Synthesis and Structures of Alkali(alkoxy) Antimonates and Bismuthates

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Dedicated to Professor Peter Paetzold on the occasion of his 60th birthday

Abstract: $\mathrm{As(O\mathit{t}Bu)_3}$ does not form adducts with alkali metal *tert*-butoxides $\mathrm{MO\mathit{t}Bu}$ (M = Li, Na, K, Rb and Cs), whereas the corresponding $\mathrm{Sb(O\mathit{t}Bu)_3}$ (**2**) and $\mathrm{Bi(O\mathit{t}Bu)_3}$ (**3**) react with $\mathrm{MO\mathit{t}Bu}$ (M = K, Rb, Cs) to yield $\mathrm{M(O\mathit{t}Bu)_4Sb}$ (M = K (**6**), Rb (**7**), Cs (**8**)) and $\mathrm{M(O\mathit{t}Bu)_4Bi}$ (M = **9**), respectively. X-ray structure determinations for **6** and **9** show them to be one-dimensional coordination polymers composed of $\mathrm{E(O\mathit{t}Bu)_4}$ (E = Sb, Bi) units linked through potassium atoms. These $\mathrm{E(O\mathit{t}Bu)_4}$ units display a ψ-trigonal-bipyramidal coordination around the metal atom (Sb–O = 1.971(2) and 2.181(2) Å, Bi–O = 2.068(8) and 2.275(8) Å). Both the structures exhibit a planar four-coordinate environment of oxygen around the potassium atoms (K–O = 2.650(2)–2.967(2) Å in **6**, 2.53(1)–3.15(1) Å in **9**). Compound **2** reacts with two equivalents of $\mathrm{KO\mathit{t}Bu}$ to afford $\mathrm{K_2Sb(O\mathit{t}Bu)_5 \cdot dioxane}$ (**10**), which contains $\mathrm{Sb_2K_2O_5}$ cage units and can be described as an $\mathrm{O_5}$ trigonal bipyramid with metal atoms inserted in the equatorial edges. Each metal atom is tetracoordinated by oxygen atoms of the cage (Sb–O = 1.979(3)–2.144(3) Å, K–O = 2.592(3)–2.778(2) Å). The dioxane molecules increase the coordination number at each potassium atom to five by forming bridges between the molecules through K–O bonds. Reaction of **2** and **3** with $\mathrm{NaO\mathit{t}Bu}$ produce the cluster compounds $\mathrm{Na_4Sb_2O(O\mathit{t}Bu)_8}$ (**4**) and $\mathrm{Na_4Bi_2O(O\mathit{t}Bu)_8}$ (**5**) in high yields. $\mathrm{K_4Sb_2O(O\mathit{t}Bu)_8}$ (**11**) is obtained in almost quantitative yield by heating $\mathrm{KSb(O\mathit{t}Bu)_4}$ in benzene for 24 h. Compounds **4**, **5** and **11** crystallise in rhombohedral lattices; the crystal structure analyses show a superposition of molecules, with an isotropic oxygen-centred $\mathrm{M_6}$ octahedron. The formation of these oxo-*tert*-butoxides is accompanied by evolution of isobutene. Addition of four equivalents of THF to **11** gives $\mathrm{K_4Sb_2O(O\mathit{t}Bu)_8 \cdot 4\,THF}$ (**12**). X-ray diffraction studies reveal a *cis* arrangement of the Sb atoms in the central $\mathrm{OSb_2K_4}$ unit. $\mathrm{K_4Sb_2O_2(O\mathit{i}Pr)_{12}}$ (**13**) is obtained as the major product on heating $\mathrm{KSb(O\mathit{t}Bu)_4}$ and subsequent reaction with isopropyl alcohol. In the crystal structure, two oxygen-centred $\mathrm{Sb_2K_2}$ tetrahedra (K–O 2.693(4) Å, Sb–O = 1.982(5) Å) linked through *i*PrO–K bonds (2.726(7)–2.738(7) Å) are observed. In the reactions of $\mathrm{KSb(O\mathit{t}Bu)_4}$ (**6**) with the metal halides $\mathrm{CaCl_2}$, TlCl and CuI, a halide ion is transferred to potassium; this results in formation of potassium halide, the corresponding alkoxide and $\mathrm{Sb(O\mathit{t}Bu)_3}$.

Keywords
alkoxides · clusters · Group 15 complexes · Lewis acids · oxygen bridges

Introduction

Although the alkoxides of the Lewis acids germanium(II), tin(II) and lead(II) easily form adducts with alkoxides of main group[1, 2] and transition metals,[3] the reports available on analogous derivatives of Group 15 elements are scarce. The tris(alkoxides) of arsenic, antimony and bismuth have been prepared by different routes, and some of these compounds, particularly those containing bismuth, have been characterised by X-ray diffraction analysis.[4–10] The bismuth alkoxides have attracted considerable attention as precursors for the sol-gel and chemical vapour deposition (CVD) techniques. The use of these alkoxides for the synthesis of mixed metal alkoxides is limited to a few examples, and there seems to be no information available on the structural features of the latter. Compounds of type $\mathrm{KSb(OR)_4}$ (R = Me, Et, *i*Pr, *n*Bu, *t*Bu) have been synthesised by Lewis acid–base reactions of the parent metal alkoxides and characterised by IR and NMR techniques.[11] The bivalent transition metals Mn, Fe, Co and Ni can be incorporated in systems of type $\mathrm{MSb(OEt)_5}$,[12] whereas $\mathrm{Sn^{II}}$ and $\mathrm{Pb^{II}}$ alkoxides form adducts with $\mathrm{Sb(OR)_3}$ of the general formula $\mathrm{M[Sb(OR)_4]_2}$[13] (these compounds have been characterised by UV, IR and NMR spectroscopy). Antimony(V) also seems to form stable adducts ($\mathrm{MSb(OR)_6}$; M = Li, Na, K; R = Me, *i*Pr, *n*Pr, *n*Bu, *t*Bu), as deduced from molecular mass and spectroscopic measurements.[14] In this paper we present our results of a systematic study of the reactivity of $\mathrm{As(O\mathit{t}Bu)_3}$ (**1**), $\mathrm{Sb(O\mathit{t}Bu)_3}$ (**2**) and $\mathrm{Bi(O\mathit{t}Bu)_3}$ (**3**) towards *tert*-butoxides of the alkali metals.

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Results and Discussion

Synthetic Procedures: $As(OtBu)_3$ (**1**) and $Sb(OtBu)_3$ (**2**) were obtained by a slightly modified procedure to that described earlier[15] [Eq. (a)]. The alkoxides **1** and **2** were crystallised from

$$ECl_3 + 3\,tBuOH + 3\,Et_3N \longrightarrow E(OtBu)_3 + 3\,Et_3NHCl \qquad (a)$$
$$E = As\ (\mathbf{1}),\ Sb\ (\mathbf{2})$$

their cooled solutions in high yields. The arsane **1** is monomeric even in the solid state and displays a three-coordinate pyramidal arsenic atom (As–O = 1.74(2) Å, O–As–O 91.5°).[16] The corresponding $Bi(OtBu)_3$ was obtained by the reaction of $BiCl_3$ with potassium alkoxide in moderate yield [Eq. (b)]. Attempts

$$BiCl_3 + 3\,KOtBu \longrightarrow \underset{\mathbf{3}}{Bi(OtBu)_3} + 3\,KCl \qquad (b)$$

to use **1** as a Lewis acid in the reaction with *tert*-butoxides of the alkali metals (MO*t*Bu; M = Li, Na, K, Rb, Cs) failed even at elevated temperatures and with long reaction times. The starting materials were recovered quantitatively. Similarly, **2** and **3** do not react with LiO*t*Bu. On the other hand, when the heavier congeners of lithium butoxides were mixed with **2** and **3**, the intensity of the signals of **2** and **3** in their ^1H NMR spectra decreased steadily with time. However, the mode of reaction with NaO*t*Bu was different to that with KO*t*Bu, RbO*t*Bu and CsO*t*Bu [Eq. (c) and (d)]. Reaction of NaO*t*Bu with **2** and **3** did

$$n\,E(OtBu)_3 + m\,NaOtBu \longrightarrow Na_4E_2O(OtBu)_8 \qquad (c)$$
$$E = Sb\ (\mathbf{4}),\ Bi\ (\mathbf{5})$$

$$E(OtBu)_3 + M(OtBu) \longrightarrow EM(OtBu)_4 \qquad (d)$$
$$E = Sb,\ M = K\ (\mathbf{6}),\ Rb\ (\mathbf{7}),\ Cs\ (\mathbf{8})$$
$$E = Bi,\ M = K\ (\mathbf{9})$$

not yield the expected simple adducts, but rather metal-rich oxoalkoxides **4** and **5** (70 and 15% yield, respectively). The reactions proceeded in two steps: 1) Addition of NaO*t*Bu to a solution of **2** or **3** in $[D_6]$benzene gave a suspension that cleared within 30 min. The ^1H NMR spectra of these solutions exhibited only one signal at $\delta = 1.42$ (**2** + NaO*t*Bu) and 1.37 (**3** + NaO*t*Bu), respectively. 2) After another 2.5 h, crystals were obtained from the solutions. These crystals were difficult to redissolve, but could be sublimed and "recrystallised" from boiling benzene. The composition of the products was confirmed by elemental and X-ray structure analysis (see below). The expected adducts $EM(OtBu)_4$ (**6, 7, 8, 9**) were, on the other hand, isolated in the case of the other alkali metal *tert*-butoxides. All adducts were slightly soluble in benzene and exhibited only one signal in their ^1H NMR spectra. Two of these adducts were characterised by X-ray structure analysis (see below).

By varying the molar ratios of KO*t*Bu and $Sb(OtBu)_3$, two alkoxide groups could formally be added to **2** [Eq. (e)]. The

$$\underset{\mathbf{2}}{Sb(OtBu)_3} + 2\,KOtBu + O(CH_2CH_2)_2O \longrightarrow \underset{\mathbf{10}}{K_2Sb(OtBu)_5 \cdot O(CH_2CH_2)_2O} \qquad (e)$$

dioxane adduct **10** was isolated in good yield. The ^1H NMR spectrum in benzene exhibited a singlet at $\delta = 1.40$ for the *t*Bu groups and multiplets for the CH_2 groups of dioxane. The structure of **10** was established by X-ray diffraction techniques.

To gain further understanding about the mechanism of formation of the oxoalkoxides **4** and **5**, the reaction of KO*t*Bu with $Sb(OtBu)_3$ (**2**) was investigated in detail. When **6** was stirred for 24 h in benzene, it was transformed to another crystalline product, which, according to the elemental analysis, had the molecular formula $K_4Sb_2O(OtBu)_8$ (**11**), a composition analogous to that of **4** and **5**. All three compounds (**4, 5** and **11**) form isotypic crystals, which have a rhombohedral lattice (see below). That isobutene was formed as one of the reaction products (besides **11**) was shown unambiguously by the characteristic resonances in the ^1H NMR spectrum of the solution. Signals assigned to *tert*-butyl alcohol and $Sb(OtBu)_3$ were also observed. Because **11** is sparingly soluble, only a qualitative equation [Eq. (f)] can be deduced on the basis of observations made

$$m\,\underset{\mathbf{6}}{KSb(OtBu)_4} \xrightarrow{\Delta T} n\,\underset{\mathbf{11}}{K_4Sb_2O(OtBu)_8} + x\,(CH_3)_2C{=}CH_2 + y\,tBuOH + z\,Sb(OtBu)_3 \qquad (f)$$

during the course of reaction. These findings indicate that the oxygen atom in the clusters **4**, **5** and **11** has its origin in the hydroxide group in $ME(OtBu)_3OH$ formed by elimination of isobutene from $ME(OtBu)_4$ [Eq. (g)]. This is also in accord with

$$ME(OtBu)_4 \longrightarrow ME(OtBu)_3OH + (CH_3)_2C{=}CH_2 \qquad (g)$$

the observation that isobutene can be detected by ^1H NMR spectroscopy before **11**, *t*BuOH and **2**. The fate of $ME(OtBu)_3OH$ is not clear; it may condense with a second molecule with elimination of water or *tert*-butyl alcohol (other reactions are also possible). A similar mechanism has been suggested for the formation of μ-oxoalkoxides, and the thermal elimination of R–O–R from metal alkoxides has also been discussed.[17] A recent report on the synthesis of $Sb_4Cl_7O(OtBu)_3$ describes the formation of isobutene and *tert*-butyl chloride during the reaction of $Sb(OtBu)_3$ with $SbCl_3$.[18] The high yields of **4** and **11** rule out the possibility of hydrolysis of $ME(OtBu)_4$ by residual water present in the reaction flasks or the solvents.

Compound **11** is more soluble in noncoordinating solvents than **4** and **5**, and its ^1H and ^{13}C NMR spectra have been recorded. The ^1H NMR spectrum contains three distinct resonances in a 1:1:2 ratio. The ^{13}C NMR is not as well resolved and shows two signals for the primary carbon atoms and one broad signal for the tertiary carbon atoms. The ^1H NMR spectrum seem to be consistent with a *cis* arrangement of the antimony atoms in the oxygen-centred K_4Sb_2O octahedron with local C_{2v} symmetry in the molecule as a whole (see section on Crystal Structures).

The four potassium atoms of the oxoalkoxide **11** can be used as acidic centres for the coordination of Lewis bases like tetrahydrofuran (THF) [Eq. (h)]. An X-ray structure analysis of **12**

$$\underset{\mathbf{11}}{K_4Sb_2O(OtBu)_8} + 4\,THF \longrightarrow \underset{\mathbf{12}}{K_4Sb_2O(OtBu)_8 \cdot 4\,THF} \qquad (h)$$

reveals the *cis* arrangement of the antimony atoms in the K_4Sb_2 octahedron and is thus consistent with the interpretation of the ^1H NMR spectrum of **11**.

Several reactions were performed in order to test the synthetic potential of **6**. The results of the biphasic reactions of **6** with

$CaCl_2$, TlCl and CuI are assembled in Equations (i), (j) and (k). They all proceed in a similar way: the halide is trapped by potassium to form KX (X = Cl, I; X-ray powder characterisation), and the corresponding metal alkoxide ($Ca(OtBu)_2$, $(TlOtBu)_4$, $(CuOtBu)_4$) and $Sb(OtBu)_3$ are liberated.

$$\underset{\mathbf{6}}{2\,KSb(OtBu)_4} + CaCl_2 \longrightarrow 2\,KCl + 2\,Sb(OtBu)_3 + Ca(OtBu)_2 \quad \text{(i)}$$

$$\underset{\mathbf{6}}{KSb(OtBu)_4} + TlCl \longrightarrow KCl + Sb(OtBu)_3 + \tfrac{1}{4}(TlOtBu)_4 \quad \text{(j)}$$

$$\underset{\mathbf{6}}{KSb(OtBu)_4} + CuI \longrightarrow KI + Sb(OtBu)_3 + \tfrac{1}{4}(CuOtBu)_4 \quad \text{(k)}$$

The thermolysis of $KSb(OtBu)_4$ [cf., Eq. (f)] followed by alcoholysis was reexamined by treating the products of the thermolysis of **6** with isopropyl alcohol. Surprisingly, the corresponding isopropyl alcoholate of **11** was not obtained; instead, an oxoalkoxide **13** was isolated in acceptable yield [Eq. (l)]. The

$$KSb(OtBu)_4 \xrightarrow{\Delta T,\, iPrOH} \underset{\mathbf{13}}{K_4Sb_4O_2(OiPr)_{12}} \quad \text{(l)}$$

compound **13** crystallised from a benzene solution and was characterised by an X-ray structure analysis. The ^1H NMR spectrum of the solution exhibited resonances for only one type of isopropyl group.

Crystal Structures: The most relevant X-ray data discussed in this section are given in the Experimental Procedure.[19] A section of the crystal structures of compounds $KSb(OtBu)_4$ (**6**) and $KBi(OtBu)_4$ (**9**) are displayed in Figures 1 and 2. Although these two compounds have identical stoichiometry, they crystallise with slightly different structures.

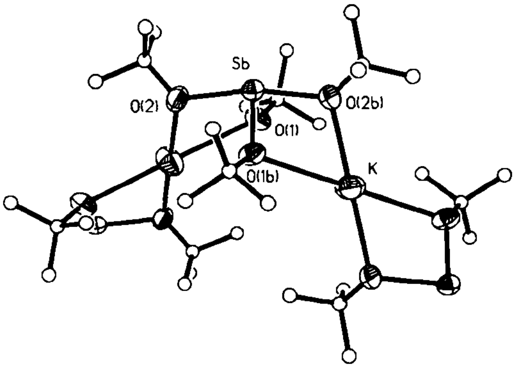

Fig. 1. A section of the one-dimensional structure of $KSb(OtBu)_4$ (**6**). The thermal ellipsoids are plotted at the 50% probability level. In all figures the carbon atoms are represented by simple circles and are not labelled.

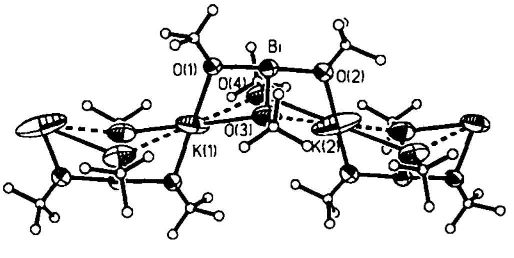

Fig. 2. A section of the one-dimensional structure of $KBi(OtBu)_4$ (**9**). The thermal ellipsoids are plotted at the 50% probability level.

The compounds **6** and **9** are composed of one-dimensional arrangements of $Sb(OtBu)_4$ or $Bi(OtBu)_4$ units linked through potassium atoms, which are each coordinated to four oxygen atoms in a single plane. In both structures the potassium atoms are situated on inversion centres. Whereas a twofold axis of symmetry runs through the antimony atom of ψ-trigonal-bipyramidal $Sb(OtBu)_4$ unit, the corresponding $Bi(OtBu)_4$, which is similar in structure, lacks this twofold axis. As expected the equatorial E–O bond lengths are shorter than the axial ones ($\Delta r(\mathbf{6}) = -0.210$, $\Delta r(\mathbf{9}) = -0.207$ Å; see also Table 1). Two of the four K–O bonds, those involving the axial oxygen atoms of the $E(OtBu)_4$ units, are short (**6**: 2.650(2), **9**: 2.530(1) Å). The longer K–O contacts (Table 1) should be considered as secondary bonds, as they are quite elongated, particularly in the case of **9** ($\Delta r(\mathbf{6}) = 0.317$, $\Delta r(\mathbf{9}) = 0.71$ Å). Whereas the fifth and sixth O···K contacts in **6** (O···K = 3.813(2) Å) are much longer than the K–O bonds, the corresponding oxygen atoms in **9** are much closer to K(1) and K(2), and form further secondary bonds (dotted lines in Fig. 2; K(2)–O(3) = 3.60(2), K(1)–O(4) = 3.49(2) Å). We suspect that these shorter distances in **9** may be responsible for the high anisotropy in the temperature factors of the potassium and oxygen atoms (see Fig. 2). In this direction the potential energy curve for the metal atoms seems to be flat; this allows a movement of the potassium atoms within the oxygen channels of the structure (Fig. 3). A similar movement of the potassium atoms is not possible within the structure of **6**, since, in this case, the gap between the bonding K–O and nonbonding K···O distances is greater than in **9** ($\Delta r = 0.84$ Å). The one-dimensional arrangement in **6** is similar to that in $KSn(OtBu)_3$, but different coordination numbers both at Sb (4 instead of 3) and K (4 instead of 5) are observed.[20]

Table 1. Some selected distances [Å] and angles [°] in $KSb(OtBu)_4$ (**6**) and $KBi(OtBu)_4$ (**9**). Symmetry operations for **6**: #1: $-x, y, 0.5-z$; #2: $x, 1-y, 0.5+z$; #3: $x, 1-y, z-0.5$; for **9**: #1: $1-x, 1-y, 1-z$; #2: $1-x, 1-y, -z$.

$KSb(OtBu)_4$			
Sb-O(1)#1	1.971(2)	O(1)#1-Sb-O(1)	88.03(13)
Sb-O(1)	1.971(2)	O(1)#1-Sb-O(2)	86.79(9)
Sb-O(2)	2.181(2)	O(1)-Sb-O(2)	84.10(9)
Sb-O(2)#1	2.181(2)	O(2)-Sb-O(2)#1	167.33(12)
K-O(2)#2	2.650(2)	O(2)#2-K-O(2)#1	180.0
K-O(2)#1	2.650(2)	O(2)#2-K-O(1)#1	120.87(6)
K-O(1)#1	2.967(2)	O(2)#1-K-O(1)#1	59.14(6)
K-O(1)#2	2.967(2)	C(1)-O(1)-Sb	126.5(2)
O(1)-C(1)	1.437(3)	C(1)-O(1)-K#3	117.7(2)
O(1)-K#3	2.967(2)	Sb-O(1)-K#3	102.93(8)
O(2)-C(2)	1.416(4)	C(2)-O(2)-Sb	123.5(2)
O(2)-K#3	2.650(2)	C(2)-O(2)-K#3	117.8(2)
		Sb-O(2)-K#3	107.76(8)
$KBi(OtBu)_4$			
Bi-O(3)	2.061(10)	O(4)-Bi-O(1)	89.5(4)
Bi-O(4)	2.075(8)	O(3)-Bi-O(2)	90.2(4)
Bi-O(1)	2.265(8)	O(4)-Bi-O(2)	91.1(4)
Bi-O(2)	2.285(9)	O(1)-Bi-O(2)	177.3(3)
K(1)-O(1)	2.559(9)	O(1)-K(1)-O(1)#1	180.0
K(1)-O(1)#1	2.559(9)	O(1)-K(1)-O(3)	62.2(3)
K(1)-O(3)	3.151(11)	O(1)#1-K(1)-O(3)	117.8(3)
K(1)-O(3)#1	3.151(11)	O(2)-K(2)-O(2)#2	180.0
K(2)-O(2)	2.500(10)	C(4)-O(1)-K(1)	129.8(8)
K(2)-O(2)#2	2.500(10)	Bi-O(1)-K(1)	105.3(3)
O(1)-C(4)	1.42(2)	C(3)-O(2)-Bi	123.5(8)
O(2)-C(3)	1.43(2)	C(3)-O(2)-K(2)	125.8(8)
O(3)-C(2)	1.44(2)	Bi-O(2)-K(2)	109.7(3)
O(4)-C(1)	1.446(14)	C(2)-O(3)-Bi	124.9(9)
		C(2)-O(3)-K(1)	115.6(8)
O(3)-Bi-O(4)	78.4(4)	Bi-O(3)-K(1)	92.5(4)
O(3)-Bi-O(1)	87.4(4)	C(1)-O(4)-Bi	124.8(9)

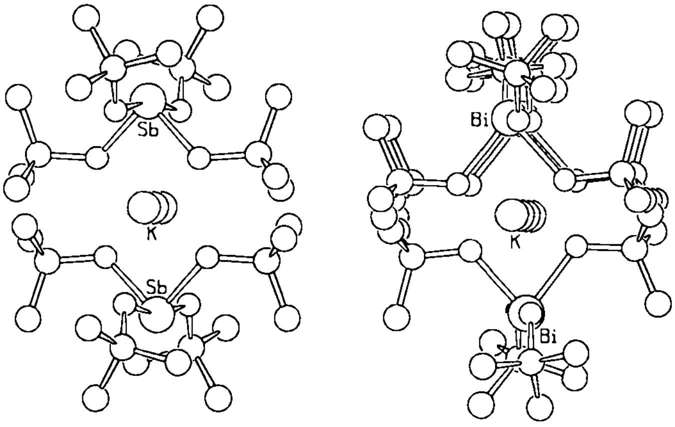

Fig. 3. Comparison of the structure **6** (left) and **9** looking down the oxygen channels. The bonds with the potassium atoms are omitted for clarity [28].

A section of the crystal structure of $K_2Sb(OtBu)_5$·dioxane (**10**) is shown in Figure 4. The inner core of the molecule consists of an O_5 trigonal bipyramid, the equatorial edges of which are centred by two potassium and one antimony atom. The SbK_2O_5 cage is bisected by a crystallographic mirror plane running through Sb, O(1), O(2) and O(3), but the overall pseudo-symmetry of the cage fragment is nearly C_{2v} (*mm*2) with the perpendicular plane incorporating the potassium atoms. Antimony is ψ-trigonal-bipyramidally coordinated by oxygen atoms; the equatorial bonds are shorter than the axial ones by 0.162 Å (see also Table 2). The potassium atoms are also trigonal-bipyramidally coordinated by oxygen atoms; the shortest bond is axial (K–O(2)). All other K–O bond lengths are in a very narrow range (2.723–2.778 Å); this suggests an interaction of the type observed in the limiting structure $[\text{dioxane}\cdot K_2OtBu]^+[Sb(OtBu)_4]^-$. The molecules are linked into a one-dimensional polymer through the oxygen atoms of the dioxane molecules. Each dioxane occupies an inversion centre of the lattice. Because of interaction with a dioxane molecule, the *tert*-butyl group on O(2) is shifted outside the SbK_2 plane, and O(2) thus occupies the apex of a K_2CO trigonal pyramid (sum of the angles: 343.6°). In contrast to O(2), the O(4) atoms are in a planar environment (sum of the angles: 360.0°). There are a number of compounds that have an M_3O_5 closed triangular polyhedron analogous to that of **10** (e.g., $KU_2(OtBu)_9$,[21] $(DME)_2Na_2Ce(OtBu)_6$,[22] etc.), but no example of a compound with a stoichiometry similar to that of **10** has been reported so far.

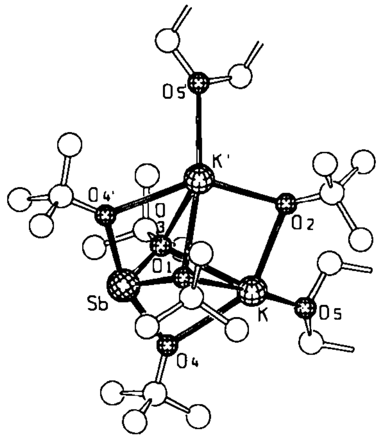

Fig. 4. A section of the dioxane-bridged structure of $K_2Sb(OtBu)_5$ · dioxane (**10**) [28].

Table 2. Some selected bond lengths [Å] and angles [°] in $K_2Sb(OtBu)_5$·dioxane (**10**). Symmetry operation: #1: x, $0.5-y$, z.

Sb-O(3)	1.979(3)	O(2)-K-O(3)	86.24(9)
Sb-O(1)	1.985(3)	O(4)-K-O(3)	59.91(8)
Sb-O(4)	2.144(3)	O(5)-K-O(3)	114.17(9)
Sb-O(4)#1	2.144(3)	O(1)-K-O(3)	57.24(8)
K-O(2)	2.592(3)	O(2)-K-Sb	104.36(7)
K-O(4)	2.717(3)	O(4)-K-Sb	36.64(5)
K-O(5)	2.723(3)	O(5)-K-Sb	135.92(7)
K-O(1)	2.778(2)	O(1)-K-Sb	33.42(6)
K-O(3)	2.777(3)	O(3)-K-Sb	33.29(6)
O(1)-C(1)	1.437(5)	C(1)-O(1)-Sb	127.1(2)
O(1)-K#1	2.778(2)	C(1)-O(1)-K#1	122.0(2)
O(2)-C(4)	1.375(6)	Sb-O(1)-K#1	96.13(9)
O(2)-K#1	2.592(3)	C(1)-O(1)-K	122.0(2)
O(3)-C(7)	1.448(6)	Sb-O(1)-K	96.13(9)
O(3)-K#1	2.777(3)	K#1-O(1)-K	82.38(9)
O(4)-C(10)	1.393(4)	C(4)-O(2)-K	126.9(2)
O(5)-C(15)	1.416(5)	C(4)-O(2)-K#1	126.9(2)
O(5)-C(14)	1.418(5)	K-O(2)-K#1	89.82(11)
		C(7)-O(3)-Sb	128.1(3)
O(3)-Sb-O(1)	84.35(12)	C(7)-O(3)-K	121.2(2)
O(3)-Sb-O(4)	83.34(7)	Sb-O(3)-K	96.31(9)
O(1)-Sb-O(4)	81.63(7)	C(7)-O(3)-K#1	121.2(2)
O(3)-Sb-O(4)#1	83.34(7)	Sb-O(3)-K#1	96.31(9)
O(1)-Sb-O(4)#1	81.63(7)	K-O(3)-K#1	82.43(10)
O(4)-Sb-O(4)#1	159.51(13)	C(10)-O(4)-Sb	131.8(2)
O(2)-K-O(4)	141.00(8)	C(10)-O(4)-K	134.0(2)
O(2)-K-O(5)	98.60(10)	Sb-O(4)-K	94.22(8)
O(4)-K-O(5)	112.09(9)	C(15)-O(5)-C(14)	108.9(3)
O(2)-K-O(1)	87.53(9)	C(15)-O(5)-K	142.7(2)
O(4)-K-O(1)	58.88(8)	C(14)-O(5)-K	107.4(2)
O(5)-K-O(1)	169.32(9)		

In Figure 5 the result of the X-ray structure determination of $K_4Sb_2O(OtBu)_8$ (**11**) is displayed (compounds $Na_4Sb_2O(OtBu)_8$ (**4**) and $Na_4Bi_2O(OtBu)_8$ (**5**) form isotypic lattices and structures). The molecules are randomly disordered in the crystal; as a result there is a superposition of different orientations. Another explanation for the findings could be twinning of three different crystalline species without a noticeable twinning obliquity. Mathematical approaches employed to solve this problem have not been successful so far.

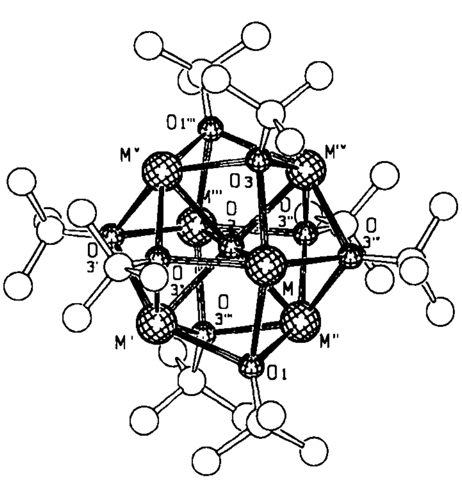

Fig. 5. Superposition of $K_4Sb_2O(OtBu)_8$ (**11**) molecules in the crystal structure ($Na_4Sb_2O(OtBu)_8$ (**4**) and $Na_4Bi_2O(OtBu)_8$ (**5**) form isotypic structures). Each M represents 2/3 of K and 1/3 of Sb [28].

An experimental alternative to the mathematical approach was then used: Four THF molecules were coordinated to the free coordination sites of the potassium atoms (see above). As a result new crystals could be isolated, which, despite of the fact that some of the THF molecules showed severe disorder in the orientation of the ring carbon atoms, were suitable for a more detailed structure analysis. Two graphical representations of the molecule $K_4Sb_2O(OtBu)_8 \cdot 4THF$ (**12**) are shown in Figures 6 and 7. The crystal point symmetry of the molecule is C_s (m) (the mirror plane runs through the central oxygen O(1), K(2) and K(3)), but the deviation from the higher C_{2v} ($mm2$) symmetry is only small (the second pseudo-symmetry plane runs through the Sb atoms). The structure of the molecule can be described as a distorted Sb_2K_4 octahedron centred by an oxygen atom. The faces of the metal cluster are trigonally capped by eight *tert*-butoxy groups. Each of the potassium atoms is coordinated by a THF donor through the oxygen atom. The two antimony atoms are in a *cis* arrangement in the octahedron around the central oxygen atom O(1). This observation is consistent with our interpretation of the NMR spectra of **11** and **12**. The shortest metal–oxygen bonds are found between Sb and the central O(1) atom, the longest between O(1) and K(1) (see also Table 3); this observation is consistent with the operation of a very remarkable *trans* effect. All oxygen atoms of the *tert*-butoxy ligands are tetracoordinated. The antimony atoms show ψ-octahedral coordination, whereas all potassium atoms are in distorted octahedral oxygen environments. Not many compounds are known with a structure comparable with that of **12**: $K_4Zr_2O(OiPr)_{10}$[23] and $Na_4Sn_2O(OtBu)_8Me_2$ also have a central quasi-octahedrally coordinated oxygen atom.[24] The latter compound is isostructural with **12**; the positions of the Sb atoms are replaced by Me–Sn.

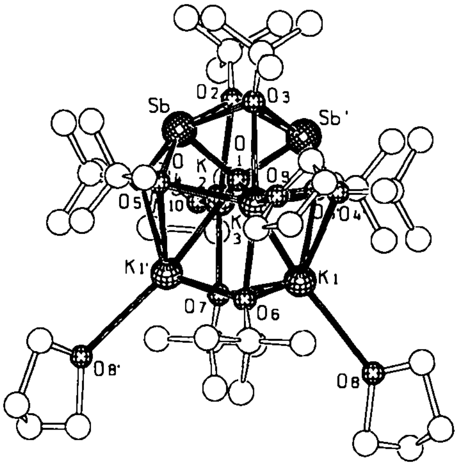

Fig. 6. Crystal structure of $K_4Sb_2O(OtBu)_8 \cdot 4THF$ (**12**) [28].

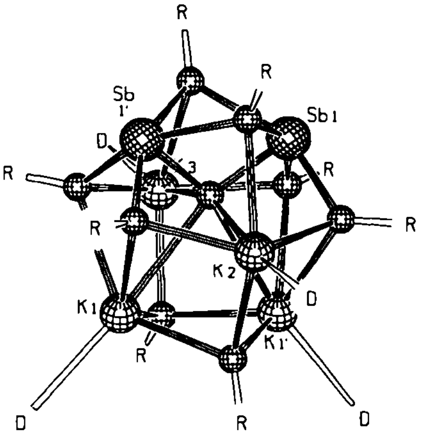

Fig. 7. The inner $K_4Sb_2O_9$ cluster of **12**; R = *tert*-butyl, D = THF.

Table 3. Selected distances [Å] and angles [°] in $K_4Sb_2O(OtBu)_8 \cdot 4THF$ (**12**). Symmetry operation: #1: $x, 0.5-y, z$.

Sb-O(1)	2.004(5)	O(7)-K(2)-O(1)	86.7(3)
Sb-O(4)	2.121(7)	O(5)#1-K(2)-O(1)	64.2(2)
Sb-O(5)	2.134(7)	O(5)-K(2)-O(1)	64.2(2)
Sb-O(2)	2.396(7)	O(7)-K(2)-O(2)	143.4(4)
Sb-O(3)	2.403(7)	O(5)#1-K(2)-O(2)	72.7(2)
K(1)-O(7)	2.647(9)	O(5)-K(2)-O(2)	72.7(2)
K(1)-O(6)	2.659(9)	O(1)-K(2)-O(2)	56.6(3)
K(1)-O(4)#1	2.800(7)	O(7)-K(2)-O(10)	103.5(7)
K(1)-O(5)#1	2.888(8)	O(5)#1-K(2)-O(10)	114.5(2)
K(1)-O(8)	3.05(2)	O(5)-K(2)-O(10)	114.5(2)
K(1)-O(1)	3.047(8)	O(1)-K(2)-O(10)	169.8(7)
K(2)-O(7)	2.526(12)	O(2)-K(2)-O(10)	113.1(7)
K(2)-O(5)#1	2.547(7)	O(6)-K(3)-O(4)#1	90.8(2)
K(2)-O(5)	2.547(7)	O(6)-K(3)-O(4)	90.8(2)
K(2)-O(1)	2.624(10)	O(4)#1-K(3)-O(4)	121.6(3)
K(2)-O(2)	2.743(10)	O(6)-K(3)-O(1)	85.7(3)
K(2)-O(10)	3.23(4)	O(4)#1-K(3)-O(1)	61.0(2)
K(3)-O(6)	2.591(12)	O(4)-K(3)-O(1)	61.0(2)
K(3)-O(4)#1	2.659(7)	O(6)-K(3)-O(3)	140.4(4)
K(3)-O(4)	2.659(7)	O(4)#1-K(3)-O(3)	71.3(2)
K(3)-O(1)	2.762(10)	O(4)-K(3)-O(3)	71.3(2)
K(3)-O(3)	2.805(10)	O(1)-K(3)-O(3)	54.7(3)
K(3)-O(9)	3.13(2)	O(6)-K(3)-O(9)	110.4(5)
O(1)-Sb#1	2.004(5)	O(4)#1-K(3)-O(9)	116.9(2)
O(1)-K(1)#1	3.047(8)	O(4)-K(3)-O(9)	116.9(2)
O(2)-Sb#1	2.397(7)	O(1)-K(3)-O(9)	163.9(5)
O(3)-Sb#1	2.403(7)	O(3)-K(3)-O(9)	109.2(5)
O(4)-K(1)#1	2.800(7)	Sb#1-O(1)-Sb	107.1(4)
O(5)-K(1)#1	2.888(8)	Sb#1-O(1)-K(2)	97.2(3)
O(6)-K(1)#1	2.659(9)	Sb-O(1)-K(2)	97.2(3)
O(7)-K(1)#1	2.647(9)	Sb#1-O(1)-K(3)	96.9(3)
		Sb-O(1)-K(3)	96.9(3)
O(1)-Sb-O(4)	83.7(3)	K(2)-O(1)-K(3)	156.1(4)
O(1)-Sb-O(5)	83.2(3)	Sb#1-O(1)-K(1)	91.76(12)
O(4)-Sb-O(5)	89.3(3)	Sb-O(1)-K(1)	161.1(3)
O(1)-Sb-O(2)	70.1(3)	K(2)-O(1)-K(1)	80.9(2)
O(4)-Sb-O(2)	153.8(2)	K(3)-O(1)-K(1)	79.5(2)
O(5)-Sb-O(2)	87.5(3)	Sb#1-O(1)-K(1)#1	161.1(3)
O(1)-Sb-O(3)	70.3(3)	Sb-O(1)-K(1)#1	91.77(12)
O(4)-Sb-O(3)	89.3(3)	K(2)-O(1)-K(1)#1	80.9(2)
O(5)-Sb-O(3)	153.5(2)	K(3)-O(1)-K(1)#1	79.5(2)
O(2)-Sb-O(3)	82.2(3)	K(1)-O(1)-K(1)#1	69.3(2)
O(7)-K(1)-O(6)	94.1(3)	Sb-O(2)-Sb#1	84.6(3)
O(7)-K(1)-O(4)#1	131.5(3)	Sb-O(2)-K(2)	85.4(3)
O(6)-K(1)-O(4)#1	86.4(3)	Sb#1-O(2)-K(2)	85.4(3)
O(7)-K(1)-O(5)#1	82.9(3)	Sb-O(3)-Sb#1	84.3(3)
O(6)-K(1)-O(5)#1	133.6(3)	Sb-O(3)-K(3)	87.1(3)
O(4)#1-K(1)-O(5)#1	63.4(2)	Sb#1-O(3)-K(3)	87.1(3)
O(7)-K(1)-O(8)	104.9(5)	Sb-O(4)-K(3)	97.1(2)
O(6)-K(1)-O(8)	109.7(4)	Sb-O(4)-K(1)#1	96.5(2)
O(4)#1-K(1)-O(8)	120.6(4)	K(3)-O(4)-K(1)#1	85.9(2)
O(5)#1-K(1)-O(8)	115.9(4)	Sb-O(5)-K(2)	96.2(2)
O(7)-K(1)-O(1)	76.4(3)	Sb-O(5)-K(1)#1	93.6(2)
O(6)-K(1)-O(1)	79.0(3)	K(2)-O(5)-K(1)#1	85.4(2)
O(4)#1-K(1)-O(1)	56.0(2)	K(3)-O(6)-K(1)#1	90.3(3)
O(5)#1-K(1)-O(1)	55.1(2)	K(3)-O(6)-K(1)	90.3(3)
O(8)-K(1)-O(1)	170.9(4)	K(1)#1-O(6)-K(1)	81.4(4)
O(7)-K(2)-O(5)#1	92.6(2)	K(2)-O(7)-K(1)#1	91.1(3)
O(7)-K(2)-O(5)	92.6(2)	K(2)-O(7)-K(1)	91.1(3)
O(5)#1-K(2)-O(5)	127.8(3)	K(1)#1-O(7)-K(1)	81.8(3)

The structure of $K_4Sb_4O_2(OiPr)_{12}$ (**13**), the biggest assembly of metal and oxygen atoms in the series of antimony alkali alkoxides, is shown in Figure 8. The crystal point symmetry of the molecule is S_4 (-4), but the distortion from D_{2d} is minimal.

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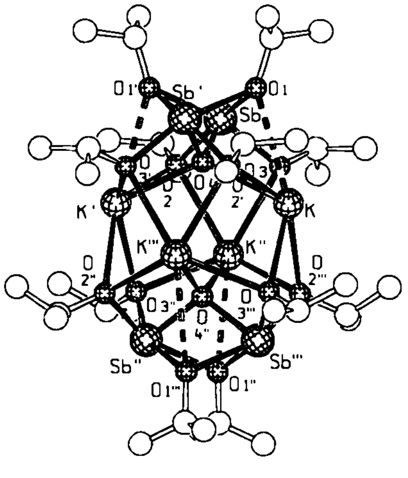

Fig. 8. Crystal structure of $K_4Sb_4O_2(OiPr)_{12}$ (**13**) [28].

The polycycle comprises two distorted Sb_2K_2 oxygen-centred tetrahedra with six face-capping isopropoxy groups interpenetrating in such a way that the potassium edges of the tetrahedra come close together and form a K_4 bisphenoid, which is stabilised by oxygen-potassium interactions. As in **12** the Sb atoms in **13** are ψ-octahedrally coordinated by oxygen atoms. The potassium atoms in **13** are in an unusual environment: they form five similar bonds to neighbouring oxygen atoms and one longer interaction to O(1) (see also Table 4). They clearly have an open coordination site, which might be accessed by nucleophiles. All oxygen atoms within the polycycle are in distorted tetrahedral environments; three of the corners are occupied by metal atoms and one by carbon. Only the central O(4) atoms are exclusively bound to metal atoms; these bonds are remarkably short (Table 4). To the best of our knowledge, no reports are available on compounds having a symmetry comparable to that of **13**. However, other oxoalkoxo metal clusters such as $Ni_5Sb_3O_2(OEt)_{15}(HOEt)_4$[25] and $Gd_2Zr_6O_2(OAc)_6(OiPr)_{20}$[26] with two oxygen atoms in a distorted tetrahedral environment of metals have been described.

Table 4. Selected distances [Å] and angles [°] of $K_4Sb_4O_2(OiPr)_{12}$ (**13**). Symmetry operations: #1: 1.5−*x*, 1.5−*y*, *z*; #2: *y*, 1.5−*x*, 0.5−*z*; #3: 1.5−*y*, *x*, 0.5−*z*.

Sb-O(4)	1.982(5)	C(1)-O(1)-Sb	119.2(8)
Sb-O(3)	2.089(6)	C(1)-O(1)-Sb#1	124.8(8)
Sb-O(2)	2.089(6)	Sb-O(1)-Sb#1	84.9(2)
Sb-O(1)	2.324(7)	C(4)-O(2)-Sb	113.8(7)
Sb-O(1)#1	2.362(7)	C(4)-O(2)-K#1	126.9(7)
K-O(4)	2.693(4)	Sb-O(2)-K#1	100.6(2)
K-O(3)	2.726(7)	C(4)-O(2)-K#2	124.7(6)
K-O(2)#1	2.738(7)	Sb-O(2)-K#2	100.8(2)
K-O(3)#3	2.827(7)	K#1-O(2)-K#2	83.7(2)
K-O(2)#3	2.845(7)	C(7)-O(3)-Sb	115.2(7)
O(1)-C(1)	1.410(12)	C(7)-O(3)-K	125.8(8)
O(1)-Sb#1	2.362(7)	Sb-O(3)-K	100.2(2)
O(2)-C(4)	1.433(12)	C(7)-O(3)-K#2	123.7(7)
O(2)-K#1	2.738(7)	Sb-O(3)-K#2	101.3(2)
O(2)-K#2	2.845(7)	K-O(3)-K#2	84.3(2)
O(3)-C(7)	1.399(12)	Sb-O(4)-Sb#1	105.8(4)
O(3)-K#2	2.827(7)	Sb-O(4)-K	104.31(6)
O(4)-Sb#1	1.982(5)	Sb#1-O(4)-K	105.18(6)
O(4)-K#1	2.693(4)	Sb-O(4)-K#1	105.18(6)
		Sb#1-O(4)-K#1	104.31(6)
O(4)-Sb-O(3)	85.0(2)	K-O(4)-K#1	130.1(3)
O(4)-Sb-O(2)	84.7(2)	O(3)-K-O(2)#1	117.0(2)
O(3)-Sb-O(2)	88.2(3)	O(4)-K-O(3)#3	109.0(2)
O(4)-Sb-O(1)	71.9(2)	O(3)-K-O(3)#3	138.2(2)
O(3)-Sb-O(1)	91.8(3)	O(2)#1-K-O(3)#3	82.7(2)
O(2)-Sb-O(1)	156.5(2)	O(4)-K-O(2)#3	109.1(2)
O(4)-Sb-O(1)#1	71.0(2)	O(3)-K-O(2)#3	82.6(2)
O(3)-Sb-O(1)#1	156.0(2)	O(2)#1-K-O(2)#3	138.3(2)
O(2)-Sb-O(1)#1	90.8(2)	O(3)#3-K-O(2)#3	61.7(2)
O(1)-Sb-O(1)#1	79.8(3)	O(4)-K-Sb	31.10(9)
O(4)-K-O(3)	61.00(14)	O(3)-K-Sb	33.57(13)
O(4)-K-O(2)#1	60.70(14)	O(2)#1-K-Sb	83.46(14)
O(2)#3-K-Sb	107.3(2)	O(3)#3-K-Sb	136.9(2)

Conclusion

The tendency of the alkali metal *tert*-butoxides to form stable adducts with $Sb(OtBu)_3$ and $Bi(OtBu)_3$ is enhanced with increasing size of alkali metal atom. The arsenic compound $As(OtBu)_3$ does not form adducts. This may be due to the bulky organic ligands, which have a greater influence with smaller central atoms like arsenic. The sequence of reactivity in the alkali metal *tert*-butoxide series is paralleled by an increase in the basicity of the oxygen atom of the *tert*-butoxy group. The formation of oxo compounds in the reaction of the alkali metal alkoxides with $E(OtBu)_3$ is very prominent with the sodium alkoxide and can also be achieved with potassium alkoxide by increasing reaction times.

Experimental Procedure

All experiments were performed under dry nitrogen in vessels connected to a vacuum line. NMR spectra were obtained on a Bruker AC 200: ^1H NMR: 200.13 MHz, δ relative to TMS; ^{13}C NMR: 50.3 MHz, δ relative to TMS. Single crystals for X-ray structure determination were checked by film methods (Weissenberg-Buerger techniques) prior to mounting on a 4-circle diffractometer (Siemens AED 2). The lattice constants were refined using 20 reflections with 2θ between 20 and 25°. In all structure determinations, $Mo_{K\alpha}$ radiation (λ = 0.7107 Å) and a graphite monochromator, together with an ω-θ scan, was used; empirical absorption corrections as well as Lorentian polarisation corrections were performed on the data. All structures were solved by direct methods [27]; all hydrogen atoms were geometrically fixed to the carbon atoms, and the overall refinement method used was full-matrix least-squares on F^2. The elemental analyses were performed by Beller, Göttingen (FRG).

$As(OtBu)_3$ (**1**), $Sb(OtBu)_3$ (**2**): Compounds **1** and **2** were obtained by a published route [15]. The procedure was modified by stirring the reaction mixture for 3 h with a considerable gain in yield. Compounds **1** and **2** were isolated by distillation at 92 °C/10 Torr and 94 °C/9 Torr, respectively (85 and 90% yield, respectively).
1: Colourless liquid; m.p. −20 °C; ^1H NMR ([D$_6$]benzene): δ = 1.38; $^{13}C\{^1H\}$ NMR: δ = 32.47 (s, C−CH_3), 75.26 (s, *C*−CH_3); $C_{12}H_{27}AsO_3$ (294.3): calcd C 48.98, H 9.25; found: C 48.47, H 8.95.
2: Colourless liquid; ^1H NMR ([D$_6$]benzene): δ = 1.39; $^{13}C\{^1H\}$ NMR: δ = 33.99 (s, C−CH_3), 74.74 (s, *C*−CH_3); $C_{12}H_{27}O_3Sb$ (341.1): calcd C 42.26, H 7.98; found: C 41.89, H 7.74.

$Bi(OtBu)_3$ (**3**): $BiCl_3$ (2.697 g, 8.6 mmol) was dissolved in THF (25 mL), and KO*t*Bu (2.878 g, 25.4 mmol) was added. After the suspension had been stirred for 24 h, the solvent was removed under reduced pressure and replaced by a mixture of hexane (20 mL) and benzene (5 mL). Undissolved particles were separated by filtration, the solvent was evaporated under reduced pressure, and the colourless residue was crystallised from a hexane/benzene mixture (5/1). No chloride was found at this stage in the product (1.51 g, 41%). Colourless solid; m.p. 168 °C; ^1H NMR ([D$_6$]benzene): δ = 1.41; $^{13}C\{^1H\}$ NMR: δ = 35.47 (s, C−CH_3), 74.26 (s, *C*−CH_3); $C_{12}H_{27}BiO_3$ (428.3): calcd C 33.65, H 6.35, Bi 48.79; found: C 33.74, H 6.37, Bi 47.84.

Reaction of $As(OtBu)_3$ (**1**) with M(O*t*Bu) (M = Li, Na, K, Rb, Cs): Arsenic compound **1** (5 mmol) was dissolved in toluene (25 mL), and equimolar amounts of the alkali metal *tert*-butoxide were added. The mixture was heated under reflux for 24 h. The ^1H NMR spectra showed no change. After evaporation of the solvent, **1** was recovered in nearly quantitative yield by distillation (95-98%). Also no reaction was observed on treating $Sb(OtBu)_3$ (**2**) with LiO*t*Bu under the same conditions.

$Na_4Sb_2O(OtBu)_8$ (**4**) and $Na_4Sb_2O(OtBu)_8$(**5**): Freshly sublimed NaO*t*Bu (0.57 g, 5.93 mmol) and **2** (1.92 g, 5.6 mmol) or **3** (2.40 g, 5.6 mmol) were stirred in benzene (25 mL) for 1 h. The solution cleared (no further **2** or **3** could be detected by ^1H NMR). After evaporation of the solvent under reduced pressure, the residue was sublimed at 120 °C/10^{-3} Torr (**4**) or 180 °C/10^{-2} Torr (**5**). The sublimed solid can be recrystallised from benzene, and 0.97 g of **4** (70 %) or 0.25 g of **5** (15 %) were obtained.

4: Colourless crystals; m.p. 255 °C (decomp.); ^{1}H NMR (of the reaction mixture): $\delta = 1.42$; $C_{32}H_{72}Na_4O_9Sb_2$ (936.4): calcd C 41.05, H 7.75; found C 41.89, H 8.09; crystal structure analysis: 0.41 × 0.31 × 0.25 mm^3, trigonal, $R\bar{3}c$, $a = b = 12.404(6)$, $c = 50.81(3)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 6771(6)$ Å^3, $Z = 6$, $D_x = 1.378$ Mg m^{-3}, $2\theta_{max} = 46.9°$, $T = 293$ K, 1087 independent reflections out of 1990, 687 $[I > 2\sigma(I)]$ reflections observed, 83 parameters, $R[I > 2\sigma(I)] = 0.038$, $wR = 0.072$, largest diff. peak and hole: 0.253 and −0.258 e Å^{-3} [19].

5: Colourless crystals; m.p. 250 °C (decomp.); ^{1}H NMR (of the reaction mixture): $\delta = 1.37$; $C_{32}H_{72}Bi_2Na_4O_9$ (1110.8): the crystals decompose on slight contact with air, so no correct analytical data could be obtained; crystal structure analysis: 0.65 × 0.40 × 0.20 mm^3, trigonal, $R\bar{3}c$, $a = b = 12.449(6)$, $c = 51.08(3)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 6856(6)$ Å^3, $Z = 6$, $D_x = 1.614$ Mg m^{-3}, $2\theta_{max} = 50.0°$, $T = 293$ K, 1351 independent reflections out of 2494, 821 $[I > 2\sigma(I)]$ reflections observed, 83 parameters, $R[I > 2\sigma(I)] = 0.037$, $wR = 0.056$, largest diff. peak and hole: 0.482 and −0.385 e Å^{-3} [19].

MSb(O*t*Bu)$_4$ [M = K (**6**), Rb (**7**), Cs (**8**)] and KBi(O*t*Bu)$_4$ (**9**): Sb(O*t*Bu)$_3$ (1.282 g, 3.83 mmol) or Bi(O*t*Bu)$_3$ (1.64 g, 3.83 mmol) were dissolved in benzene (25 mL), and equimolar amounts of KO*t*Bu, RbO*t*Bu or CsO*t*Bu were added. After 30 min of stirring, the suspension cleared. After another 2.5 h, a precipitate formed. The solvent was removed completely, and the residue was dissolved in dioxane (20 mL). From this solution 0.91 g of **6** (53 %), 0.88 g of **7** (46 %), 1.19 g of **8** (57 %) or 0.77 g of **9** (37 %) were obtained by crystallisation.

6 (see also ref. [11]): Colourless crystals; m.p. 259 °C (decomp.); ^{1}H NMR (of the reaction mixture): $\delta = 1.44$; ^{13}C NMR: $\delta = 34.7$ (s, CCH_3), 71.5 (s, CCH_3); $C_{16}H_{36}KO_4Sb$ (453.3): calcd C 42.37, H 7.94; found C 41.76, H 7.86; crystal structure analysis: 1.44 × 0.25 × 0.25 mm^3, monoclinic, $C2/c$, $a = 15.529(8)$, $b = 12.577(6)$, $c = 11.510(6)$ Å, $\alpha = \gamma = 90°$, $\beta = 95.09(4)°$, $V = 2239(2)$ Å^3, $Z = 4$, $D_x = 1.345$ Mg m^{-3}, $2\theta_{max} = 48.0°$, $T = 293$ K, 1758 independent reflections, 1627 $[I > 2\sigma(I)]$ reflections observed, 120 parameters, $R[I > 2\sigma(I)] = 0.024$, $wR = 0.061$, largest diff. peak and hole: 0.468 and −0.542 e Å^{-3} [19].

7: Colourless crystals; m.p. 250 °C (decomp.); ^{1}H NMR (of the reaction mixture): $\delta = 1.39$; $C_{16}H_{36}O_4Sb$ (499.7): calcd C 38.46, H 7.26; found C 38.21, H 7.22.

8: Colourless crystals; m.p. > 270 °C (decomp.); ^{1}H NMR (of the reaction mixture): $\delta = 1.41$; $C_{16}H_{36}CsO_4Sb$ (547.1): calcd C 35.13, H 6.63; found C 34.22, H 6.63.

9: Colourless crystals; m.p. 220 °C (decomp.); ^{1}H NMR (of the reaction mixture): $\delta = 1.36$; $C_{16}H_{36}BiKO_4$ (540.5): calcd C 35.56, H 6.71; found C 34.61, H 6.64; crystal structure analysis: 0.88 × 0.56 × 0.20 mm^3, triclinic, $P\bar{1}$, $a = 9.942(7)$, $b = 10.357(7)$, $c = 12.097(9)$ Å, $\alpha = 102.89(5)°$, $\beta = 91.75(6)°$, $\gamma = 104.73(5)°$, $V = 1169(1)$ Å^3, $Z = 2$, $D_x = 1.535$ Mg m^{-3}, $2\theta_{max} = 49.96°$, $T = 293$ K, 3389 independent reflections, 2816 $[I > 2\sigma(I)]$ reflections observed, 203 parameters, $R[I > 2\sigma(I)] = 0.057$, $wR = 0.149$, largest diff. peak and hole: 2.225 and −2.275 e Å^{-3} (absorption effect).

$K_2Sb(OtBu)_5 \cdot O(CH_2CH_2)_2O$ (**10**): KO*t*Bu (1.203 g, 10.72 mmol) and Sb(O*t*Bu)$_3$ (1.62 mL, 5.36 mmol) were added to benzene (25 mL). The suspension was stirred for 5 h, and the solution cleared. After removal of the solvent by condensation in vacuum, the solid residue was dissolved in dioxane (20 mL),and 1.9 g of **10** (54.3 %) was obtained by crystallisation. Colourless crystals; m.p. 239 °C; ^{1}H NMR: $\delta = 1.40$ (*t*Bu), 3.36 (dioxane); dioxane was removed from the crystals on a vacuum line prior to the analysis: $C_{20}H_{45}K_2O_5Sb$ (565.3): calcd C 42.46, H 8.02; found C 41.45, H 8.05; crystal structure analysis: 1.20 × 0.38 × 0.25 mm^3, monclinic, $P2_1/m$, $a = 9.962(5)$, $b = 17.620(9)$, $c = 10.316(5)$ Å, $\alpha = \gamma = 90°$, $\beta = 111.34(3)°$, $V = 1687(2)$ Å^3, $Z = 2$, $D_x = 1.287$ Mg m^{-3}, $2\theta_{max} = 45°$, $T = 293$ K, 2286 independent reflections, 2116 $[I > 2\sigma(I)]$ reflections observed, 212 parameters, $R[I > 2\sigma(I)] = 0.026$, $wR = 0.071$, largest diff. peak and hole: 0.582 and −0.460 e Å^{-3} [19].

$K_4Sb_2O(OtBu)_8$ (**11**) and $K_4Sb_2O(OtBu)_8 \cdot 4THF$ (**12**): KO*t*Bu (3.104 g, 27.7 mmol) and Sb(O*t*Bu)$_3$ (4.17 mL, 13.83 mmol) in toluene (25 mL) were stirred for 24 h under reflux. Every hour the evolution of isobutene [$\delta = 1.59$ (t, $^4J \approx 1.2$, 6H, C=C−CH$_3$), 5.04 (m, $^4J \approx 1.2$, 2H, C=CH$_2$)], **2** and *tert*-butyl alcohol were recorded by ^{1}H NMR spectroscopy. After approximately 14 h the amount of isobutene no longer increased (in an alternative experiment **2** and KO*t*Bu were heated for 20 h, and the volatile components were condensed in the cooled trap of the vacuum line; again isobutene, **2** and *tert*-butyl alcohol were detected by NMR spectroscopy). The solvent was seperated by condensation, and the residue was crystallised from THF (20 mL). At this stage 6.24 g of the THF adduct **12** (70 %) was obtained (crystal structure determination). The crystals can be liberated from the coordinated THF at 60 °C/10^{-3} Torr to yield 4.56 g of a colourless solid **11** (66 %).

11: Colourless solid; m.p. 306 °C (decomp.); ^{1}H NMR: $\delta = 1.30$, (s, 12H, CH$_3$), 1.35 (s, 6H, CCH$_3$), 1.49 (s, 6H, CCH$_3$); ^{13}C{^{1}H} NMR: $\delta = 34.08$ (s, CCH_3), 34.36 (s, CCH_3), 70.58 (broad s, CCH_3); $C_{32}H_{72}O_9K_4Sb_2$ (1000.8): calcd C 38.40, H 7.25; found C 37.22, H 6.93; crystal structure analysis: 0.56 × 0.56 × 0.38 mm^3, trigonal, $R\bar{3}c$, $a = b = 12.560(6)$, $c = 51.89(3)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 7089(6)$ Å^3, $Z = 6$, $D_x = 1.407$ Mg m^{-3}, $2\theta_{max} = 45.04°$, $T = 293$ K, 1041 independent reflections out of 1872, 748 $[I > 2\sigma(I)]$ reflections observed, 83 parameters, $R[I > 2\sigma(1)] = 0.035$, $wR = 0.082$, largest diff. peak and hole: 0.242 and −0.262 e Å^{-3}.

Crystal structure analysis of **12**: 1.56 × 0.81 × 0.44 mm^3, orthorhombic, $Pnma$, $a = 21.037(11)$, $b = 17.412(9)$, $c = 18.452(9)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 6759(6)$ Å^3, $Z = 4$, $D_x = 1.267$ Mg m^{-3}, $2\theta_{max} = 45.0°$, $T = 293$ K, 4367 independent reflections out of 4871, 3143 $[I > 2\sigma(I)]$ reflections observed, 284 parameters, $R[I > 2\sigma(I)] = 0.072$, $wR = 0.23$, largest diff. peak and hole: 1.648 and −0.634 e Å^{-3}.

Reactions of KSb(O*t*Bu)$_4$ (**6**) with CaCl$_2$, TlCl and CuI: Sb(O*t*Bu)$_3$ (1.85 g, 5.43 mmol) and KO*t*Bu (0.61 g, 5.43 mmol) were dissolved in toluene (25 mL). After the mixture had been stirred for 4 h, equimolar amounts of TlCl or CuI or half molar amounts of CaCl$_2$ were added. The suspension was heated at reflux for 24 h. The residue was seperated by filtration and characterised in all cases as KCl or KI by powder X-ray diffraction. The solution was concentrated by evaporation. The colourless crystalline products were characterised by X-ray powder diffraction (Ca(O*t*Bu)$_2$ and (CuO*t*Bu)$_4$) and by comparison with diffraction patterns of authentic compounds. In the case of (TlO*t*Bu)$_4$, a singlet was recorded in the ^{1}H NMR spectrum ($\delta = 1.42$), and correct analytical data were obtained (C_4H_9OTl (277.5): calcd C 17.31, H 3.14, found C 17.29, H 3.27). Finally, Sb(O*t*Bu)$_3$ could be isolated in all cases by distillation in almost quantitative yield (1.76–1.84 g, 95–99 %).

Thermolysis of KSb(O*t*Bu)$_4$ (**6**) and reaction with isopropyl alcohol: KO*t*Bu (1.21 g, 10.8 mmol) and Sb(O*t*Bu)$_3$ (3.26 mL, 10.8 mmol) in benzene (25 mL) were heated for 48 h under reflux. The solvent was removed in vacuo, and isopropyl alcohol (25 mL) was added to the residue. The mixture was heated to 70 °C for 1 h. After removal of the isopropyl alcohol in vacuo, the residue was recrystallised from benzene to give 1.35 g of $K_4Sb_4O_2(OiPr)_{12}$ (**13**) as colourless platelets (36 %). Colourless crystals (decomp. 230 °C); ^{1}H NMR: $\delta = 1.29$ (d, ^3J(H,H) = 6.1 Hz, 6H, CH−CH_3), 4.24 (m, ^3J(H,H) = 6.1 Hz, 1H, CH−CH$_3$); $C_{36}H_{84}K_4O_{14}Sb_4$ (1384.4): calcd C 31.23, H 6.11; found C 31.58, H 6.20; crystal structure analysis: 0.56 × 0.25 × 0.20 mm^3, tetragonal, $P4_2/n$, $a = b = 13.775(11)$, $c = 15.208(13)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2886(4)$ Å^3, $Z = 2$, $D_x = 1.593$ Mg m^{-3}, $2\theta_{max} = 45.0°$, $T = 293$ K, 1886 independent reflections, 1473 $[I > 2\sigma(I)]$ reflections observed, 153 parameters, $R[I > 2\sigma(I)] = 0.045$, $wR = 0.097$, largest diff. peak and hole: 0.646 and −0.784 e Å^{-3}.

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