A structural study of alkaline earth metal complexes with hybrid disila-crown ethers†

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Compounds consisting of [M(1,2-disila-[3n]crown-n)]2+ (M = Mg, Ca, Sr, Ba; n = 5, 6) and [Ba(1,2-disila-benzo[18]crown-6)]2+ cations and different anions were obtained by equimolar reaction of the hybrid disila-crown ethers 1,2-disila[15]crown-5 (1), 1,2-disila[18]crown-6 (2) and 1,2-disila-benzo[18]crown-6 (7) with alkaline earth metal salts. Even with strongly coordinating anions such as Br− or I− stable complexes could be obtained, showing the good coordination ability of these ligands. The structures of all coordination compounds were determined via single crystal X-ray diffractions (XRD). By means of DFT calculations, the complexation ability of 1,2-disila[15]crown-5 (1) towards magnesium bromide was determined to be considerably higher compared to [15]crown-5. The opposite case was observed in solution as the exchange of calcium cations between [18]crown-6 and 1,2-disila[18]crown-6 (2) was studied via dynamic proton nuclear magnetic resonance (NMR) spectroscopy.

Introduction

Within the scope of developing macrocycles, there has also been an increased interest in ring compounds which are made of an inorganic skeleton.1–3 Unlike crown ether complexes, coordination compounds with cyclosiloxanes are very rare. They are mostly constituted of a weakly coordinating anion such as AlF4− (AlF4− = [Al[O(CF3)3]4]−), [SbF6]− or [InH(CH2C6H4CH2)]− as counterion where the charge is widely spread over a non-nucleophilic, chemically robust moiety.2,4–6 The Zr(n) compound [Zr(D6)Br2][Zr2Br9]2 (D = Me2SiO) is a unique example of a cyclosiloxane complex with a more strongly coordinating halide anion.7

One model to describe the reduced basicity of siloxanes is the negative hyperconjugation. An occupied p-orbital of the oxygen atom donates electron density into the σ*−orbital of the silicon–methyl bond, which strengthens the Si–O bond. The complexity of metal ions leads to a competing polarization.2,8 According to Weinhold and West, negative hyperconjugation plays a major role in permethylated siloxanes, which was recently shown via natural-bond-orbital-analysis.9,10 Another approach to explain the low basicity of siloxanes consists of an ionic consideration of the Si–O bond.11–13 Despite the high anionicity of the O atoms, siloxanes do not exhibit an increased coordination ability owing to the energetically unfavoured further polarisation of the already polar Si–O bond. In this respect changes in the nO → σ*Si–C interaction play a significant role.8 Recent work suggests that repulsion between the positively polarized Si atom and the metal ion is eminentely important beside the negative hyperconjugation to explain the low coordination ability of cyclosiloxanes.14

Furthermore, extraction experiments have shown that the complexation abilities of ring contracted crown ethers like [17]crown-6 and sila[17]crown-6 are notably smaller than those of common crown ethers revealing that not only electronic effects but also the conformation of the macrocycle determines the complexation ability of such compounds.15,16

These facts motivated us to incorporate a Si2Me4 unit rather than one SiMe2 in between the oxygen atoms of crown ethers (Scheme 1). Less attention has been paid to this function and its coordination chemistry even though it is known for quite some time.17,18 However, in our recent work on hybrid disila-crown ethers we were able to synthesize crown ethers of the type 1,2-disila[3n]crown-n and their alkali metal complexes. The reaction of 1,2-dichloro-1,1,2,2-tetramethylidisilane and the appropriate glycole yielded the hybrid crown ether.

Scheme 1 Binding modes of siloxanes (left) and disila-crowns (right) in metal complexes.
Complexation with selected alkali metal salts in dichloromethane (DCM) then yielded their alkali metal complexes (Scheme 2). By means of DFT calculations as well as dynamic proton NMR experiments, we revealed a comparable complexation ability of these crown ethers and their organic analogues.\(^1\)\(^9\)\(^{18}\)\(^9\) We therefore assume that the reduced complexation ability of siloxanes is rather the result of structural and electrostatic factors. As the next step in understanding the coordination chemistry of disila-crown ethers we herein report the incorporation of alkaline earth metal cations.

### Results and discussion

Treatment of 1 with MgBr₂ in trifluorotoluene led to the coordination compound \([\text{Mg}[1,2\text{-disila}[15\text{-crown-5}]]\text{Br}_2]\) (3). Neat 3 is a white powder which can be recrystallized after dissolution in DCM and layering with n-pentane. The resulting colourless plates were analysed via XRD. 3 crystallizes in the orthorhombic space group \(Pbc\alpha\). The magnesium cation is coordinated by all oxygen atoms of the cyclic ligand as well as by two bromide ions giving a coordination number of seven (Fig. 1). The oxygen atoms are in almost coplanar arrangement with the magnesium cation, which is apparent from the Br₁-Mg₁-Br₂-angles of approximately 90°. The MgBr₂ fragment is in well-nigh linear shape showing a Br₁-Mg₁-Br₂ angle of 178.5(1)°. This is consistent with the \([\text{Mg}(\text{THF})_2\text{Br}_2]\) (THF = tetrahydrofuran) complex, whose Br-Mg-Br-angle is 178.0(1)°.\(^{20}\)

The O-Mg-O-angles differ from 67.5(1) to 81.5(1)°. The O₁-Mg₁-O₅-angle is enlarged as a result of the Si-Si bond of 232.2(1) pm. The methyl groups are taking an almost elliptic arrangement, which can be seen in the C-Si-Si-C torsion angles of 9.3(1)° and 6.2(1)°. This eclipsed arrangement was also reported for different cyclosiloxane and disila-crown ether complexes.\(^{2,4,14,19,21}\) The O-Mg-bond lengths vary from 223.3(2) to 235.1(2) pm. Hence they are slightly longer than the O-Mg-bond lengths in related compounds with [15]crown-5 as ligand (see Table 1) and quite as long as those of \([\text{Mg}[18\text{-crown-6}](\text{Cl}-\text{H}-\text{Cl})_2]\).\(^{22}\) However, the O-Mg-bond lengths of fully carbon substituted oxygen atoms in 3 are comparable to those which are half carbon and half silicon substituted, so there is no hint for lower complexation ability of the silicon bonded oxygen atoms.

The shortest O-Mg bond is attributed to the silicon bonded oxygen atom O5 whereas the longest O-Mg bond is observed for the fully carbon substituted oxygen atom O3. The relative binding affinity of the hybrid ligand 1 towards magnesium bromide was further studied by quantum chemical calculations and is presented in Scheme 3. The exchange of magnesium bromide from [15]crown-5 to 1,2-disila[15]crown-5 (1) was calculated by means of DFT using the BP86 functional and def2-TZVP basis sets with inclusion of dispersion interactions together with charge compensation and is energetically favoured by 217.63 kJ mol\(^{-1}\). This result implies a significantly better coordination ability of 1 compared to [15]crown-5 and is in well accordance to previous calculations for 1,2-disila[12] crown-4 towards Li\(^{+}\).\(^{19}\) Unfortunately, the results of quantum chemical calculations could not be underlined with

### Scheme 2 Synthesis of hybrid disila-crown-ethers and their alkali metal complexes.

### Table 1 Selected bond lengths [pm] for compounds 3–5 and their related crown ether complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(O_{\text{Coord}}-\text{M}) [pm]</th>
<th>CN(^a)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>223.3(2)-235.1(2) 7</td>
<td>3</td>
<td>b</td>
</tr>
<tr>
<td>[Mg[15]<a href="SCPh%E2%82%83">crown-5</a>]₂</td>
<td>214.3(3)-219.2(4) 26</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>[Mg[15]<a href="H%E2%82%82O">crown-5</a>]₂[NO₃]₂</td>
<td>201.7(2)-235.7(8) 27</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>[Mg[15]<a href="NCS">crown-5</a>]₂</td>
<td>214.2(2)-239.9(7) 28</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>[Mg[15]<a href="CuCl%E2%82%82">crown-5</a>(CH₃CN)]</td>
<td>211.7(4)-219.1(3) 29</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>[Sr[18]<a href="OTf">crown-6</a>(H₂O)]</td>
<td>255.5(1)-265.7(1) 10</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>[Ca[18]<a href="H%E2%82%82O">crown-6</a>]₂</td>
<td>264.9(5)(^5)</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>[Ca[15]<a href="NCS">crown-5</a>]₂[O₃]</td>
<td>251.2(2)-258.5(2) 28</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>[Ca[15][crown-5][NO₃]₂]</td>
<td>247.4(3)-258.1(4) 27</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>[Sr[18]<a href="NO%E2%82%83">crown-6</a>]₂</td>
<td>266.5(5)-275.5(3) 10</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>[Sr[18]<a href="H%E2%82%82O">crown-6</a>]₂[CuCl₂]</td>
<td>268.2(8)-268.0(8) 10</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>[Sr[18]<a href="MeCN">crown-6</a>]₂[BPh₃]</td>
<td>267.2(3)-270.0(3) 9</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>[Sr[18]<a href="hmpa">crown-6</a>]₂[Sn(SnPh₃)]₂</td>
<td>262.4(2)-271.4(2) 9</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>[Sr[18]<a href="hmpa">crown-6</a>]₂[Sn(SnPh₃)]₂</td>
<td>258.9(4)-273.6(4) 8</td>
<td>44</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Coordination number. \(^b\) This work. \(^5\) All symmetry generated.
experimental data such as dynamic $^1$H NMR spectroscopy. 3 does only barely dissolve in DCM and thus no proton NMR study was possible for this compound.

The heavier calcium cation was incorporated by treating 2 with Ca(OTf)$_2$ (OTf = F$_3$CSO$_3$) in DCM. The resulting coordination compound [Ca(1,2-disila[18]crown-6)(OTf)$_2$] (4) was obtained as colourless powder. After recrystallization from dichloromethane, single crystals suitable for XRD were obtained in shape of colourless rods. 4 crystallizes in the monoclinic space group $P2_1/n$. This coordination compound shows a mismatch: one of the crown ether oxygen atoms does not participate in the coordination of the central atom. The crown acts as “pseudo-1,2-disila[15]crown-5”, so overall five crown ether oxygen atoms around the calcium cation. The mismatch, the O$_{crown}$–Ca bond lengths in 4 are slightly shorter than those of complexes of [18]crown-6 and close to [15]crown-5 complexes of calcium (see Table 1). In case of this mismatched crown ether complex, we observed a significantly lower complexation ability of 2 in comparison to [18]crown-6 which was confirmed by means of dynamic $^1$H NMR spectroscopy (see Scheme 4). An equimolar reaction of 2, [18]crown-6 and Ca(OTf)$_2$ was carried out. The percentage of coordinated and free ligand was calculated from the average chemical shifts in the mixture according to

$$\delta_{\text{average}} = \frac{n_{\text{coordinated}}\delta_{\text{coordinated}} + n_{\text{noncoordinated}}\delta_{\text{noncoordinated}}}{n_{\text{total}}}$$

Chemical shifts of compound 4 are significantly high-field shifted in the 1 : 1 mixture of 4 and [18]crown-6, whereas the singlet of [18]crown-6 is significantly down-field shifted (see Scheme 4, spectrum c). As calculated with the above given equation, the ratio of 4 to [Ca([18]crown-6)OTf$_2$] is 14 : 86. This result is contradicted to experimental data which was observed

![Diagram](image-url)

**Fig. 2** Molecular structure of 4 in the crystal. Thermal ellipsoids represent a probability level of 50%. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm]: O1–Ca1 244.9(1), O2–Ca1 245.8(1), O3–Ca1 247.9(1), O4–Ca1 232.4(1), O5–Ca1 243.6(1), O6–Ca1 247.5(1), O7–Ca1 247.5(1), O3–Ca1 234.8(1), O4–Ca1 248.1(1), O6–Ca1 245.8(1), O7–Ca1 246.3(1), Si1–O6 169.6(1), Si2–O1 169.1(1). Selected bond angles [°]: O1–Ca1–O6 76.1(1), O7–Ca1–O1 85.5(1), O7–Ca1–O2 84.6(1), O7–Ca1–O3 78.3(1), O7–Ca1–O5 99.4(1), O7–Ca1–O6 81.6(1), O7–Ca1–O10 63.0(1).

Hence this angle is slightly smaller than the expected 180° angle which is found in [Ca(CH$_3$CH$_2$OH)$_4$OTf]$_2$. The O7–Ca1–O(1,2,3,5,6) bond angles differ from 78.3(1) to 99.41(1)° leading to a distorted arrangement of the crown ether oxygen atoms around the calcium cation. The mismatch is obviously caused by the small ion diameter of Ca$^{2+}$, which is 200 pm, and the enlarged cavity of the ligand 2 compared to [18]crown-6. The coordination pattern of 4 is known for different crown ether complexes. However, no mismatched calcium complexes of [18]crown-6 are known to date. Due to the mismatch, the O$_{crown}$–Ca bond lengths in 4 are slightly shorter than those of complexes of [18]crown-6 and close to [15]crown-5 complexes of calcium (see Table 1). In case of this mismatched crown ether complex, we observed a significantly lower complexation ability of 2 in comparison to [18]crown-6 which was confirmed by means of dynamic $^1$H NMR spectroscopy (see Scheme 4). An equimolar reaction of 2, [18]crown-6 and Ca(OTf)$_2$ was carried out. The percentage of coordinated and free ligand was calculated from the average chemical shifts in the mixture according to

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![Diagram](image-url)

**Scheme 4** Segments of 300 MHz $^1$H NMR Spectra in CD$_2$Cl$_2$ of (a) 1,2-disila[18]crown-6, (b) [Ca(1,2-disila[18]crown-6)(OTf)$_2$] (c) [18]crown-6/1,2-disila[18]crown-6/Ca(OTf)$_2$ ratio 1:1:1 (d) [Ca([18]crown-6)OTf$_2$] and (e) [18]crown-6.
for the system 1,2,7,8-tetrasila[12]crown-4/LiPF$_6$/[12]crown-4 but attention should be paid to the enlarged cavity size of 2.

As reported for different supramolecules, the coordination ability of such compounds highly depends on the characteristics of the host-molecule. Especially the size complementarity between cation and host cavity influences the magnitude of the binding constant. The molecular structure of [Ca[[18]crown-6][OTf]$_2$][H$_2$O] reveals that [18]crown-6 enables all six oxygen atoms for the coordination to the metal ion rather than only five as in 4. This is presumably the key advantage of [18]crown-6 over the corresponding disila crown ether 2.

The halide complex [Sr(1,2-disila[18]crown-6)I$_2$] (5) was synthesized by reaction of 2 with SrI$_2$ in trifluorotoluene. After recrystallization, 5 was obtained as colourless blocks which were suitable for XRD. 5 crystallizes in the monoclinic space group $C2/c$ with one solvent molecule DCM. In contrast to 4, all crown ether oxygen atoms are coordinating to the larger strontium cation (Fig. 3). With two additional iodine atoms, the strontium cation has a coordination number of eight. No crown ether complex of the halide salt SrI$_2$ is known to date. No strontium cation (Fig. 3). With two additional iodine atoms, all crown ether oxygen atoms are coordinating to the larger strontium cation (Fig. 3). With two additional iodine atoms, all six oxygen atoms for the coordination to the metal ion as the half carbon and half silicon a small advantage of [18]crown-6 over the corresponding disila crown ether 2. 24 The twisted arrangement of the ligand enables all oxygen atoms to participate in the coordination. The O–Sr–I1 bond angles differ from 86.1(1) to 96.9(1)° stronger than for example the O–Mg1–Br1 bond angles in 3. In addition, the Sr(OSiMe$_2$I)$_2$ fragment shows an envelope conformation where the disilane-unit is buckling with Sr–O–O–Si torsion angles of 151.0(1) and 146.8(1)°. The methyl groups are again in an almost eclipsed arrangement with C–Si–Si–C torsion angles of 5.1(1) and 6.2(1)°. The I–Sr–I1 bond angle of 177.4(1)° is very close to 180° showing a well-nigh linear coordination of the SrI$_2$-fragment, which is also observed for [Sr(DME)$_3$(THF)$_3$] (DME = 1,2-dimethoxyethane), whose I–Sr–I bond angle is 178.6(1)°. 40

With bond lengths of 320.1(1) and 320.5(1) pm, the Sr–I bonds are similar to those of different ether adducts such as for example [Sr(DME)$_3$I$_2$]$_2$ (diglyme = bis(2-methoxyethyl)ether) or [Sr(DME)$_2$(THF)$_2$I$_2$]. Again all carbon substituted oxygen atoms show almost the same bond lengths to the metal ion as the half carbon and half silicon affected oxygen atoms (270.0(2) to 277.7(2) pm). However, the O6–Sr1 bond is the longest one, but should be considered with respect to the twisting of the crown ether. The Sr–O$_{crown}$ bonds of [Sr[[18]crown-6][NO$_3$]$_2$]$_2$ and [Sr[[18]crown-6][HOSO$_4$]$_2$] are marginally shorter. 27,32 The cationic crown compounds [Sr[[18]crown-6][hmpa]$_2$]$_2$ (hmpa = hexamethylphosphoramide) and [Sr[[18]crown-6]L]$_2$ (L = H$_2$O, CH$_3$CN) show notably smaller Sr–O$_{crown}$ bond lengths (see also Table 1). 33,34,39

Finally, the heaviest non-radioactive alkaline earth metal was incorporated into the macrocycle by treating 2 with Ba(OTf)$_2$ in DCM. After recrystallization, [Ba(1,2-disila[18]crown-6)OTf$_2$]$_2$ (6) crystallizes in the triclinic space group $P1$ with two independent molecules within the asymmetric unit. The metal ion is coordinated by all of the crown ether oxygen atoms as well as by the two triflate groups. One triflate group is coordinating as bidentate ligand giving the barium cation a total coordination number of nine (Fig. 4). With its ion diameter of 270 pm the barium cation is larger than the strontium cation, but the crown is still twisting as shown by the O5–Ba1–O10 and O6–Ba1–O10 bond angles, which are 78.1(1) and 77.4(1)°.

Fig. 3 Molecular structure of 5 in the crystal. Thermal ellipsoids represent a probability level of 50%. Hydrogen atoms and one solvent molecule DCM are omitted for clarity. Selected bond lengths [pm]: O1–Sr1 273.8(1), O2–Sr1 273.8(1), O3–Sr1 270.2(1), O4–Sr1 273.5(1), O5–Sr1 271.0(1), O6–Sr1 277.7(2), I1–Sr1 320.1(1), I2–Sr1 320.5(1), S1–O1 167.6(2), S2–O6 167.7(2), S1–S2 233.4(1). Selected bond angles [°]: O1–Sr1–I1 88.0(1), O2–Sr1–I1 93.2(1), O3–Sr1–I1 96.9(1), O4–Sr1–I1 87.0(1), O5–Sr1–I1 86.1(1), O6–Sr1–I1 93.2(1), I1–Sr1–I2 177.4(1), S1–O1–O6–Si2 151.0(1), S1–O6–O1–S1 146.8(1).
The O1–4–Ba1–O10 angles are much closer to 90°. The $O_{\text{Crown}}$–Ba bond lengths of 277.5(1) to 285.9(1) pm are in accordance with those of different [18]crown-6 complexes with barium. Nevertheless these distances are dependent on several factors such as coordination number, donor strength and the steric demand of coligands (see Table 2).

Similar to the compounds 3–5, the silicon bonded oxygen atoms do not differ significantly concerning the oxygen metal distance in comparison to the fully carbon substituted oxygen atoms. Again an eclipsed arrangement of the methyl groups at the silicon atoms is found. With 2.3(1) and 2.7(1)° the C–Si–Si–C torsion angles are even smaller. The monodentate coordinating triflate group binding to the metal ion has a O(10)–Si(1)–O(15) distance of 263.0(7) pm, the C–Si(2)–Si–C(3) torsion angle is 157.0(1)°. The second triflate group is chelating, the other one bonds to the metal ion only by a single oxygen atom. In comparison to O9, whose atomic distance to the metal ion is 263.0(7) pm, the O10–Ba1 atomic distances of 282.8(4) and 279.1(6) pm, respectively, are even longer. The torsion angles of related complexes (see Table 2).

As previously shown for 6, the metal ion in 8 is coordinated by all of the crown ether oxygen atoms as well as two triflate groups. The barium ion is only slightly shifted out of the center of the crown ether. The transannular angles of 157.0(1)° to 170.0(1)° are close to 180°, so the barium cation fits well into the cavity of 7.

In contrast to 6, the twisting of the crown is absent. The crown ether is rather bent with the benzylic as well as the disilane unit buckling to one side. With 277.5(2)–289.9(2) pm, the $O_{\text{Crown}}$–Ba distances have almost the same lengths as in 6. So have those of related compounds (see Table 2). Similar to 6, one triflate group is chelating, the other one bonds to the metal ion only by a single oxygen atom. In comparison to O9, whose atomic distance to the metal ion is 263.0(7) pm, the chelating oxygen atoms of the triflate group have O10–Ba1 and O12–Ba1 atomic distances of 282.8(4) and 279.1(6) pm, respectively. The methyl groups of the SiMe3 units are only slightly contorted to each other and show torsion angles of 16.8(1)° and 18.3(1)°.

According to recently published work another key role in understanding the complexation ability of silicon based crown ethers analogues is the repulsion between the positively

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### Table 2: Selected bond lengths [pm] for compounds 6, 8 and their related crown ether complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$O_{\text{Crown}}$–Ba [pm]</th>
<th>CN$^a$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{[Ba(18\text{crown}-6)(hmpa)$_2$]BF$_4$}$</td>
<td>277.2(2)–281.3(2)</td>
<td>8</td>
<td>34</td>
</tr>
<tr>
<td>$\text{[Ba(18\text{crown}-6)(hmpa)$_2$]SnPh$_3$}$</td>
<td>277(1)–280(1)</td>
<td>8</td>
<td>35</td>
</tr>
<tr>
<td>$\text{[Ba(18\text{crown}-6)(HCPH)$_2$]BF$_4$}$$^a$</td>
<td>275.0(2)–280.2(3)</td>
<td>8</td>
<td>41</td>
</tr>
<tr>
<td>$\text{[Ba(18\text{crown}-6)(PPH)$_2$]BF$_4$}$</td>
<td>271.7(2)–280.7(2)</td>
<td>8</td>
<td>42</td>
</tr>
<tr>
<td>$\text{[Ba(18\text{crown}-6)(hmpa)$_2$(SeMes)$_2$}]$</td>
<td>276.7(3)–280.3(2)</td>
<td>8</td>
<td>43</td>
</tr>
<tr>
<td>6</td>
<td>277.5(1)–285.9(1)</td>
<td>9</td>
<td>46</td>
</tr>
<tr>
<td>8</td>
<td>277.5(2)–289.9(2)</td>
<td>9</td>
<td>47</td>
</tr>
<tr>
<td>$\text{[Ba(18\text{crown}-6)(NCS)$_2$]H$_2$O}$</td>
<td>280.8(6)–287.5(5)</td>
<td>9</td>
<td>44</td>
</tr>
<tr>
<td>$\text{[Ba(18\text{crown}-6)(O$_2$P(OEt)$_2$Bu)$_2$]Cl}$$^b$</td>
<td>281(2)–290(2)</td>
<td>9</td>
<td>45</td>
</tr>
<tr>
<td>$\text{[Ba(18\text{crown}-6)(O$_2$CCF$_2$)$_2$]py}$</td>
<td>282.0(5)–284.5(7)</td>
<td>10</td>
<td>46</td>
</tr>
<tr>
<td>$\text{[Ba(18\text{crown}-6)(pta)$_2$]BF$_4$}$$^c$</td>
<td>278.6(3)–283.1(3)</td>
<td>10</td>
<td>47</td>
</tr>
<tr>
<td>$\text{[Ba(18\text{crown}-6)(pta)$_2$]BPh$_4$}$$^c$</td>
<td>292.9(4)–317.1(4)</td>
<td>10</td>
<td>47</td>
</tr>
<tr>
<td>$\text{[Ba(18\text{crown}-6)(H$_2$O)$_2$]Cl}$</td>
<td>277.0(2)–285.4(1)</td>
<td>10</td>
<td>48</td>
</tr>
<tr>
<td>$\text{[Ba(18\text{crown}-6)(O$_2$CH)$_2$]BF$_4$}$$^c$</td>
<td>275.3(2)–283.5(2)</td>
<td>10</td>
<td>49</td>
</tr>
<tr>
<td>$\text{[Ba(18\text{crown}-6)(NO$_2$)$_2$H$_2$O}$</td>
<td>283(1)–290.8(8)</td>
<td>11</td>
<td>27</td>
</tr>
</tbody>
</table>

$^a$ Coordination number. $^b$ Mes$^*$ = 2,4,6-tris(1H-1,2,4-triazol-1-yl)mesityl. $^c$ This work. $^d$ pta = 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dione. $^e$ DB = dibenzo.
charged metal ion and the positively polarized silicon atoms. The use of \( \text{Si}_2\text{Me}_4 \) rather than one \( \text{SiMe}_2 \) allows lower repulsion, which can be seen in the average Si–M distances. This might also be an explanation for the higher coordination ability of these hybrid disila-crown ethers in comparison to cyclosiloxanes which we reported before. Further calculations would be helpful to quantify though. Experimental data of metal complexes with disila units, however, features longer average Si–M distances than the sila units in siloxanes. While \([\text{Li}(1,2\text{-disila}[12]\text{crown-4})\text{OTf}]\) has average M–Si distances of 3.21 pm, they are shortened to 2.72–2.75 pm in the cyclosiloxane complexes \([\text{Li}(\text{D}_{6})\text{AlF}]\) and \([\text{Li}(\text{D}_{6})\text{AlF}_{9}]\). \( \text{Al}^{\text{III}} = \{\text{Al}[(\text{CF}_3\text{Cl})_2\text{Ph}]_2\}^{\text{−}} \).\(^2,19\) \([\text{K}(1,2\text{-disila}[18]\text{crown-6})\text{PF}_6]\) has Si–M average distances of 392.4(1) pm.\(^19\) \([\text{K}([\text{D}]_7)]\) has average distances of 358–365 pm, so these are shortened as well.\(^4,21\) Analogous observations were made in the comparison of alkaline earth metal complexes reported in this work like 5 and 6 with siloxane complexes such as \([\text{Sr}(\text{NBN-SiMe}_2\text{OSiMe}_2\text{O})_2]\) or \([\text{Ba}(\text{THF})_6\text{dmpz}][\text{(OSiMe}_2\text{O})_2]\) (dmpz = 3,5-di-methylpyrazolate).\(^51,52\) Still no complexes of common cyclosiloxanes and alkaline earth metal salts are known today, so the reported complexes in this work are the first crown-type structures containing an alkaline earth metal as well as ligands bearing Si–O donors.

Conclusions

In a recent work, we described the synthesis of hybrid disila-crown ethers of the type 1,2-disila[3n]crown-n (1: n = 5, 2: n = 6) and the formation of alkaline metal complexes.\(^19\) Within this study, we reported the synthesis of 1,2-disila-benzo[18] crown-6 (7) using similar conditions.

By equimolar reaction of alkaline earth metal salts with the disila-crown ethers 1, 2 and 7, we obtained the alkaline earth metal complexes 3–6 and 8. The structures of all coordination compounds were determined via X-ray crystallographic studies. The \( \text{O}_{\text{crown}}\text{–M} \) bond lengths indicate that all carbon substituted oxygen atoms show almost the same bond lengths to the metal ion as the half carbon and half silicon affected oxygen atoms, so that on a structural level no reduced complexation ability of these \( \text{O–Si}_2\text{Me}_4\text{–O} \) fragments can be observed. The variation of ion diameter and cavity size of the crown then gives interesting coordination patterns: in compound 4, the cavity diameter of 2 is too large for the calcium ion resulting in a mismatch structure. This structure reveals that it’s not inevitably the silicon affected oxygen atom which does not participate in the coordination but according to proton NMR-studies, the complexation ability of 1,2-disila[18] crown-6 (2) was determined to be significantly lower than those of [18]crown-6. The size complementarity between cation and host cavity significantly influences the complex stabilities.

Beside the trilicate complexes 4, 6 and 8, we also obtained complexes with strongly coordinating anions such as \( \text{Br}^- \) or \( \text{I}^- \) (compound 3 and 5). These results show a better coordination ability of disila-bridged donor atoms in comparison to \( \text{R}_2\text{Si} \) bridges, which results from longer Si–M distance within the metal complexes and a reduced cyclic stress. Furthermore DFT calculations (BP86 functional and def2-TZVP basis set) revealed that the coordination ability of 1,2-disila[15]crown-5 (1) towards magnesium bromide is considerably higher compared to [15]crown-5. Nonetheless, all disila-substituted crown ether oxygen atoms of the type Si–Si–O–Si would still be useful to give more meaningful results in how far disila-affected crown ethers can challenge organic crown compounds. Most recent work hints a considerably higher complexation ability of the partially silicon substituted crown ether 1,2,4,5-tetrasila[12]crown-4 towards \( \text{Li}^- \) than [12]crown-4.\(^53\)

Thus, further investigations for this kind of crown ethers and a stepwise synthesis of a fully silicon substituted crown ether are intended for the future.

Experimental section

General

All working procedures were carried out with rigorous exclusion of oxygen and moisture using Schlenk techniques under inert gas atmosphere. Solvents were dried and freshly distilled before use. Compounds 1, 2 and the organic fragment of 7 were synthesized using methods described in literature.\(^19,50\) Alkaline earth metal salts were stored and handled under argon atmosphere using a glovebox. NMR spectra were recorded on a Bruker AV III HD 300 MHz or AV III 500 MHz. Infrared (IR) spectra of the respective samples were measured using attenuated total reflectance (ATR) mode on a Bruker Model Alpha FT-IR. MS-spectrometry was measured on JEOL AccuTOF-GC (LIFDI) or LTQ-FT (ESI). Elemental analysis was performed on a Vario MicroCube. Fluorine-containing compounds led to ongoing damage of the elemental analyser and were not measured.

Synthesis of \([\text{Mg}(1,2\text{-disila}[15]\text{crown-5})\text{Br}_2](3)\). 0.244 g 1,2-disila[15]crown-5 (0.79 mmol) are dissolved in 15 ml trifluoro-toluene, and 0.146 g (0.79 mmol) MgBr\(_2\) are added. The suspension is stirred for four days and then filtered. The residue is washed with 4 ml DCM, and the filtrate is freed of the solvent. The resulting solid is washed with three portions of 5 ml n-pentane, dissolved in 2 ml DCM and layered with 10 ml n-pentane. After two days, 3 is obtained as colourless blocks (0.12 g, 30%). Elemental Analysis [%] found (calc.): C 28.83 (29.26) H 6.18 (5.73).

1H NMR: (300 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) = 0.44 (s, 12H, Si(CH\(_3\))\(_2\)), 3.77–3.80 (m, 4H, CH\(_2\)), 3.86 (s, 8H, CH\(_3\)), 3.95–3.98 (m, 4H, CH\(_2\)) ppm; 13C\(^{1}\)H NMR: (75 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) = −0.8 (s, Si(CH\(_3\))\(_2\)), 61.8 (s, CH\(_3\)), 68.1 (s, CH\(_2\)), 68.5 (s, CH\(_2\)), 69.9 (s, CH\(_3\)) ppm; 29Si\(^{1}\)H NMR: (99 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) = 18.0 (s, Si(CH\(_3\))\(_2\)) ppm; MS: LIFDI(\( \pm \)m/z): 411.051 [M – Br\(_2\)] ppm; IR (cm\(^{−1}\)): 2948 (m), 2884 (w), 1634 (w), 1467 (m), 1345 (w), 1297 (w), 1243 (m), 1084 (s), 1058 (s), 1046 (s), 959 (s), 922 (m), 896 (m), 824 (m), 803 (m), 774 (w), 730 (w), 696 (w), 639 (w), 568 (w).

Synthesis of \([\text{Ca}(1,2\text{-disila}[18]\text{crown-6})\text{OTf}_2]\) (4). 0.192 g 1,2-disila[18]crown-6 (0.79 mmol) are dissolved in 15 ml DCM,
and 0.146 g (0.79 mmol) CaOTf₂ are added. The suspension is stirred vigorously overnight and then filtered. The residue is washed with 2 mL DCM and the filtrate is freed of the solvent. The resulting solid is washed with three portions of 5 mL n-pentane, dissolved in 5 mL DCM and layered with 10 mL n-pentane. After two days, 4 is obtained as colourless rods (0.187 g, 39%).

³¹H NMR: (300 MHz, CD₂Cl₂) δ = 0.41 (s, 12H, Si(CH₃)₂), 3.80–3.84 (m, 4H, CH₂), 3.87–3.89 (m, 12H, CH₂), 3.94–3.97 (m, 4H, CH₂) ppm; \(^{13}\)C\(^{1}\)H NMR: (75 MHz, CD₂Cl₂) δ = 0.9 (s, Si(CH₃)₂), 62.9 (s, CH₂), 69.7 (s, CH₂), 70.3 (s, CH₂), 70.7 (s, CH₂), 72.7 (s, CH₂), 120.7 (q, \(_{JC} = 318\) Hz, CF₃) ppm; \(^{29}\)Si\(^{1}\)H NMR: (99 MHz, CD₂Cl₂) δ = 19.7 (s, (Si(CH₃)₂) ppm; \(^{19}\)F NMR: (282 MHz, CD₂Cl₂) δ = −79.3 (s, CF₃) ppm; MS LIFDI(+) m/z (%): 375.165 [1,2-disila[18]crown-6 + Na]+ (100), 541.088 [M – OTf] (40); IR (cm\(^{-1}\)): 2954 (w), 2887 (w), 1471 (w), 1357 (w), 1305 (s), 1240 (s), 1219 (s), 1164 (s), 1059 (s), 1028 (s), 933 (s), 868 (m), 838 (s), 817 (s), 795 (s), 775 (s), 760 (s), 726 (s), 634 (s), 579 (m), 514 (s), 460 (w).

**Synthesis of [Sr(1,2-disila[18]crown-6)]₆** (5). 0.355 g 1,2-disila[18]crown-6 (1.00 mmol) are dissolved in 20 mL trifluorotoluene, and 0.343 g (0.79 mmol) SrAl₂ are added. The suspension is stirred under exclusion of light for 12 h and then filtered. The residue is washed with 2 mL DCM, and the filtrate is freed of the solvent. The resulting solid is washed with three portions of 5 mL n-pentane, dissolved in 3 mL DCM and layered with 15 mL n-pentane. After two days, 5 is obtained as colourless plates (0.227 g, 33%). Elemental Analysis [%] found: C 24.23 (23.96) H 5.05 (4.65).

³¹H NMR: (300 MHz, CD₂Cl₂) δ = 0.46 (s, 12H, Si(CH₃)₂), 3.81–3.84 (m, 4H, CH₂), 3.90 (s, 4H, CH₂), 3.91–3.96 (m, 8H, CH₂), 4.05–4.08 (m, 4H, CH₂) ppm; \(^{13}\)C\(^{1}\)H NMR: (75 MHz, CD₂Cl₂) δ = 0.0 (s, Si(CH₃)₂), 63.1 (s, CH₂), 70.4 (s, CH₄), 70.5 (s, CH₂), 70.5 (s, CH₂), 73.0 (s, CH₂) ppm; \(^{29}\)Si\(^{1}\)H NMR: (99 MHz, CD₂Cl₂) δ = 18.2 (s, Si(Me)₂) ppm; MS: LIFDI(+) m/z (%): 566.984 [M – 1]+ (100); IR (cm\(^{-1}\)): 2943 (w), 2881 (w), 1457 (w), 1353 (w), 1320 (w), 1245 (m), 1082 (s), 1039 (s), 972 (s), 957 (s), 930 (s), 919 (s), 862 (s), 841 (s), 823 (s), 797 (s), 769 (s), 729 (s), 696 (m), 657 (w), 628 (m), 532 (w), 461 (w).

**Synthesis of [Ba(1,2-disila[18]crown-6)OTf₂** (8). 0.164 g 1,2-disila[18]crown-6 (0.41 mmol) are dissolved in 15 mL DCM, and 0.178 g (0.28 mmol) BaOTf₂ are added. The suspension is stirred for 6 h and then filtered. The residue is washed with 2 mL DCM and the filtrate is freed of the solvent. The resulting solid is washed with four portions of 5 mL n-pentane, dissolved in 4 mL DCM and layered with 15 mL n-pentane. After two days, 8 is obtained as colourless blocks (0.120 g, 35%).

³¹H NMR: (300 MHz, CD₂Cl₂) δ = 0.36 (s, 12H, Si(CH₃)₂), 3.81–3.88 (m, 8H, CH₂), 4.03–4.06 (m, 4H, CH₂), 4.24–4.27 (m, 4H, CH₂), 6.93–7.03 (m, 4H, CH₂) ppm; \(^{13}\)C\(^{1}\)H NMR: (75 MHz, CD₂Cl₂) δ = −0.9 (s, Si(CH₃)₂), 63.4 (s, CH₂), 68.4 (s, CH₂), 73.4 (s, CH₂), 112.3 (s, CH₂), 120.8 (q, \(_{JC} = 319\) Hz, C₃F₃) ppm; \(^{19}\)F NMR: (282 MHz, CD₂Cl₂) δ = −78.7 (s, CF₃) ppm; \(^{29}\)Si\(^{1}\)H NMR: (99 MHz, CD₂Cl₂) δ = 17.7 (s, Si(CH₃)₂) ppm; MS LIFDI(+) m/z (%): 687.031 [M − OTf²] (100), 1523.014 [2M − OTf²] (100); IR (cm\(^{-1}\)): 2945 (w), 2885 (w), 1596 (w), 1506 (s), 1477 (m), 1456 (w), 1357 (s), 1300 (s), 1240 (s), 1220 (s), 1171 (s), 1115 (s), 1063 (s), 1034 (s), 1023 (s), 961 (s), 941 (s), 914 (s), 865 (m), 852 (s), 837 (s), 819 (s), 795 (s), 772 (s), 756 (s), 737 (s), 634 (s), 604 (m), 583 (m), 573 (m), 528 (m), 513 (s), 454 (w).

**Computational details**

Calculations were performed with the program system TURBOMOLE V7.0.1.\(^{54}\) The resolution of identity (RI) approxi-
mation, dispersion corrections, and the conductor-like screening model (COSMO) were applied throughout, the latter with default settings. For all calculations, the BP86 functional was chosen, utilizing a def2-TZVP basis set.55

Crystal structures

Single crystal X-ray diffraction was carried out using Bruker D8 Quest (3, 6, 8) or IPDS 2 diffractometer (4, 5) at 100–110 K with MoKα radiation and X-ray optics or graphite monochromatization, respectively (λ = 0.71073). The structures were solved by direct methods and refinement with full-matrix-leastsquares against F² using SHELXT- and SHELXL-2015 on OLEX2 platform,56–58 Triflate groups were refined with help of DSR.59

Crystallographic data for compounds 3–6 and 8 are denoted as follows: CCDC No. 1497469 (3), 1497467 (4), 1497468 (5-DCM), 1497471 (6) and 1497470 (8).

Crystal data of 3. C₁₂H₂₈Br₂MgO₅Si₂, orthorhombic, Pbca, Z = 8, 100 K, a = 10.8339(6) Å, b = 14.1089(7) Å, c = 27.7505(14) Å, V = 4241.8(4) Å³, ρ = 1.543 g cm⁻³, multiscan absorption correction using SADABS-2014,60 μ = 3.980 mm⁻¹, T min, T max = 0.622, 0.745, 2θ range 4.77–50.5⁰, reflections measured 22 357, independent reflections 3841 [R(int) = 0.0724], 203 parameters, R-index [I ≥ 2σ(I)] 0.0322, wR2 (all data) 0.0553, GOOF 1.023, Δρ max, Δρ min 0.40/–0.61 e Å⁻³.

Crystal data of 4. C₁₄H₂₆CaF₄O₈Si₂Si₂, monoclinic, P2₁/n, Z = 4, 100 K, a = 8.9460(18) Å, b = 34.272(7) Å, c = 9.6976(19) Å, β = 103.04⁰, V = 2896.6(11) Å³, ρ = 1.584 g cm⁻³, numerical absorption correction using X-AREA and X-RED32,61 μ = 0.535 mm⁻¹, T min, T max = 0.874, 0.951, 2θ range 4.48–49.62⁰, reflections measured 13 664, independent reflections 4991 [R(int) = 0.0780], 358 parameters, R-index [I ≥ 2σ(I)] 0.0408, wR2 (all data) 0.1089, GOOF 1.008, Δρ max, Δρ min 0.73/–0.67 e Å⁻³.

Crystal data of 5-DCM. C₁₅H₃₄Cl₄O₈Si₂, monoclinic, C2/c, Z = 8, 100 K, a = 14.037(3) Å, b = 10.896(2) Å, c = 37.359(8) Å, β = 99.19(3)⁰, V = 5641(2) Å³, ρ = 1.834 g cm⁻³, numerical absorption correction using X-AREA and X-RED32,61 μ = 4.400 mm⁻¹, T min, T max = 0.482, 0.709, 2θ range 4.756–52.01⁰, reflections measured 15 303, independent reflections 5516 [R(int) = 0.0290], 257 parameters, R-index [I ≥ 2σ(I)] 0.0191, wR2 (all data) 0.0360, GOOF 0.800, Δρ max, Δρ min 0.60/–0.61 e Å⁻³.

Crystal data of 6. C₁₆H₃₂BaF₄O₁₂Si₂S₂, triclinic, P1, Z = 4, Z' = 2, 100 K, a = 9.7531(4) Å, b = 17.5485(8) Å, c = 18.5666(8) Å, α = 72.5040(10)⁰, β = 86.902(2)⁰, γ = 89.5490(10)⁰, V = 3026.2(2) Å³, μ = 1.617 g cm⁻³, multiscan absorption correction using SADABS-2014,60 μ = 1.617 mm⁻¹, T min, T max = 0.544, 1.00, 2θ range 4.518–61.68⁰, reflections measured 103 763, independent reflections 8198 [R(int) = 0.0254], 991 parameters, R-index [I ≥ 2σ(I)] 0.0237, wR2 (all data) 0.0509, GOOF 1.093, Δρ max, Δρ min 1.03/–2.70 e Å⁻³.

Crystal data of 8. C₂₀H₃₂BaF₄O₁₂Si₃₂, orthorhombic, P2₁2₁2₁, Z = 4, 110 K, a = 9.0173(4) Å, b = 10.3761(5) Å, c = 35.6495(16) Å, V = 3333.5(3) Å³, μ = 1.665 g cm⁻³, numerical absorption correction using SADABS-2014,60 μ = 1.473 mm⁻¹, T min, T max = 0.668, 0.904, 2θ range 4.542–57.452⁰, reflections measured 32 181, independent reflections 8616 [R(int) = 0.0346], 525 parameters, R-index [I ≥ 2σ(I)] 0.0274, wR2 (all data) 0.0481, GOOF 1.037, Δρ max, Δρ min 0.59/–0.60 e Å⁻³, Flack parameter 0.002(6).

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