Silicon Crown Ethers

DOI: 10.1002/anie.200701822

Silicon Analogues of Crown Ethers and Cryptands: A New Chapter in Host–Guest Chemistry?**

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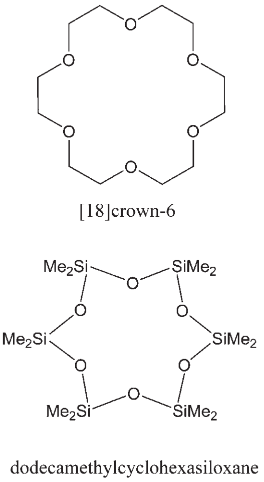
Keywords:
crown compounds · cryptands · cyclosiloxanes · host–guest systems · weakly coordinating anions

The synthesis of macrocyclic polyethers was first reported by Pedersen in the 1960s.[1] Subsequent studies on their selective ligation of alkali-metal cations has led to the development of host–guest chemistry, and in 1987 Pedersen's seminal work was recognized by the award of the Nobel Prize in Chemistry, jointly with Lehn and Cram.[2] The discovery of silicon-containing macrocyclic ethers, known as dimethylcyclosiloxanes, $(Me_2SiO)_n$ (abbreviated $\mathbf{D}_n$),[3] predates that of the so-called crown ethers by more than twenty years.[4] An analogy can be drawn between these macrocyclic inorganic ligands and the crown ethers, as they feature oxygen atoms linked by $-SiMe_2-$ rather than $-CH_2CH_2-$ units (Figure 1).



[18]crown-6

dodecamethylcyclohexasiloxane

Figure 1. Comparison of a representative crown ether and a typical cyclosiloxane.

There have been few studies of the coordination of these silicon analogues to metal ions. This is not surprising in light of the reluctance of silicon ethers, for example, $(Me_3Si)_2O$, to participate in adduct formation, even with Lewis acids such as BCl_3 or BF_3.[5,6] The first reported investigation of the complexation behavior of $\mathbf{D}_n$ ligands appeared in the 1970s.[7] The authors of that work observed the lack of a "crown effect" in attempts to use $\mathbf{D}_7$ or $\mathbf{D}_8$ to accelerate the rate of the anionic ring-opening polymerization (ROP) of a cyclotrisiloxane, $(R^1R^2SiO)_3$ ($R^1 = Me$, $R^2 =$ 3,3,3-trifluoropropyl), and claimed that this was due to a lower electron density on the oxygen atoms of $\mathbf{D}_7$ and $\mathbf{D}_8$ compared to that in organic ethers.

In the 1990s two examples of potassium complexes of $\mathbf{D}_7$ were reported to form in the serendipitous interaction of highly reactive reagents with silicone grease.[8] The first example was described by Churchill et al.;[9] the product was obtained unexpectedly during the recrystallization of $K[InNp_3H]$ (Np = neopentyl) from heptane containing a small quantity of silicone grease. Colorless crystals were isolated and shown by single-crystal X-ray diffraction (XRD) studies to have the composition $[K]_3[K\mathbf{D}_7][InNp_3H]_4$. A few years later, Smith and co-workers reported the crystal structure of a similarly adventitious product.[10] The recrystallization of $K[C(SiMe_3)_2\{SiMe_2(CH{=}CH_2)\}]$ from methylcyclohexane/Et_2O in a vessel sealed with a glass stopper lubricated with silicone grease yielded single crystals of $[K\mathbf{D}_7][C(SiMe_3)_2\{SiMe_2(CH{=}CH_2)\}]$. It has been suggested that the formation of the fourteen-membered ring in both cases results from a templation effect of the potassium ion.[8] In both complexes, the potassium cation resides in the middle of a cavity and the ligand and metal ion form an approximately planar motif (Figure 2).

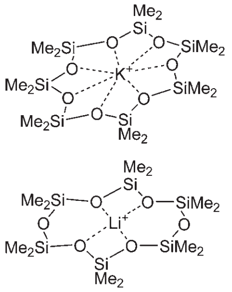


Figure 2. Binding modes of $\mathbf{D}_n$ ligands in alkali-metal complexes.

More recently, Passmore and co-workers reported the surprising formation of crystals of $[Li\mathbf{D}_6][Al_F]$ ($Al_F = Al\{OC(CF_3)_3\}_4$) from the attempted synthesis of a cyclic selenium cation, $Se_6Ph_2^{2+}$.[11] The reaction vessel containing the necessary reagents was stoppered with a ground-glass joint lubricated with silicone grease. While no trace of the target compound was detected, colorless crystals of $[Li\mathbf{D}_6][Al_F]$ were isolated and characterized by single-crystal XRD. The structural parameters of $[Li\mathbf{D}_6][Al_F]$ are notably different than those of the aforementioned potassium

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[**] Financial support from the NSERC (Canada), Alberta Ingenuity, and the Killam Foundation (University of Calgary) is gratefully acknowledged. We thank Prof. J. Passmore for communicating unpublished results (Ref. [18]) and Dr. C. von Hänisch for providing a copy of Ref. [19] prior to publication.

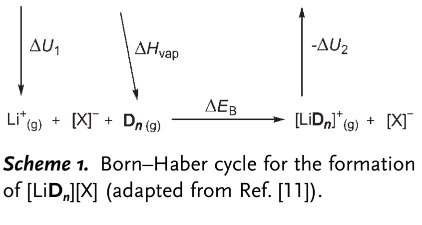
complexes because, in addition to the smaller ring size, only four out of six oxygen atoms are coordinated to the metal ion (Figure 2). The exact mechanism of formation of these complexes remains uncertain.[12]

Several questions were prompted by the serendipitous discovery of alkali-metal complexes of cyclodimethylsiloxanes. First and foremost, can $M\mathbf{D}_n^+$ complexes be prepared directly from the interaction of an alkali-metal cation with the appropriate cyclodimethylsiloxane? In 2006 this challenge was addressed through the direct synthesis of three complexes of the type $[\mathrm{Li}\mathbf{D}_n][\mathrm{X}]$ by the treatment of lithium salts of weakly coordinating anions (WCAs), $\mathrm{Li[Al_F]}$ or $\mathrm{Li[Al_{PhF}]}$ $(=\mathrm{Al\{OC(CF_3)_2Ph\}_4})$,[13] with $\mathbf{D}_n$ ligands ($n=5$, 6). These simple reactions proceed in dichloromethane at room temperature to give the corresponding pseudo-crown complexes as colorless crystalline solids [Eq. (1); $\mathrm{X}=\mathrm{Al_F}$, $n=5$ or 6; $\mathrm{X}=\mathrm{Al_{PhF}}$, $n=6$].[11]

$$\mathrm{Li[X]} + \mathbf{D}_n \xrightarrow[\mathrm{RT}]{\mathrm{CH_2Cl_2}} [\mathrm{Li}\mathbf{D}_n][\mathrm{X}] \tag{1}$$

These seminal findings raised the issue of thermochemical considerations in the formation of these host–guest complexes. Is this type of reaction feasible for more common alkali-metal salts such as lithium halides? Passmore et al. probed this question with ab initio methods by calculating the binding energy (ΔE_B) of Li^+ with $\mathbf{D}_n$ in the gas phase and constructing Born–Haber cycles for the overall reaction with various anions (Scheme 1).[11]

These energy calculations rationalize the use of WCAs in the synthetic approach outlined in Equation (1). For instance, when $\mathrm{X}=\mathrm{I}^-$ the lattice energy terms are $\Delta U_1 = 730\ \mathrm{kJ\,mol^{-1}}$ and $\Delta U_2 = 372\ \mathrm{kJ\,mol^{-1}}$, whereas for $\mathrm{X}=[\mathrm{Al_F}]^-$ the corresponding contributions are $\Delta U_1 = 368\ \mathrm{kJ\,mol^{-1}}$ and $\Delta U_2 = 318\ \mathrm{kJ\,mol^{-1}}$. The lattice energy of LiI is much larger than that of the host–guest complex and so the overall enthalpy change is positive ($\Delta H = +66\ \mathrm{kJ\,mol^{-1}}$). The lattice energy of $\mathrm{Li[Al_F]}$, however, is comparable to that of $[\mathrm{Li}\mathbf{D}_6][\mathrm{Al_F}]$ and the overall enthalpy change is negative ($\Delta H = -242\ \mathrm{kJ\,mol^{-1}}$). In summary, WCAs minimize changes in lattice energy and they also reduce the possibility of unfavorable cation–anion interactions that would perturb the complexation of the metal ion.



Scheme 1. Born–Haber cycle for the formation of $[\mathrm{Li}\mathbf{D}_n][\mathrm{X}]$ (adapted from Ref. [11]).

Another interesting aspect of these new pseudo-crown-ether complexes is the bonding description of the rings compared to their organic analogues. One obvious difference between these two systems is the ring conformation when coordinated to a metal ion. Whereas puckering is observed in the complexes of organic crown ethers with all the oxygen atoms pointing towards the metal ion, the known silicon analogues all feature the metal ion in the centre of a planar ring. The parent cyclosiloxane ligands are known to be puckered rings, so why are the metal complexes planar? Perhaps a more fundamental question is: why are the silicon analogues of crown ethers, and silicon ethers in general, much less able to coordinate to metal ions?

Gillespie and Robinson[14] argue that the large difference in electronegativity between silicon and oxygen results in spatially diffuse electron pairs on the oxygen atom which are weakly basic compared to more localized electron pairs such as in organic ethers, where the electronegativity difference is not so pronounced. An alternative explanation invokes the participation of negative hyperconjugation through donation of p-orbital electron density from the oxygen atom to a Si–C antibonding molecular orbital ($\mathrm{p^2(O)}\rightarrow\sigma^*(\mathrm{Si{-}CH_3})$, Figure 3).[11] This interaction would reduce the capacity of the oxygen atom to bind to metal ions and concomitantly strengthen the Si–O bond and weaken the Si–C bond. Upon coordination of an oxygen atom to a lithium cation, polarization towards the oxygen atom would diminish the influence of this interaction (Figure 3). The crystal structures of $[\mathrm{Li}\mathbf{D}_6][\mathrm{Al_F}]$ and $[\mathrm{Li}\mathbf{D}_6][\mathrm{Al_{PhF}}]$ support this proposal: normal Si–O bond lengths are observed for non-coordinated oxygen atoms (compared to the values in gaseous $\mathbf{D}_6$ as determined by electron diffraction[15]); the coordinated oxygen atoms, however, show elongated Si–O bonds (by ca. 0.04 Å).

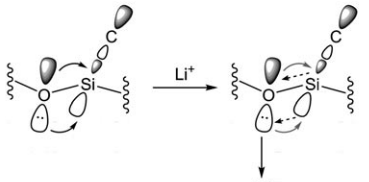


Figure 3. The $\mathrm{p^2(O)}\rightarrow\sigma^*(\mathrm{Si{-}CH_3})$ interaction and its polarization by Li^+ (adapted from Ref. [11]).

In a subsequent study, the reactions of multidentate $\mathbf{D}_n$ ligands with silver hexafluoroantimonate were investigated.[16] The reaction of $\mathbf{D}_5$ with $\mathrm{Ag[SbF_6]}$ in liquid $\mathrm{SO_2}$ produced a colorless product, the major component of which was shown to be $[\mathrm{Ag}\mathbf{D}_7][\mathrm{SbF_6}]$. $^{29}\mathrm{Si}$ NMR spectroscopy revealed that an equilibrium mixture of $[\mathrm{Ag}\mathbf{D}_n]^+$ cations ($n=6$, 7, 8) was formed; similar mixtures were also obtained when other $\mathbf{D}_n$ ligands ($n=3$, 4, 6) were used.[17,18] Ab initio calculations suggest that the formation of $[\mathrm{Ag}\mathbf{D}_7]^+$ is favored over that of $[\mathrm{Ag}\mathbf{D}_6]^+$ because of the more exothermic enthalpy change ΔE_B (by ca. $25\ \mathrm{kJ\,mol^{-1}}$) for the former species (see Scheme 1 for a definition of ΔE_B). In contrast to the structure of $[\mathrm{K}\mathbf{D}_7]^+$ (Figure 2), the silver complex $[\mathrm{Ag}\mathbf{D}_7]^+$ embodies only five Ag–O contacts, three of which are strong while the other two are weak (Figure 4).

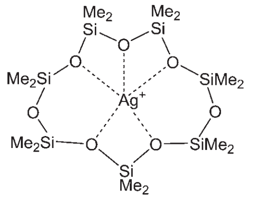


Figure 4. Binding mode of $\mathbf{D}_7$ in an Ag^+ complex.

In a very recent related study, the group of von Hänisch has achieved the first encapsulation of an alkali-metal cation by an inorganic cryptand **L** ($\mathbf{L} = [\mathrm{P_2\{O(Si}i\mathrm{Pr_2)_2\}_2\{SiMe_2(OSiMe_2)_2\}}]$) that incorporates a siloxane framework.[19] The relationship between **L** and [2,1,1]cryptand is illustrated in Figure 5; the $\text{-}\mathrm{CH_2CH_2}\text{-}$ groups are replaced by

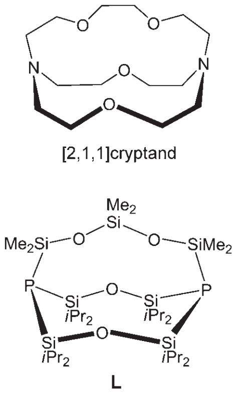


Figure 5. Comparison of [2,1,1]cryptand with the hexadentate inorganic cryptand **L**.

SiR_2, and the P atoms are substituted for the N atoms.

The formation of the Li^+ complex of **L** was achieved by direct synthesis employing the Li^+ salt of the WCA $[Al_F]^-$. The X-ray crystal structure of [Li**L**][Al_F] reveals coordination to three oxygen atoms (two long and one short Li–O interaction) and two weak Li–P interactions (Figure 6). The existence of [Li**L**][Al_F] was also confirmed in the gas phase (ESI-MS) and in solution (the ^{7}Li NMR spectrum comprises a 1:2:1 triplet).[19] Density functional theory (DFT) calculations indicate that, consistent with the lower basicity of siloxanes,[6] $\mathbf{D_6}$ has a binding energy towards Li^+ that is approximately 100 kJ mol^{-1} smaller than that of 18-crown-6,[11] while the binding affinity of **L** is comparable to that of $\mathbf{D_6}$.[19] The bonding in [Li**L**][Al_F] results primarily from the electrostatic interaction of Li^+ with donor electron pairs on three O and two P centers.

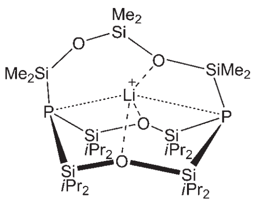


Figure 6. Binding mode of **L** in a Li^+ complex.

In summary, these recent findings highlight the importance of thermodynamic considerations in the formation of stable ionic metal complexes of cyclic dimethylsiloxanes and explain why previous attempts to make such complexes by direct reaction of the inorganic macrocycle with alkali-metal halides were doomed to failure. They also provide a cogent example of the effectiveness of WCAs in minimizing lattice-energy changes and cation–anion interactions.[13]

What are the implications for host–guest chemistry? Cyclophosphazenes $(Me_2PN)_n$, which are formally isoelectronic with the cyclosiloxanes $(Me_2SiO)_n$, also form an extensive homologous series of macrocyclic ligands.[20] The largest structurally characterized example is the twenty-four-membered ring $(Me_2PN)_{12}$.[21] To date the known complexes of these multidentate N-donor ligands are limited to late transition metals, for example, the neutral complexes $[\{(Me_2PN)_6\}MCl_2]$ (M = Pt, Pd)[22] and the ionic complex $[\{(Me_2PN)_8\}Co(NO_3)][NO_3]$[23] in which the cyclophosphazene behaves as a bi- or tetradentate ligand, respectively. The endocyclic coordination chemistry of cyclophosphazenes deserves to be revisited in the light of recent findings.[11,24]

Although the weaker basicity of cyclosiloxanes compared to that of organic polyethers will likely restrict the range of metal-ion complexes of $\mathbf{D}_n$, the observation of metal-templated ring transformations may be of considerable significance.[16,25] For instance, the series of polysilathianes $(R_2SiS)_n$ is limited to dimeric ($n = 2$) and trimeric ($n = 3$) ring systems even for small substituents (R = Me).[26] Templation of these S-donor ligands (or their Se analogues)[27] by soft metal cations may promote ring transformations to give larger Si–E (E = S, Se) rings.

Finally, the implications for ROP merit investigation. The cyclic systems $(Me_2SiO)_n$ ($n = 3, 4$) are known to serve as precursors for polydimethylsiloxane under the influence of cationic initiators, but the involvement of metal complexes in this ROP process has not been established.[28] Poly(dialkylphosphazenes), for example, $(Me_2PN)_n$ ($n = 5\times10^4$–2×10^5), are currently made by condensation methods from acyclic precursors;[29] the generation of these soluble inorganic polymers from cyclic precursors by metal-templated ROP is an interesting possibility.

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