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## The Hetero-Cubane Structures of the Heavy Alkali Metal *tert*-Amyloxides [MOCMe<sub>2</sub>Et]<sub>4</sub> (M = K, Rb, Cs)

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The series of alkali metal (Li – Cs) alkoxides of *tert*-pentanol (1,1-dimethylpropan-1-ol) has been prepared by reaction of the corresponding metal with the alcohol in *n*-hexane or *n*-heptane. The compounds were purified by vacuum sublimation and crystallised in *n*-hexane to produce crystals suitable for single-crystal X-ray diffraction studies. The structures of the potassium, rubidium, and cesium compounds revealed tetrameric units with additional intra- and intermolecular interactions between the metal atom and alkoxide methyl groups increasing with the size of the involved metal.

### Introduction

The ambiguous character of alkali metal alkoxides, the salt-like metal-oxygen interactions in combination with an organic lipophilic alkyl/alcohol group, makes them an important component in many chemical reactions. These compounds are easily accessible and in the case of the lighter alkali metals or simple alcohols often commercially available. The comparable low sensitivity towards air and inertness towards most organic solvents makes them easy to handle under inert-gas conditions. Alkali metal alkoxides have been used in a large variety of reactions: As precursor for metal oxides,<sup>1</sup> in the Williamson ether synthesis,<sup>2</sup> as moderate base<sup>3</sup> in organic reactions, and as additive in polymerisation reactions.<sup>4</sup> In 1950, Morton discovered the activating role of sodium *iso*-propoxide in deprotonations of ethene with pentylsodium.<sup>5</sup> Potassium *tert*-butoxide in connection with *n*-butyllithium was used efficiently in superbasic<sup>6</sup> mixtures of the Lochmann-Schlosser bases.<sup>7</sup> In a similar reaction, alkyllithium and a heavier alkali metal alkoxide react in a metal exchange reaction to produce the (often insoluble) alkali metal alkyl compound. By this method it was possible to isolate the sodium, potassium, rubidium, and caesium compounds of bis(trimethylsilyl)methane<sup>8</sup> and trimethylsilylmethane.<sup>9</sup> When used in Lochmann-Schlosser superbasic mixtures, the alkali metal alkyl compound is not isolated and separated from the corresponding soluble lithium alkoxide. The formed suspension is directly used to metalate/deprotonate organic substrates such as benzene.<sup>10</sup> The chemical nature of these freshly prepared reagents could not be identified for decades.

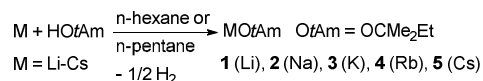
This may be attributed to the poor solubilities and fierce reactivity of such systems. Both the activation of alkyllithium by lithium alkoxide or the existence of mixed aggregates such as [LiOtBu-KnBu] were discussed.<sup>11</sup> The use of the neopentyl group as alkyl component with increased alkane-solubility allowed the isolation and characterisation of mixed aggregates including lithium and potassium atoms, in connection with neopentyl and *tert*-butoxy groups side by side.<sup>12</sup> Another soluble systems using 2-ethylhexyllithium and potassium *tert*-amyloxide<sup>13</sup> was used in metalation reactions, but no characterisation was reported. The use of branched and better soluble alkali metal alkoxides such as *tert*-amyloxides<sup>14</sup> [MOtAm] in superbases leads to increased alkoxy concentrations and often better results compared to corresponding *tert*-butoxides. This is why Lochmann described such mixtures as superbases of the second generation.<sup>15</sup> The combination of neopentyllithium and excess potassium *tert*-amyloxide,<sup>4</sup> organic groups with increased alkane-solubility, leads to the formation of a soluble potassium mixed aggregate consisting of three potassium *tert*-amyloxide units and one neopentylpotassium unit.<sup>16</sup> In contrast to more bulky alkoxides such as 3-methyl-3-pentoxide or 3-ethyl-3-pentoxide,<sup>14d,14e</sup> *tert*-amyloxide offered a good balance of increased solubility (compared to *tert*-butoxide) with an acceptable minimum of structural disorder enabling detailed structural studies. For a better understanding of the interaction of *tert*-amyloxides with alkali metal alkyl compounds, the knowledge about the structures is of importance. To the best of our knowledge, only three metal *tert*-amyloxides are reported, including neodymium,<sup>17</sup> iron,<sup>18</sup> and gallium.<sup>19</sup> Despite their numerous uses in chemistry and to some extent commercial availability no structures of alkali metal *tert*-amyloxides were found. This is in contrast to the corresponding *tert*-butoxides with numerous reported structures. LiOtBu is found in disordered hexamers,<sup>20</sup> but also an octameric form is reported.<sup>21</sup>

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† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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**Scheme 1.** Formation of alkali metal *tert*-amyloxides using alkali metal and *tert*-pentanol.

NaOtBu forms mixtures of hexamers and nonamers,<sup>20</sup> but recently a purely hexameric form was reported.<sup>22</sup> KOtBu,<sup>1</sup> RbOtBu,<sup>1</sup> and CsOtBu<sup>23</sup> are found as regular heterocubanes.<sup>24</sup> Some mixed bimetallic alkali metal alkoxides were also characterised.<sup>16,25</sup> *tert*-Amyloxides are also called *tert*-pentoxides, *tert*-amylates, 2-methyl-2-butoxides, *tert*-pentylates, 1,1-dimethylpropoxides, or *tert*-amoxide. The increasing use of their alkali metal compounds, even on industrial scale, and their advantageous properties makes it desirable to gain additional structural information.

## Results and discussion

### Preparation of alkali metal *tert*-amyloxides

The alkali metal *tert*-amyloxides [MOtAm] were prepared following a procedure for the preparation of KOtAm (Scheme 1).<sup>3</sup> Pieces of excess alkali metal were stirred in *n*-hexane (*n*-heptane in the case of sodium), and *tert*-pentanol (*tert*-amylalcohol) was quickly added. The mixture was heated for several days, in the meantime the metal dissolved partially accompanied by the formation of molecular hydrogen. In the case of potassium, rubidium, and caesium the formation of a colourless, crystalline solid was observed which in some cases resulted in the partial solidification of the mixture. This precipitation is presumed to be a complex of alkali metal alkoxide and *tert*-pentanol.<sup>4</sup> In similar reactions of *tert*-butanol with potassium or rubidium the solid was isolated and characterised as polymeric chains of [KOtBu-HOtBu]<sub>∞</sub> and [RbOtBu-HOtBu]<sub>∞</sub>.<sup>1</sup> As the reaction proceeded the precipitated intermediate redissolved. After cooling the excess metal was removed and all solvent was distilled off. The obtained crystalline solids (LiOtAm, **1**; NaOtAm, **2**; KOtAm, **3**; RbOtAm, **4**; CsOtAm, **5**) were purified in a vacuum sublimation with pressures of about 5·10<sup>-2</sup> mbar using temperatures between 160–180°C (except **3**: 120°C) with good to excellent yields.<sup>5</sup>

### NMR spectroscopy

The good solubility of the alkali metal *tert*-amyloxides enables their characterisation by NMR spectroscopy even in weakly coordinating solvents such as [D<sub>6</sub>]benzene or [D<sub>12</sub>]cyclohexane (Table 1 and 2). The NMR spectra of compounds **4** and **5** in deuterated benzene are in good agreement with spectra found in literature.<sup>26</sup> To obtain reference data of these compounds in a solvent which is inert towards deprotonation by highly basic systems such as Lochmann-Schlosser superbases we also carried out NMR spectroscopy in deuterated cyclohexane.

**Table 1:** <sup>1</sup>H, <sup>13</sup>C, <sup>7</sup>Li, and <sup>133</sup>Cs NMR spectroscopic data [ppm] of compounds **1**, **2**, **3**, **4**, and **5** in deuterated [D<sub>6</sub>]benzene at 21°C.

	<sup>1</sup> H			<sup>13</sup> C			<sup>7</sup> Li/ <sup>133</sup> Cs	
	Me	Et	tert-C	Me	Et	tert-C		
<b>1</b>	1.24	0.99	1.51	32.5	10.9	41.5	69.3	0.94
<b>2</b>	1.10	0.99	1.34	34.2	10.4	42.2	67.8	—
<b>3</b>	1.01	0.98	1.29	34.9	10.4	41.9	68.4	—
<b>4</b>	1.05	0.99	1.34	34.9	10.4	41.8	68.9	—
<b>5</b>	1.15	1.04	1.41	34.7	10.5	41.6	70.1	202.1

**Table 2:** <sup>1</sup>H, <sup>13</sup>C, <sup>7</sup>Li, and <sup>133</sup>Cs NMR spectroscopic data [ppm] of compounds **1**, **2**, **3**, **4**, and **5** in deuterated [D<sub>12</sub>]cyclohexane at 21°C.

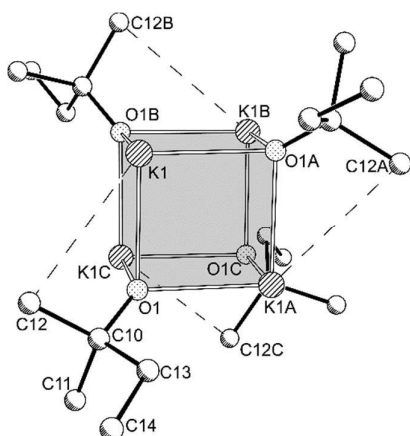
	<sup>1</sup> H			<sup>13</sup> C			<sup>7</sup> Li/ <sup>133</sup> Cs	
	Me	Et	tert-C	Me	Et	tert-C		
<b>1</b>	1.12	0.90	1.39	32.6	11.1	41.9	69.7	1.31
<b>2</b>	1.00	0.89	1.25	34.3	10.5	42.6	68.2	—
<b>3</b>	0.91	0.83	1.20	34.7	10.3	42.3	68.9	—
<b>4</b>	0.93	0.83	1.20	34.6	10.3	42.2	69.4	—
<b>5</b>	0.98	0.84	1.24	33.8	10.2	41.5	70.1	211.2

The data obtained from both series of measurements is very similar for the corresponding *tert*-amyloxide compounds. Therefore no conclusions can be made about changes of oligomerisation depending on the different Lewis donor properties of benzene and cyclohexane. The strongest effect in this regard would be expected for caesium compounds, due to its comparable strong arene-metal interactions.<sup>27</sup> A corresponding result is found for <sup>133</sup>Cs NMR spectra<sup>28</sup> of compound **5**: 202.1 ppm in [D<sub>6</sub>]benzene, and 211.2 ppm in [D<sub>12</sub>]cyclohexane. Compared to <sup>133</sup>Cs chemical shifts of similar caesium compounds measured in [D<sub>8</sub>]THF in literature (3-methylpentoxide:<sup>29</sup> 196.9 ppm, and 3-ethyl-3-heptoxide:<sup>30</sup> 191.7 ppm), a trend involving O-donor (THF), π-donor (benzene), and non-donor (cyclohexane) can be observed.

### X-ray crystallography

All five compounds<sup>31</sup> **1**, **2**, **3**, **4**, and **5** show very good to moderate solubility in *n*-hexane. Additionally, because of their high thermal stability in this solvent these compounds could be easily crystallised from hot *n*-hexane. X-ray crystallography of lithium compound **1**, which crystallises in the trigonal space group *P* $\bar{3}$  was not successful, due to problems concerning crystallographic disorder. In hexameric lithium compounds such as (LiOtBu)<sub>6</sub><sup>20</sup> and (LinBu)<sub>6</sub><sup>32</sup> the six lithium atoms are disordered over eight positions. In compound **1** this obstacle is joined by additional rotational disorder of the OtAm group, resulting in a disorder between the involved methyl and ethyl groups. Exactly the same two problems were also encountered in sodium compound **2**, preventing a satisfying refinement of both (presumably hexameric) structures in space group *C2/m*. Compared to the *tert*-butoxy compounds of potassium, rubidium, and caesium, which crystallise in cubic space groups,<sup>24</sup> the introduction of the less symmetric OtAm group should also result in lower crystallographic symmetry. However, the potassium, rubidium, and caesium compounds of OtAm are also found to consist of tetrameric units: [MOtAm]<sub>4</sub>, M = K (**3**), Rb (**4**), and Cs (**5**). Potassium compound

**3** crystallised at  $-30^{\circ}\text{C}$  in the highly symmetric tetragonal space group  $P\bar{4}2_1c$  (Figure 1).



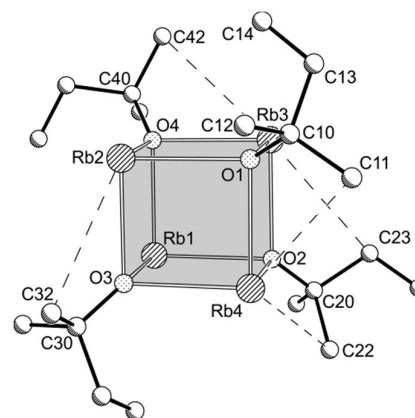
**Figure 1.** Molecular structure of tetrameric  $[\text{KOtAm}]_4$ , **3**. Hydrogen are omitted for clarity. Symmetry operator A:  $-x+1, y, -z$ ; B:  $-x+1, -y+1, z$ ; C:  $x, -y+1, -z$ . The  $\text{K}_4\text{O}_4$  cube is shaded for emphasis. Intramolecular short  $\text{K}\cdots\text{methyl}$  contacts are shown as dashed lines.

**Table 3:** Structural parameters of compounds **3**, **4**, and **5** in comparison to the corresponding *tert*-butoxy compounds  $\text{KOtBu}$ ,<sup>3</sup>  $\text{RbOtBu}$ ,<sup>1</sup> and  $\text{CsOtBu}$ .<sup>23</sup> (distances: [Å]; angles: [°]). For **3**, **4**, and **5** the minimum and maximum values are given.

MOR	M–O	M $\cdots$ Me	O–M–O	M–O–M
<b>3</b>	2.6232(13)	3.699	90.18(6)	89.82(6)
	2.6023(12)	3.498(2)	90.29(4)	89.16(4)
	2.6412(12)	3.509(2)	90.84(4)	89.70(4)
$\text{RbOtBu}$	2.757(4)	3.691	89.11(17)	90.89(16)
<b>4</b>	2.735(11)	3.34(4)	88.1(3)	89.2(3)
	2.802(10)	3.71(3)	91.3(3)	91.9(3)
$\text{CsOtBu}$	2.924	3.865	90.92	89.08
<b>5</b>	2.879(11)	3.71(2)	86.0(3)	90.7(3)
	2.938(10)	3.91(2)	89.1(3)	94.1(3)

The four potassium atoms and the four oxygen atoms of the *OtAm* groups form a regular cube with the metal atoms placed on diagonal corners of the quadratic faces of the cube (Table 3). The three K–O distances are found in a small range between 2.6023(12) and 2.6416(12) Å, the angles involving the atoms in the cubane structure are close to  $90^{\circ}$  (O–K–O: 90.29(4) to 90.84(4) $^{\circ}$ ; K–O–K: 89.16(4) to 89.70(4) $^{\circ}$ ). Interestingly, the *OtAm* group does not show any rotational disorder. Several intramolecular and intermolecular interactions of the potassium with alkoxy methyl groups can be observed, the shortest of these interactions are in the range of 3.498(2) and 3.509(2) Å. When the crystallisation of **3** was attempted at room temperature a polymorphic form was obtained in the monoclinic space group  $P2_1/c$  (**3a**). Disorder of one of the four *OtAm* groups and an overall lower quality of the collected data makes it reasonable to restrict the discussion to the tetragonal form. The structure of the homometallic potassium neopentyl/*tert*-amyloxide mixed aggregate<sup>16</sup>  $[\text{K}_4\text{Np}(\text{OtAm})_3]$  can be derived from tetrameric **3** by replacement of one *OtAm* group by a neopentyl group. This

alkyl group, which is responsible for the superbasic behaviour of this compound, also leads to dimerisation resulting in  $[\text{K}_4\text{Np}(\text{OtAm})_3]_2$  and therefore a substantial different solubility in alkanes in comparison to **3**.



**Figure 2.** Molecular structure of tetrameric  $[\text{RbOtAm}]_4$ , **4**. Hydrogen and disordered units of minor occupancy are omitted for clarity. The  $\text{Rb}_4\text{O}_4$  cube is shaded for emphasis. Intramolecular short  $\text{Rb}\cdots\text{methyl}$  contacts are shown as dashed lines.

**Table 4:** Crystallographic parameters of compounds **3**, polymorphic **3a**, **4**, and **5**.

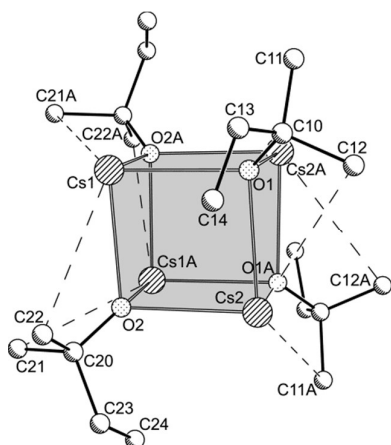
Compound	<b>3</b>	<b>3a</b>	<b>4</b>	<b>5</b>
Formula	$\text{C}_5\text{H}_{11}\text{OK}$	$\text{C}_5\text{H}_{11}\text{ORb}$	$\text{C}_5\text{H}_{11}\text{ORb}$	$\text{C}_5\text{H}_{11}\text{OCs}$
$M_r$ [g mol $^{-1}$ ]	126.24	126.24	172.61	220.05
Crystal system	tetragonal	monoclinic	monoclinic	monoclinic
Space group	$P\bar{4}2_1c$	$P2_1/c$	$Ia$ (Cc)	$P2/c$
$a$ [Å]	8.251(1)	21.876(4)	19.509(16)	19.114(3)
$b$ [Å]	8.251(1)	8.181(2)	8.686(6)	8.875(2)
$c$ [Å]	20.346(3)	16.896(3)	20.161(17)	20.401(3)
$\alpha$ [°]	90	90	90	90
$\beta$ [°]	90	111.92(1)	116.48(2)	117.10(1)
$\gamma$ [°]	90	90	90	90
$V$ [Å $^3$ ]	1385.1(2)	2805.2(10)	3058(4)	3080.6(9)
$Z$	8	16	16	16
$\rho_{\text{calcd}}$ [g cm $^{-3}$ ]	1.211	1.196	1.500	1.898
measured reflections	7105	29399	12649	37696
independent reflections	1664	6662	5571	7562
$R(\text{int})$	0.0365	0.0903	0.0742	0.0828
$R1$	0.0222	0.0719	0.0406	0.0695
(all data)	(0.228)	(0.1172)	(0.1737)	(0.0965)
$wR2$	0.0568	0.1439	0.0818	0.2090
(all data)	(0.0571)	(0.1588)	(0.1045)	(0.2364)
CCDC Number <sup>31</sup>	1837111	1837112	1837113	1837114

In compound **4** (Figure 2), which crystallises in the monoclinic space group  $Ia$  (equivalent to space group Cc) three of the four *OtAm* groups are disordered over two positions. Despite the lower symmetry, the  $\text{Rb}_4\text{O}_4$  cubane structure is fairly regular with O–Rb–O and Rb–O–Rb angles close to  $90^{\circ}$  (Table 3). In

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comparison to **3**, more short intramolecular and intermolecular interactions of rubidium with methyl groups of the OtAm units can be observed (Rb...Me: 3.34(4) to 3.71(3) Å).



**Figure 3.** Molecular structure of tetrameric [CsOtAm]<sub>4</sub>, **5**. Hydrogen and disordered units of minor occupancy are omitted for clarity, only one of the two crystallographically independent units is shown. Symmetry operator A:  $-x+1, y, -z+0.5$ . The Cs<sub>4</sub>O<sub>4</sub> cube is shaded for emphasis. Intramolecular short Cs...methyl contacts are shown as dashed lines.

Compound **5**, which crystallises in the monoclinic space group *P2/c*, is found in two crystallographic independent units. One of four OtAm groups shows disorder. **5** also forms reasonably regular Cs<sub>4</sub>O<sub>4</sub> cubane structures, despite the less symmetric structural environment. Compared to **3** and **4**, it shows considerably more intra- and intermolecular Caesium...methyl contacts (Cs...Me: 3.71(2) to 3.91(2) Å). These additional intermolecular interactions, caused by the increased size of caesium, may be the reason for the considerably lower solubility of **5** in non-coordinating solvents such as *n*-hexane.

## Conclusions

The potassium, rubidium, and caesium compounds of *tert*-amylalcohol were identified as tetramers in the solid state by single crystal X-ray crystallography. This is in accordance with the corresponding *tert*-butoxy compounds, which were identified as tetramers in highly symmetric crystalline environment. However, the *tert*-amyloxy group can introduce disorder and asymmetries into the crystalline arrangement. This property and the increased lipophilicity of the organic group in such 'amphiphile' alkali metal alkoxy compounds may contribute to the increased solubility compared to the corresponding *tert*-butoxy compounds.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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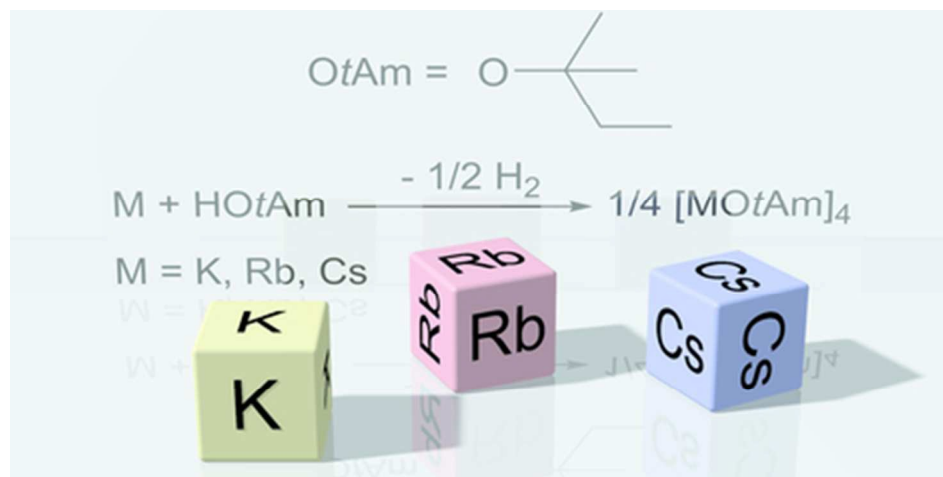
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§ See supporting information for experimental details, crystallographic and NMR spectroscopic data

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Hetero-cubane structures were revealed for the *tert*-amyloxide compounds of potassium, rubidium, and caesium.



39x19mm (300 x 300 DPI)