)–Sb(2b)–Sb(1) 134.9, C(13)–Sb(3)–Sb(2b)–Sb(1) 117.84.

In crystals of **3**·0.5C_6H_6 the coordination of the triantimonide as a bridging tridentate ligand is realized. Not only the terminal but also the central antimony atoms are coordinated to neighbouring potassium cations and helical chains, [K(L){(t-Bu$_2$Sb)$_2$Sb}]$_n$ result. The C_6H_6 molecules lie between the chains. A section of this unique structure is depicted in Fig. 3.

The Sb_3K heterocycle is slightly folded with an Sb_3–Sb_2K dihedral angle of 160.8°. The central antimony atom is in a trigonal pyramidal environment (sum of bond angles at Sb(2) = 338.59°). The bond lengths, bond angles and conformation of the ligand in **3**·0.5C_6H_6 (Sb–Sb 275.94 pm, Sb(1)–Sb(2)–Sb(3) 87.59(2)°, $\Phi_1 = 1.84$; $\Phi_2 = 22.22°$) are similar to the corresponding values for **2**·C_6H_6 or **4**. The coordination number about each potassium is completed to six by three nitrogen atoms of a ($Me_2NCH_2CH_2)_2NMe$ ligand. The Sb–K bond lengths in **3**·0.5C_6H_6 (Sb(1)–K(1)* 415.7(4), Sb(3)–K(1)* 399.7(6), Sb(2)–K(1) 383.3(6) pm) vary in a large range. The shortest bond results from the monodentate coordination of the central antimony atom; the longer bonds represent the asymmetric bidentate coordination through the terminal atoms. All Sb–K bonds lie between the sum of the covalent (368.0 pm) and van der Waals radii (500.0 pm) for Sb and K. Shorter K–Sb bonds (348.6–361.8 pm) were found in [K(thf)$_{1/4}$(*cyclo*-Et_4C_4Sb)] [6].

The solid-state structure of **5** consists of a centrosymmetric dimer in which two [(t-Bu)$_2$SbSb(t-Bu)]$^-$ anions are coordinated through the antimonido atoms as bridging ligands to two potassium ions (Fig. 4). The central K_2Sb_2 unit has a rhombic shape, (K(1)–Sb(2)–K(1)* 101.37(3), Sb(2)–K(1)–Sb(2)* 78.63(3)°), with almost equal Sb–K bond lenghts, (K(1)–Sb(2) 356.55(9), K(1)–Sb(2)* 359.26(11) pm). The potassium ions are five-coordinate with two antimony ligands and one triamine. An unexpected aspect of the structure of **5**

Table 1
Crystal data, data collection, and structure refinement parameters for $\mathbf{2}\cdot C_6H_6$, $\mathbf{3}\cdot 0.5C_6H_6$, and **5**

	$\mathbf{2}\cdot C_6H_6$	$\mathbf{3}\cdot 0.5C_6H_6$	**5**
Empirical formula	$C_{25}H_{59}N_3NaSb_3\cdot C_6H_6$	$C_{25}H_{59}KN_3Sb_3\cdot 0.5C_6H_6$	$C_{21}H_{50}KN_3Sb_2$
Formula weight	868.10	845.16	627.24
Temperature (K)	173(2)	173(2)	173(2)
Mo−K_α (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$
Color	Red	Orange	Orange
Unit cell dimensions			
a (pm)	1248.8(10)	1234.4(4)	1047.7(2)
b (pm)	1876.5(3)	2065.2(5)	1666.6(3)
c (pm)	3486.4(3)	1602(2)	1790.5(4)
α (°)	90	90	90
β (°)	91.660(10)	111.47(5)	106.24(3)
γ (°)	90	90	90
V (nm^3)	8.1665(16)	3.80(1)	3.0016(10)
Z	8	4	4
Absorptions coefficient (mm^{-1})	2.002	2.245	1.948
Absorptions correction	DIFABS	DIFABS	DIFABS
Diffractometer	Siemens P4	Siemens P4	Stoe IPDS
$F(000)$	3488	1692	1272
Crystal size (mm^3)	0.5 × 0.4 × 0.2	0.8 × 0.8 × 0.2	0.4 × 0.3 × 0.3
Total majority to θ	99.6%	98.3%	97.8%
Index ranges	$-16 \leq h \leq 1$, $-24 \leq k \leq 1$, $-45 \leq l \leq 45$	$-14 \leq h \leq 1$, $-24 \leq k \leq 24$, $-18 \leq l \leq 19$	$-12 \leq h \leq 12$, $-20 \leq k \leq 20$, $-21 \leq l \leq 21$
Reflections collected	11 472	15 457	40 585
Independent reflections	9372 [$R_{int} = 0.0357$]	6713 [$R_{int} = 0.1117$]	5811 [$R_{int} = 0.0782$]
Refinement method	Full-matrix least-squares on F^2 [18]		
Data/restraints/parameters	9372/0/372	6713/0/336	5811/0/260
Final R [a] indices [$I > 2\sigma(I)$]	$R_1 = 0.0491$, $wR_2 = 0.1251$	$R_1 = 0.0623$, $wR_2 = 0.1272$	$R_1 = 0.0278$, $wR_2 = 0.0455$
R [a] indices (all data)	$R_1 = 0.0713$, $wR_2 = 0.1502$	$R_1 = 0.1228$, $wR_2 = 0.1514$	$R_1 = 0.0564$, $wR_2 = 0.0503$
Goodness-of-fit on F^2	1.028	0.984	0.877
Largest difference peak and hole (e Å^{-3})	1.434 and −2.097	1.191 and −1.279	0.653 and −0.359
Treatment of hydrogen atoms	Refined with a riding model and common isotopic temperature factor		

[a] Definition of the R values: $R_1 = \Sigma\ ||F_o| - |F_c||/\Sigma\ |F_o|$; $wR_2 = [w\ \Sigma\ (F_o^2 - F_c^2)^2/\Sigma\ w(F_o^2)^2]^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

is the trigonal pyramidal coordination of the antimonido atoms Sb(2) and Sb(2)* (sum of Sb_2K and SbK_2 angles at Sb(2), respectively Sb(2)* 358.89°), which is very unusual for four-coordinate antimony atoms and contrasts with the distorted tetrahedral geometry of the arsenido atoms in [Li(thf)(t-Bu_3As_2)]$_2$ [11]. This difference may result from steric effects. The most straightforward interpretation for the coordination geometry in **5** is to consider a sp^2 hybridization for the Sb(2), respectively Sb(2)* atoms. Two of the hybrid orbitals contain the lone pairs of electrons for the coordinative bond to the potassium ion, one is used for the Sb−Sb bond. The remaining unhybridized p orbital of Sb(2) is involved in the bond to the C(9) carbon atom of the t-Bu group (C(9)−Sb(2)−Sb(1) 94.88(9), C(9)−Sb(2)−K(1)* 93.740(9), C(9)−Sb(2)−K(1) 90.02(9)°). An alternative interpretation would be to assume no hybridization at Sb(2) and to consider a p orbital orthogonal to the Sb−Sb bond for the interaction with the K atoms.

A common feature of the crystal structures of the antimonides **2**–**5** and [Ph_4Sb_3]$^-$ [7] are the relative short Sb−Sb bond lenghts (275.5(1)–276.7(1) pm). They are shorter than the Sb−Sb single bond lengths in **1** (281.7(2)–282.1(2) pm) [15] but significantly longer than a Sb−Sb double bond (264.2(1) pm in {2,4,6-[($Me_3Si)_2CH]_3C_6H_2$}$_2Sb_2$ [16]). The shortening may rather be a consequence of the participation of s orbitals in the hybridization of the bonding orbitals of the antimonido atoms than result from (p–d)π bonding [7]. Relative short single bonds were also reported for complexes containing the [($R_2P)_2P$]$^-$ [10], [R(H)PPR]$^-$ [12], or [R_2PNR]$^-$ [13] ligands.

3. Experimental

NMR spectra were run on Bruker DPX 200 spectrometer. Chemical shifts are reported in δ units (ppm)

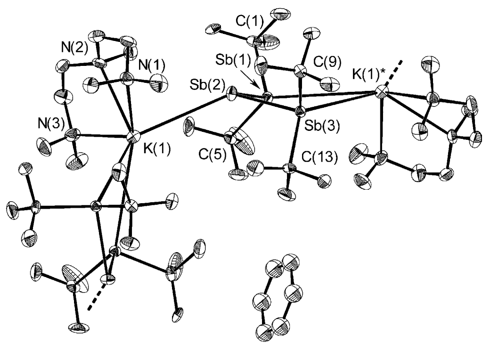


Fig. 3. ORTEP-like representation of a section of the structure of **3**·$0.5C_6H_6$ (H atoms omitted) at 30% probability showing the atomic numbering scheme. Bond lenghts (pm) and angles (°): K(1)–Sb(2) 383.3(6), K(1)*–Sb(1) 415.7(4), K(1)*–Sb(3) 399.7(6), Sb(2)–Sb(3) 276.65(11), Sb(1)–Sb(2) 276.3(3), Sb–C 221.3(11)–225.1(11), K(1)–N 287.9(10)–297.4(9), K(1)–Sb(2)–Sb(3) 130.24(5), K(1)–Sb(2)–Sb(1) 120.97(8), Sb(1)–Sb(2)–Sb(3) 87.60(5), Sb(2)–Sb(1)–C 101.6(3)–102.2(3), Sb(2)–Sb(3)–C 99.7(3)–103.0(3), C(1)–Sb(1)–C(5) 105.0(4), C(9)–Sb(3)–C(13) 104.7(4), Sb(3)*–K(1)–Sb(2) 130.24(10), Sb(1)*–K(1)–Sb(2) 121.03(8), Sb(2)–Sb(1)–K(1)* 104.09(8), Sb(2)–Sb(3)–K(1)* 108.12(6), C–Sb(1)–K(1)* 104.0(3)–135.6(3), C–Sb(3)–K(1)* 113.8(3)–124.3(3), N–K(1)–N 60.3(3)–61.7(3), C(1)–Sb(1)–Sb(2)–Sb(3) 125.03, C(5)–Sb(1)–Sb(2)–Sb(3) 126.87, C(9)–Sb(3)–Sb(2)–Sb(1) 137.16, C(13)–Sb(3)–Sb(2)–Sb(1) 114.94.

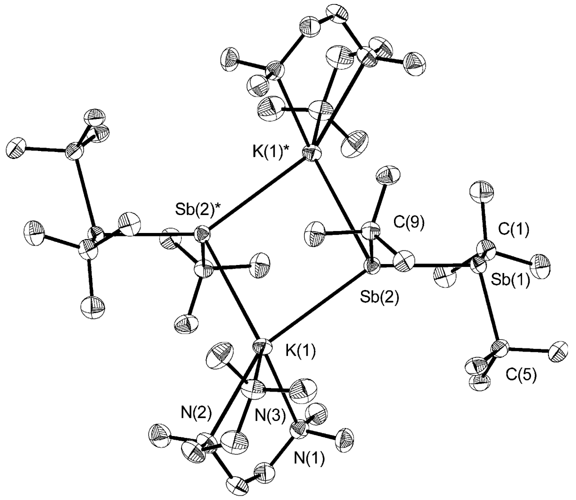


Fig. 4. ORTEP-like representation of **5** at 30% probability showing the atomic numbering scheme. Bond lenghts (pm) and angles (°): K(1)–Sb(2) 356.55(9), K(1)–Sb(2)* 359.26(11), Sb(1)–Sb(2) 276.13(10), Sb–C 222.6(4)–225.0(3), K–N 282.9(3)–288.9(3), K(1)–Sb(2)–K(1)* 101.37(3), Sb(2)–K(1)–Sb(2)* 78.63(3), Sb(1)–Sb(2)–K(1) 113.85(2), Sb(1)–Sb(2)–K(1)* 143.669(18), Sb(1)–Sb(2)–C(9) 94.88(9), Sb(2)–Sb(1)–C 100.01(1)–103.53(9), C(1)–Sb(1)–C(5) 102.77(14), C(9)–Sb(2)–K(1)* 93.70(9), C(9)–Sb(2)–K(1) 90.02(9).

referenced to C_6D_5H (7.15 ppm, ^1H) and C_6D_6 (128.0 ppm, ^{13}C). Mass spectra were recorded on Finnigan MAT CH7 (A) spectrometer. The pattern of antimony-containing ions was compared with theoretical values. The reactions and manipulations were performed in an inert atmosphere of Ar using dried solvents distilled under Ar. *cyclo*-(*t*-Bu_4Sb_4) (**1**) was prepared according to reported procedures [17].

3.1. Preparation of [Na(L)(t-Bu_4Sb_3)] (L = ($Me_2NCH_2CH_2$)$_2$NMe) (2)

Compound **1** (1.0 g, 1.4 mmol) was reacted for 4 h with 0.4 g (17.4 mmol) small pieces of Na in 40 ml thf. Afterwards 0.58 ml (2.77 mmol) $(Me_2NCH_2CH_2)_2NMe$ were added and stirred for 1 h until room temperature (r.t.). After filtration and removal of the solvent under reduced pressure 0.08 g of a red solid (82–88 °C dec.) was obtained. After recrystallization from C_6H_6 at 7 °C 0.058 g (58%) of **2**·C_6H_6 formed as red crystals. ^1H-NMR (200 MHz, C_6D_6): δ 1.77 (s, 36H; $C(CH_3)_3$), 2.07 (s, 12H; $N(CH_3)_2$), 2.10 (s, 3H; NCH_3), 2.15–2.21 (m, 8H; CH_2). ^{13}C-NMR (50MHz, C_6D_6): δ 30.42 (s, 4C; $C(CH_3)_3$), 34.88 (s, 12C; $C(CH_3)_3$), 43.14 (s, 1C; NCH_3), 46.02 (s, 4C; $N(CH_3)_2$), 56.94 (s, 2C; CH_2), 58.35 (s, 2C; CH_2).

3.2. Preparation of [K(L)(t-Bu_4Sb_3)] (L = ($Me_2NCH_2CH_2$)$_2$NMe) (3)

To a solution of **1** (1.0 g, 1.4 mmol) in 40 ml thf 0.3 g (7.7 mmol) small pieces of K were added and stirred with reflux for 1 h. At this temperature 0.43 ml (2.1 mmol) $(Me_2NCH_2CH_2)_2NMe$ were added and the red–brown solution further stirred until r.t., than filtered through a frit covered with kieselguhr. Removal of the solvent under reduced pressure gave 0.76 g (68%) of **3** as a red–brown solid (90–110 °C dec.). Crystals of **3**·$0.5C_6H_6$ suitable for X-ray analysis were grown by cooling solutions of **3** in C_6H_6 at 7 °C for 1 day. ^1H-NMR (200 MHz, C_6D_6): δ 1.81 (s, 36H; $C(CH_3)_3$), 2.10 (s, 12H; $N(CH_3)_2$), 2.14 (s, 3H; NCH_3), 2.26–2.34 (m, 8H; CH_2). ^{13}C-NMR (50 MHz, C_6D_6): δ 24.80 (s, 4C; $C(CH_3)_3$), 34.89 (s, 12C; $C(CH_3)_3$), 43.61 (s, 1C; NCH_3), 45.73 (s, 4C; $N(CH_3)_2$), 56.40 (s, 2C; CH_2), 57.83 (s, 2C; CH_2).

3.3. Preparation of [K(L)(t-Bu_3Sb_2)] (L = ($Me_2NCH_2CH_2$)$_2$NMe) (5)

The reaction of 1.0 g (1.4 mmol) **1** with 0.3 g (7.7 mmol) K in 40 ml of thf for 2 h was performed in an analogous way to the synthesis of **3**. After addition of 0.88 ml (4.2 mmol) $(Me_2NCH_2CH_2)_2NMe$ and further stirrring for 1 h at r.t. the reaction mixture was filtered and the solution concentrated to 15 ml. Cooling at 7 °C for 1 day gives 0.46 g (53%) of **5** as orange crystals (80–90 °C dec.). MS (CI_{neg}, NH_3): 415 (100) $[t\text{-}Bu_3Sb_2]^-$. ^1H-NMR (200 MHz, C_6H_6): δ 1.55 (s, 18H; $C(CH_3)_3$), 1.57 (s, 9H; $C(CH_3)_3$), 2.11 (s, 12H; $N(CH_3)_2$), 2.17 (s, 3H, NCH_3), 2.34–2.46 (m, 8H, CH_2). ^{13}C-NMR (50 MHz, C_6D_6): δ 30.52 (s, 4C; $C(CH_3)_3$), 31.03 (s, 2C, $C(CH_3)_3$), 34.99 (s, 12C; $C(CH_3)_3$), 35.61 (s, 6C, $C(CH_3)_3$), 43.26 (s, 1C; NCH_3), 46.12 (s, 4C; $N(CH_3)_2$), 57.05 (s, 2C; CH_2), 58.45 (s, 2C; CH_2).

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 184805–184807 for compounds **5**, **3**$\cdot 0.5C_6H_6$ and **2**$\cdot C_6H_6$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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