Multi-electron reduction of bowl-shaped polyaromatic hydrocarbons: structural studies

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ABSTRACT

We have focused our work on the structural characterization of multi-charged fullerene fragments, focusing on their aggregation patterns with different alkali metals, as well as geometrical deformations, resulting from charge acquisition and metal binding. We have contributed to this field and recently accomplished the first structural characterization of alkali metal salts of mono-, di-, tri-, and tetrareduced corannulene. This dissertation reveals the binding preferences of Group 1 metals towards the non-planar π-surface of corannulene bearing various negative charges. For corannulene monoanion, the lightest alkali metals, Li⁺ and Na⁺, tend to yield solvent-separated ion pairs, whereas the heavier Rb⁺ and Cs⁺ ions prefer to form contact-ion pairs with a remarkable face selectivity in binding (exo-η⁶ vs. endo-η⁵, respectively). It was also demonstrated that Rb⁺–π interactions can be completely excluded by providing full metal ion encapsulation by crown ether. In addition, the first corannulene dianions have been recently crystallized with Li⁺, Na⁺, K⁺, and Cs⁺ counterions, showing a fascinating variation of metal binding modes based on X-ray crystallographic studies. The different binding modes of the corannulene dianion were also detected by ¹H NMR, EPR, and UV-vis spectroscopy. The first crystallographic characterization of C₂₀H₁₀⁻³ has also been accomplished in this work revealing that corannulene trianions show preference for self-assembly. They form novel and unique supramolecular aggregates with four alkali metal ions sandwiched between two triply-reduced bowls, [M₄(C₂₀H₁₀⁻³)]²⁻ (M = K or Cs).

For the tetrareduced corannulene, the formation of the supramolecular [Li₅(C₂₀H₁₀⁻⁴)]³⁻ sandwich, in which five Li⁺ ions are jammed between two corannulene decks, has been revealed by X-ray crystallographic and NMR studies. In
addition, it has been demonstrated that the sandwich aggregation is retained upon re-
crystallization of \([\text{Li}_5(\text{C}_{20}\text{H}_{10}^{4-})_2]^{3-}\) from THF in the presence of strong O-donors such as crown ethers and diglyme. However, the use of neat diglyme, for reduction of \(\text{C}_{20}\text{H}_{10}\)
with lithium, has prevented the high-order self-assembly of \(\text{C}_{20}\text{H}_{10}^{4-}\), according to our NMR investigations. The reduction of corannulene with lithium metal in DME revealed the formation of a unique \([\text{Li}_6/(\text{OR})_6/\text{Li}_6]^{6+}\) cluster core stabilized by two corannulene tetraanions, forming a remarkable penta-decker supramolecular aggregate. In addition, the unique reactivity and synergistic effect of mixed-metal reduction reactions of corannulene were investigated, revealing novel supramolecular aggregates in the solid-state accompanied by unprecedented shifts in \(^7\text{Li}\) NMR spectra.
ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to my scientific advisor and mentor, Prof. Marina A. Petrukhina. It has been a true privilege to have the opportunity to work in her laboratory and to be able to learn from her valuable and constructive suggestions during the development of this research project. I would like to thank her for always being patient, helpful, and understanding through any ups and downs, both on a personal and professional level. Her passion, enthusiasm, and knowledge of chemistry helped and encouraged me even through the most challenging moments of my graduate career. She has embedded beneficial qualities into my personality, which have helped me build confidence and motivated me to always strive to achieve the best in everything I undertake. She was without doubt the most influential person throughout my Ph.D. study.

I would like to thank my doctoral committee members, Prof. Eric Block, Prof. Evgeny V. Dikarev, Prof. Rabi A. Musah, and Prof. Paul J. Toscano. I appreciate the time and effort they spent in revising my research proposal and dissertation. Additionally, I would like to acknowledge Prof. Dikarev and Prof. Toscano for their inorganic lectures, which helped me better understand the organometallic component of my research project.

I want to thank our previous post-doctoral associate, Dr. Alexander V. Zabula, for helping me develop and perfect my synthetic skills. I was fortunate to be able to learn from such a talented chemist as him.

A special thanks to our X-ray Crystallographer, Dr. Alexander S. Filatov, for always being approachable and willing to explain challenging concepts. I have had the pleasure of working with him through my undergraduate career, which motivated me to pursue a Ph.D. in chemistry.
I want to thank Dr. Andrey Yu. Rogachev for computational studies shown throughout this work and Dr. Vladimir M. Grigoryants for recording EPR spectra.

I would like to thank all the staff of the Department of Chemistry, especially Brian Gabriel and Michele Janishak, for their expertise, which made reaching the end of my graduate studies a smooth process. Additionally, thank you to Dr. David S. Burz for always helping with instrumental and mechanical problems. He was always able to fix anything brought to him, which allowed the research process to continue uninterrupted.

I would also like to thank the former and present members of Prof. Petrukhina’s lab. I was lucky to be able to work with such a well-rounded group of people. Each has played a significant role in my graduate career and I wish them all luck in their future endeavors.

I want to thank my parents for always presenting me with opportunities and demonstrating the meaning of hard work. The values they have instilled into me were found to be priceless throughout my life. Also, I want to thank my sister, Kayleigh, for helping me understand the importance of separating priorities and making sure each is fulfilled.

Last but certainly not least, a special thank you to my husband, Matthew. He has the ability to motivate me when I need it the most. Without his support and encouragement, this degree would have not been possible.
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1. Bowl-Shaped Polyaromatic Hydrocarbons

1.1 Introduction

Buckybowls are a class of polycyclic aromatic hydrocarbons (PAHs) with a bowl-shaped open carbon framework structurally related to fullerenes.\textsuperscript{1,2,3,4,5} The first and smallest buckybowl, corannulene (C\textsubscript{20}H\textsubscript{10}, 1), was prepared by a tedious seventeen-step synthesis in 1966 by Barth and Lawton.\textsuperscript{6} Corannulene remained largely unexplored until two decades later when the first ball-like all carbon molecule, C\textsubscript{60}, was discovered by future Nobel Prize winners, Kroto, Heath, and Smalley in 1985 in the products of graphite vaporization.\textsuperscript{7} This sparked a renewed interest in corannulene, which represents the \( \frac{1}{3} \) subunit of C\textsubscript{60}. Although corannulene is still not commercially available, alternative and more efficient synthetic methods have been developed since 1966, leading to an increased desire for exploration of this unique buckybowl and its properties.\textsuperscript{8,9,10,11}

All geodesic polyarenes, both open (e.g. bowls) and closed (e.g. fullerenes), are characterized by curved \( \pi \)-systems composed of pyramidalized carbon atoms.\textsuperscript{12} The C\textsubscript{60}-fullerene, consists of 20 six-membered rings and 12 five-membered rings; the five-membered rings provide the curvature (Figure 1). C\textsubscript{60} has a curved but fully conjugated polycyclic 60 \( \pi \)-electron system with an empty space inside.

![Figure 1. Buckminsterfullerene, C\textsubscript{60} (left), and corannulene, C\textsubscript{20}H\textsubscript{10} (right).](image-url)
The discovery of fullerenes triggered a very broad interest in the chemistry of buckybowls because of the role non-planar carbon-rich polyarenes can play in multidisciplinary fields, such as electrical materials science, catalysis, and pharmaceutics. Additionally, the industrial production of C_{60} generates fullerene waste. During decomposition, fullerenes may undergo fragmentation to form buckybowls, which will then enter the environment. Thus, knowledge about their physical and chemical properties is of great importance.

Other open geodesic polyaromatic molecules comprised of five- and six-membered rings that map onto the C_{60} surface are sumanene, C_{21}H_{12}; hemibuckminsterfullerene, C_{30}H_{12}; circumtrindene, C_{36}H_{12}; and indeno[1,2,3-cd]circumtrindene, C_{42}H_{14} (Figure 2).

![Figure 2. Sumanene (a), hemibuckminsterfullerene (b), circumtrindene (c), and indeno[1,2,3-cd]circumtrindene (d).](image)

Buckybowls, such as the fullerene fragments shown above, serve as key models for theoretical and experimental studies of fullerenes and nanotubes. It was demonstrated that curved PAHs can serve as prospective starting materials for the complete synthesis.
of fullerenes and caps of nanotubes. Furthermore, the discovery of fullerenes and fullerene fragments has opened a new research area in organometallic and coordination chemistry: the study of metal binding to non-planar $\pi$-surfaces. Buckybowls share with fullerenes the convex three-dimensional unsaturated carbon surface. Contrary to fullerenes, buckybowls also possess an open concave $\pi$-carbon face that is sterically available for binding, making them exceptional $\pi$-ligands for further investigation.

1.2 Synthesis of Corannulene

Corannulene has been a desirable synthetic target since Lawton and Barth successfully prepared it by a tedious seventeen-step synthesis. Although the overall yield was quite low and only a limited amount of corannulene was available for further studies, the reported $^1$H NMR spectrum indicated the magnetic equivalence of all ten rim hydrogen atoms. Moreover, some electrochemical studies showed a reversible reduction of corannulene to its radical anion and most likely a dianion. Most importantly, the single crystal X-ray study revealed that corannulene was indeed bowl-shaped.

A major breakthrough occurred in 1991 when Scott and coworkers developed a new convenient method, flash vacuum pyrolysis (FVP), for the synthesis of this remarkable compound, C$_{20}$H$_{10}$ (Scheme 1). Using this procedure, corannulene can now be prepared in milligram quantities.
Flash vacuum pyrolysis is a synthetic tool, in which planar PAHs are heated to very high temperatures (900-1100 °C). Under FVP conditions, aromatic rings in PAHs are capable of bending and stretching, thus producing reactive intermediate species. Practically, the precursor sample is sublimed in a quartz tube, under reduced pressure, and the converted product is collected near the cold trap. A flow of nitrogen is used to help large molecules pass through the hot zone. The pressure is generally kept in the range of 0.1–1.0 mmHg.²

Several limitations with the FVP method quickly arose:²,²⁰

- The amount of starting material that can be used is low
- The precursors are volatile
- The yields are low
- Functionalization of the framework is prohibited
• Some starting materials may polymerize before sublimation takes place

Regardless of the indisputable success of the FVP method for the production of C_{20}H_{10}, a synthesis resulting in higher yields was necessary in order to obtain corannulene in gram quantities. Solution phase synthesis of corannulene resurfaced in 2001 after being dormant for several years. Based on the non-pyrolytic procedure established by Siegel to form 2,5-dimethylcorannulene, Sygula et al. developed an approach to produce corannulene from tetrabromocorannulene (Scheme 2).^{21,22}

**Scheme 2:**

The work by Sygula offered a practical method for the synthesis of corannulene, resulting in a reproducible overall yield of approximately 70%. Several synthetic advantages are observed when using tetrabromocorannulene as a precursor to corannulene. The procedure is a macro-scale synthesis, which has the potential to produce corannulene in moderate quantities. A brief reflux of 15 minutes is all that is required to produce tetrabromocorannulene from octabromofluoranthene. The resulting tetrabromocorannulene can be converted without difficulty to a number of derivatives of corannulene by standard coupling procedures. Additionally, tetrabromocorannulene can
be easily debrominated to the parent corannulene in 90% yield by refluxing with KI and Zn powder in ethanol. Unlike previous work, the current procedure does not entail any time consuming high dilution techniques nor anhydrous/oxygen-free conditions; therefore, this procedure is the most convenient large-scale synthesis of C_{20}H_{10} available today.\textsuperscript{11,22} With help from our collaborators at Boston College, the synthesis developed by Sygula \textit{et al.} has been adapted in our laboratory.\textsuperscript{11}

Recently, an even more efficient synthesis of C_{20}H_{10} has been developed by Siegel \textit{et. al} to obtain corannulene in kilogram quantities. Among the benefits of this procedure are that the amounts of solvent and reagents (per gram of product) were greatly reduced. In addition, improvements of product purification were reported, without the need of column chromatography.\textsuperscript{23}

### 1.3 Coordination of Corannulene and Other Fullerene Fragments

Complexes of transition metals with curved polyaromatic hydrocarbons have attracted substantial interest in recent years due to their fundamental and practical importance. From a coordination viewpoint, bowl-shaped polyarenes are unique and intriguing π-ligands, which provide interior and edge carbon atoms for binding, along with the concave and convex unsaturated carbon surfaces (Figure 3).\textsuperscript{17} For example, several specific C=C bond sites can be considered for corannulene such as the rim, hub, flank, and spoke carbon atoms.
Both $\sigma$- and $\pi$-metal complexes of corannulene with transition metals have been isolated and structurally and spectroscopically characterized.\textsuperscript{17} Organometallic corannulene derivatives with nickel and platinum $\sigma$-bonded to the edge have been prepared by oxidative addition of bromocorannulenes to Ni(COD)$_2$/2PEt$_3$ or Pt(PEt$_3$)$_4$. It was demonstrated that the corannulene core can undergo organometallic reactions on the rim carbon, which are comparable to planar aromatic systems.\textsuperscript{24} Further research into corannulene coordination chemistry has taken place, including structural investigation of multisubstituted halo- and ethynylcorannulenes.\textsuperscript{25,26}

In 1997, Siegel’s group isolated and spectroscopically characterized the first $\pi$-metal complex of corannulene, $[(\eta^6$-C$_{20}$H$_{10})$Ru(C$_5$Me$_5$)]$^+$.\textsuperscript{27} Shortly after, Sygula et al. demonstrated by NMR spectroscopy the formation of two new complex species: [Ir(C$_5$Me$_5$)($\eta^6$-corannulene)]$^{2+}$ and [Ir(C$_5$Me$_5$)($\eta^6$-tetramethylcorannulene)]$^{2+}$.\textsuperscript{28} This showed potential for coordination of corannulene to a variety of transition metals.

The first structural characterization of $\eta^6$-coordinated corannulene, [((RuCp*)$_2$($\mu_2$-$\eta^6$:$\eta^6$-C$_{20}$H$_{10}$)(PF$_6$)$_2$)], was accomplished by Angelici and coworkers in 2004 (Figure 4).\textsuperscript{29} This work demonstrated the influence transition metals have on non-planar PAHs.
metal binding of the RuCp* units to corannulene significantly affected the shape of the bowl, nearly flattening its surface completely.²⁹ By now, the class of η⁶-corannulene metal complexes has expanded drastically. Recently, complexes of the type [(η⁶-arene)M(η⁶-C₂₀H₁₀)]X₂ (M = Ru or Os; X = BF₄⁻, PF₆⁻, or SbF₆⁻; η⁶-arene = C₆Me₆, C₆HMe₅, C₆EtMe₅, or cymene) have been prepared.³⁰ X-ray diffraction studies have indicated the strong preference of convex metal coordination in all discrete complexes having a single metal bound to corannulene in a η⁶-mode.¹⁷

Figure 4. Transition metal η⁶-complexes involving the convex surface of corannulene of Ru⁺ (a), Rh⁺ and Ir⁺ (b), and η²-η²-η²-η¹-bound Ag⁺ (c).

In 2005, three silver(I) complexes, consisting of Ag⁺ cations bound to the rim position of corannulene in an η² and η¹-fashion, were structurally characterized. The metal was found outside the bowl, reinforcing the fact that metal atoms favor coordination to corannulene in a convex manner (Figure 4).³¹

In our laboratory, gas phase, solvent-free complexation reactions of arenes with volatile electrophilic metal complexes, such as Rh(II), Ru(II), and Ru(I) complexes, were used to investigate the preferred binding sites of corannulene.¹⁷,³²-³⁵ This micro-scale deposition technique was very efficient in isolation of single crystals of corannulene-
based metal complexes, which allowed their first X-ray structural characterization. Our
group demonstrated the preference of the strong Lewis acidic complexes of Rh(II) and
Ru(I) to coordinate to corannulene at the rim carbon atoms in an $\eta^2$-fashion.\textsuperscript{17} These gas
phase coordination reactions were later expanded by our group to bowls larger than
corannulene, such as C\textsubscript{20}H\textsubscript{9}Br,\textsuperscript{32} C\textsubscript{28}H\textsubscript{14},\textsuperscript{33} C\textsubscript{26}H\textsubscript{12},\textsuperscript{34} C\textsubscript{30}H\textsubscript{12},\textsuperscript{35} and C\textsubscript{40}H\textsubscript{50}\textsuperscript{17} (Table 1).\textsuperscript{17}
<table>
<thead>
<tr>
<th>Formula</th>
<th>Side view,(^a)</th>
<th>Coordination modes,(^b)</th>
<th>Bowl depth in a free form (Å)</th>
<th>Bowl depth in a complexed form (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(<em>{20})H(</em>{10})</td>
<td><img src="image" alt="C({20})H({10}) side view" /></td>
<td><img src="image" alt="Coordination modes" /></td>
<td>0.875(2)</td>
<td>(\mu_2-\eta^2:\eta^2) 0.839(3) (\mu_3-\eta^2:\eta^2:\eta^2) 0.861(3) (\eta^1) 0.940(4) (\eta^2) 0.860(1)</td>
</tr>
<tr>
<td>C(_{20})H(_9)Br</td>
<td><img src="image" alt="C(_{20})H(_9)Br side view" /></td>
<td><img src="image" alt="Coordination modes" /></td>
<td>0.862 (calc)(^c)</td>
<td>(\mu_2-\eta^2:\eta^2) 0.808(2) (\mu_3-\eta^2:\eta^2:\eta^2) –</td>
</tr>
<tr>
<td>C(<em>{28})H(</em>{14})</td>
<td><img src="image" alt="C({28})H({14}) side view" /></td>
<td><img src="image" alt="Coordination modes" /></td>
<td>0.830(3)</td>
<td>(\mu_3-\eta^2:\eta^2:\eta^2) 0.770(3)</td>
</tr>
<tr>
<td>C(<em>{26})H(</em>{12})</td>
<td><img src="image" alt="C({26})H({12}) side view" /></td>
<td><img src="image" alt="Coordination modes" /></td>
<td>1.065(4)</td>
<td>(\mu_4-\eta^2:\eta^2:\eta^2:\eta^1) 1.148(6)</td>
</tr>
<tr>
<td>C(<em>{30})H(</em>{12})</td>
<td><img src="image" alt="C({30})H({12}) side view" /></td>
<td><img src="image" alt="Coordination modes" /></td>
<td>2.41(4)(^c)</td>
<td>(\mu_4-\eta^2:\eta^2:\eta^2:\eta^1) –</td>
</tr>
</tbody>
</table>

\(^a\) Hydrogen atoms are omitted for clarity.  
\(^b\) Only one metal atom of each dimetal unit is shown.  
\(^c\) Severe disorder of C\(_{20}\)H\(_9\)Br and C\(_{30}\)H\(_{12}\) precludes obtaining accurate bowl depth values in the X-ray structures of their complexes.
Despite all prior examples of the preferential coordination of metal centers to the convex surfaces of buckybowls, the inside concave carbon face can also be engaged in metal coordination. In 2007, the first concave-bound complex of cyclopentadienyl iron and sumanene, C_{21}H_{12}, was synthesized. The metalation of sumanene was achieved by ligand exchange with a cyclopentadienyl group of ferrocene, resulting in the \( \pi \)-bowl \textit{endo} complex, \([(\eta^5-C_5H_5)Fe(\eta^6-C_{21}H_{12})]\) (Figure 5).  

![Figure 5. Endo bound \([(\eta^5-C_5H_5)Fe(\eta^6-C_{21}H_{12})]^+ cation.](image)

Shortly thereafter in 2010, the ruthenium analog, \([(\eta^5-C_5H_5)Ru(\eta^6-C_{21}H_{12})]^+\), was synthesized in a similar way to the iron complex. However, the Ru complex exhibits both \textit{endo} and \textit{exo} binding of the metal center to the corannulene core in solution. Nevertheless, in the solid state, the Ru metal center is coordinated to C_{20}H_{10} on the concave surface. The major and minor species observed by NMR were assigned to the concave and convex sumanene Ru-complexes, respectively. The preference for inversion between the concave and convex isomers was suggested to depend on the solvent and/or temperature. The discovery of both \([(\eta^5-C_5H_5)Fe(\eta^6-C_{21}H_{12})]^+\) and \([(\eta^5-C_5H_5)Ru(\eta^6-C_{21}H_{12})]^+\) by Hirao \textit{et al.} demonstrates that buckybowls serve as excellent multisite ligands capable of both concave and convex binding of metal centers to their curved \( \pi \)-carbon surfaces.
1.4 Redox Properties of Corannulene

Reduction of non-planar polycyclic carbon-rich compounds with alkali metals, structural deformation of the resulting carbanions and their supramolecular aggregation have been the subject of intensive research during the last 20 years. It has been demonstrated that carbon allotropes with curved \( \pi \)-surfaces can substitute graphite and serve as prospective anode materials for the fabrication of Li-ion batteries. In this regard, bowl-shaped carbon-rich polyaromatic hydrocarbons have been widely used as useful and effective models for investigation of fullerenes and nanotubes and their alkali metal intercalated products.

The first observation of a corannulene anion was reported back in 1967, soon after the preparation. Barth and Lawton first visualized neutral corannulene as an “annulene-within-annulene”. In other words, \( \text{C}_{20}\text{H}_{10} \) was thought to consist of cyclopentadienyl ([5]-annulene) anion (6\( \sigma \)/5C) and [15]annulene cation (14\( \sigma \)/15C). The lowest unoccupied molecular orbital (LUMO) of this unique bowl-shaped molecule is rather low-lying and doubly degenerate. This accounts for the interesting redox behavior of \( \text{C}_{20}\text{H}_{10} \), which can accept up to four electrons. Over the past few decades, considerable research into multiple reduction stages of corannulene by different alkali metals (Li, Na, K, Rb, and Cs) has been underway using optical absorption, ESR, and nuclear magnetic spectroscopy. Although the formation of multiply-charged anions of corannulene ranging from \( \text{C}_{20}\text{H}_{10}^- \) to \( \text{C}_{20}\text{H}_{10}^{4-} \) has been detected in solutions, their crystallographic investigation was lagging behind due to their extreme sensitivity towards air and moisture. Previously, the solid-state characterization of bowl-shaped carbanions...
has been restricted to the lithium salts of the acepentalene and tribenzacepentalene dianions.\textsuperscript{47}

1.4.1 Monoanions

The variable-temperature ESR studies for the Li and Na-doped corannulene monoanion in THF were previously reported by Sato \textit{et al}.\textsuperscript{46b} It was found that the ESR signals at room temperature for the C\textsubscript{20}H\textsubscript{10}\textsuperscript{−} anions with solvent separated Li\textsuperscript{+} (or Na\textsuperscript{+}) cations are composed of 11 equally spaced peaks with hyperfine coupling constants (Figure 6), whereas the ESR spectra at low temperatures are more complicated owing to the lowering of the symmetry for the corannulene-monoanion (Jahn-Teller effect).

\textbf{Figure 6.} ESR spectrum of Li\textsuperscript{+} and Na\textsuperscript{+}-dopped corannulene monoanions (in THF).

1.4.2 Dianions

The corannulene dianions, generated using lithium or potassium as the reducing agent, were investigated by variable-temperature \textsuperscript{1}H NMR studies. The resonance signals in the \textsuperscript{1}H NMR spectra for the protons of the paratropic corannulene dianion appear only at low temperatures as very broad signals at $\delta = -5.6$ ppm (Figure 7).\textsuperscript{38b}
1.4.3 Trianions

The paramagnetic C\textsubscript{20}H\textsubscript{10}\textsuperscript{3−} radical was detected by ESR spectroscopy by \textit{in-situ} reduction of corannulene with lithium metal in THF.\textsuperscript{38b} It is the only evidence of the existence of this species in solution, as the initially reported UV-vis spectroscopic data for the C\textsubscript{20}H\textsubscript{10}\textsuperscript{3−} trianion\textsuperscript{38c} was later re-assigned to the tetrareduced state of corannulene.\textsuperscript{38b}

1.4.4 Tetraanions

The self-assembly of the tetraanion of corannulene in solution was predicted by NMR spectroscopy and attracted substantial interest within the past few decades. Low resolution \textsuperscript{7}Li NMR spectroscopy studies revealed two signals of almost equal intensity at \textdegree60°C (Figure 8).\textsuperscript{38a} One broad band appears at −4.5 ppm, whereas, a much narrower band appears at −11.7 ppm. The authors conclude that the peak at −4.5 ppm can be
attributed to the exterior Li ions. While, the signal at $-11.7$ ppm comes from lithium cations that are sandwiched between two tetrareduced corannulene moieties.$^{38a}$

![Variable-temperature $^7$Li NMR spectra for C$_{20}$H$_{10}$$_{4}^-$](image)

**Figure 8.** Variable-temperature $^7$Li NMR spectra for C$_{20}$H$_{10}$$_{4}^-$. $^{38a}$

Based on these data, the structure was proposed to have eight lithium ions which distribute themselves above, below, and between the two corannulene tetraanions (Figure 9).$^{38a}$ In addition to NMR studies, semi-empirical calculations have also supported the aggregation of corannulene tetraanions to form a dimeric supramolecular aggregate.

![Formal representation of corannulene tetraanions (disks) and eight lithium cations (balls) in a dimer](image)

**Figure 9.** Formal representation of corannulene tetraanions (disks) and eight lithium cations (balls) in a dimer.$^{38a}$
One setback with the postulated dimer shown in Figure 9 is the incompatibility of this picture with the observed equivalence of the two tetraanion partners in each dimer based on $^1$H and $^{13}$C NMR data. Despite this discrepancy, this assignment has served as a model for the aggregation of the reduced buckybowls and fullerenes with Li$^+$ since then.\textsuperscript{40} This model has never been proven. No investigations concerning the solid state structure of the unique corannulene-based dimer or any highly reduced anions of buckybowls were reported, owing to their exceptional sensitivity towards air and moisture. We therefore set up to closely look into these processes and target the isolation of solid crystalline products for structural investigations.
1.5 References


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33 Petrukhina, M. A.; Andreini, K. W.; Tsefrikas, V. M.; Scott, L. T., Unprecedented Complexation of Two Transition Metals to the Concave Surface of a Geodesic Polyarene: $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]_3(\text{dibenzo}[a,g]\text{corannulene})_2\}$. Organometallics 2005, 24, 1394–1397.


2. Controlled Reduction of Corannulene

2.1 Introduction

The addition of electrons to corannulene initially results in generation of an intense green solution (monoanion), which subsequently endures higher reduction and transforms to a deep purple solution (di- and/or trianion). Finally, the furthest reduction stage of corannulene, with Li metal only, can be detected by the appearance of a brown solution (tetraanion). Considering the low molecular weight of Li and micro-scale of reduction reactions, it is impracticable to weigh the suitable amount of the metal to obtain the mono-, di-, and trianion of C_{20}H_{10}. However, we are able to reduce corannulene to the tetraanion stage and add the appropriate amount of neutral corannulene in order to obtain the desired anionic species (Scheme 3, Reactions 1-3).

Scheme 3:

- **Monoanions**: \[3\text{C}_{20}\text{H}_{10} + \text{C}_{20}\text{H}_{10}^{4-} \rightarrow \text{4C}_{20}\text{H}_{10}^{-} \quad (1)\]
- **Dianions**: \[\text{C}_{20}\text{H}_{10} + \text{C}_{20}\text{H}_{10}^{4-} \rightarrow \text{2C}_{20}\text{H}_{10}^{2-} \quad (2)\]
- **Trianions**: \[\text{C}_{20}\text{H}_{10} + 3\text{C}_{20}\text{H}_{10}^{4-} \rightarrow \text{4C}_{20}\text{H}_{10}^{3-} \quad (3)\]
- **Tetraanions**: \[\text{excess Li} + \text{C}_{20}\text{H}_{10} \rightarrow \text{C}_{20}\text{H}_{10}^{4-} \quad (4)\]

In contrast to Li, other alkali metals, such as Na, K, and Rb, are believed to reduce corannulene to the dianionic state (over a 24 hour time period). The dianion, C_{20}H_{10}^{2-}, can be readily obtained by reacting corannulene with an excess of these alkali metals (Scheme 4, Reaction 2). When the monoanion of corannulene is the desired product, we simply add one equivalent of neutral corannulene to the in-situ generated dianions (Scheme 4, Reaction 1).
Scheme 4:

\[
\begin{align*}
\text{Monoanions:} & \quad C_{20}H_{10}^+ + C_{20}H_{10}^{2-} \rightarrow 2C_{20}H_{10}^- \\
\text{Dianions:} & \quad \text{excess } M + C_{20}H_{10} \rightarrow C_{20}H_{10}^{2-} \\
&M: \text{Na, K, Rb}
\end{align*}
\]

Using cesium as the reducing agent, the highest reduction state is thought to be the trianion.\(^2\) Due to the higher molecular weight of Cs, it is realistic to weigh the suitable amount of the metal to obtain the mono-, di-, and trianion of \(C_{20}H_{10}\) in a controlled fashion.

It should be noted that previously, very broad signals of the resulting tetraanions (with K, Rb, and Cs) have been detected in the \(^1\)H NMR spectra at low temperatures, indicating possible mixing with a paramagnetic trianion radical or an energetically close triplet state.\(^{1d,3}\) In our experience, even with very extended time (up to two months), the tetraanions were not observed as a major product with these metals.

The solvents used in reduction reactions were also given substantial attention. It is well known that the use of different coordinating solvents can affect the metal binding to the aromatic system.\(^4\) These procedures can be performed in tetrahydrofuran (THF), dimethoxyethane (DME), dioxane, or diglyme (Figure 10). However, we found that reaction times in DME must be limited in order to prevent the Li-induced solvent fragmentation (Section 5.4).\(^5\)
Tetrahydrofuran, dimethoxyethane, and diglyme are the most efficient solvents that have been used in our laboratory thus far. Additional coordinating solvents, such as tetramethylethylenediamine and trimethylamine, have been tried; however corannulene is only sparingly soluble in these solvents. Moreover, reactions can be performed with or without the addition of different crown ethers (Figure 11). Typically, 12-crown-4 (C$_{8}$H$_{16}$O$_{4}$) is used for Li, 15-crown-5 (C$_{10}$H$_{20}$O$_{5}$) is used for Na, and 18-crown-6 (C$_{12}$H$_{24}$O$_{6}$) is used for K.

**Figure 10.** Tetrahydrofuran (a), dimethoxyethane (b), 1,4-dioxane (c), and diglyme (d). Hydrogen atoms are omitted.

**Figure 11.** 12-crown-4 (a), 15-crown-5 (b), and 18-crown-6 (c). Hydrogen atoms are omitted.
2.2 Monoanions

2.2.1 Lithium Salts

2.2.1.1 [Li(DME)₃][C₂₀H₁₀⁻]

Various crystallization techniques have been applied and lead to the successful isolation of several new lithium salts of monoreduced corannulene (1⁻).⁶ The first corannulene monoanions with lithium countercations were obtained as dark green blocks, in moderate yield, from the DME solution layered with hexanes. According to an X-ray diffraction study, the resulting [Li(DME)₃][1⁻] (2) product crystallizes in the Pn space group. This is the first example of a polar space group for charged buckybowls (Figure 12). Two crystallographically independent [Li(DME)₃]⁺ cations and C₂₀H₁₀⁻ anions with essentially close geometrical parameters (within the limits of experimental error) have been observed in the unit cell. One ion pair is depicted in Figure 12. The [Li(DME)₃]⁺ cation is solvent-separated from 1⁻ and has its metal center in an octahedral environment. The Li···O separations for the hexacoordinated Li⁺ ions are (2.071(6)–2.202(7) Å).

![Figure 12](image_url)

**Figure 12.** Molecular structure of 2 (a) along with the space filling depiction of the solid state packing (b) blue and purple colors are attributed to the corannulene monoanions and counterions, respectively).
The isolation of the “naked” C_{20}H_{10}^{−} anion allows the evaluation of geometric parameters for monoreduced corannulene without the influence of metal binding. The hub C–C bond lengths of the “naked” C_{20}H_{10}^{−} anion (av. 1.403 Å) are slightly shortened in 2 compared to the parent bowl (av. 1.415 Å).\textsuperscript{7} The spoke C–C bonds (av. 1.407 Å) are slightly elongated vs. those in neutral corannulene (av. 1.379 Å), whereas considerable elongation of the rim C–C bonds (1.4178 Å) is observed compared to C_{20}H_{10} (1.383 Å). The addition of one negative charge causes only slight flattening of the bowl depth of corannulene (0.841(5) Å vs. 0.875(2) Å for neutral C_{20}H_{10}) (Table 2).\textsuperscript{7}

**Table 2.** Key distances (in Å) for neutral C_{20}H_{10} and C_{20}H_{10}^{−} in 2.

<table>
<thead>
<tr>
<th></th>
<th>C_{20}H_{10}^{0}</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>hub</td>
<td>1.411(2)–1.417(2)</td>
<td>1.389(5)–1.425(5)</td>
</tr>
<tr>
<td>spoke</td>
<td>1.376(2)–1.381(2)</td>
<td>1.392(5)–1.417(5)</td>
</tr>
<tr>
<td>flank</td>
<td>1.441(2)–1.450(2)</td>
<td>1.388(5)–1.462(5)</td>
</tr>
<tr>
<td>rim</td>
<td>1.377(2)–1.387(2)</td>
<td>1.396(6)–1.453(6)</td>
</tr>
<tr>
<td>bowl depth</td>
<td>0.875(2)</td>
<td>0.841(5)</td>
</tr>
</tbody>
</table>

Notably, rather short separations are found between the hydrogen atoms of DME molecules of [Li(DME)\textsubscript{3}]\textsuperscript{+} with the concave and convex faces of C_{20}H_{10}^{−} (2.67 and 2.75 Å, respectively) in the crystal lattice of 2 (Figure 12b). The C_{20}H_{10}^{−} bowls are aligned in
the direction of one dipole in the solid state (Figure 12b), and that may provide interesting conductive properties of 2 owing to its non-reduced dipole moment.8

2.2.1.2 [Li(15-crown-5)]2[C20H10−]

Crystals of [Li(15-crown-5)]2[1−]2 (3) were obtained from the THF solution by slow diffusion of hexanes. An X-ray diffraction study of 3 revealed the presence of the “naked” 1− anions and the centrosymmetric dicationic [Li(15-crown-5)]22+ moiety (Figure 13a). In the [Li(15-crown-5)]22+ dimer, the pentacoordinated Li+ ions are bound to four oxygen atoms of 15-crown-5 ether (2.039(4)−2.216(4) Å). The resulting Li···O distances are similar to the separations for the hexacoordinated Li+ ions in 2 (2.071(6)−2.202(7) Å). Moreover, lithium ions gain electron density from the oxygen atom of the neighboring [Li(15-crown-5)]+ fragment with the short Li···O contact of 1.951(3) Å.

Figure 13. Molecular structure of 3 (a) along with the space filling depiction of the solid state packing (b).
Although the rotational disorder of the corannulene monoanion in 3 precludes accurate measurements of its geometrical parameters, it is clearly seen that both the convex and concave faces of C_{20}H_{10}^- are involved in weak intermolecular interactions with hydrogen atoms of the crown ether moieties. The shortest C−H crown···π separation is measured at 2.61 Å (Figure 13b). The occupation of the open concave cavity by non-metal species was previously observed for functionalized corannulene cations, illustrating good host capabilities of this π-bowl.

### 2.2.2 Sodium Salts

#### 2.2.2.1 [Na(18-crown-6)][C_{20}H_{10}^-] and [Na(THF)_2(18-crown-6)][C_{20}H_{10}^-]

Numerous crystallization techniques have been applied and lead to the successful isolation of several new sodium salts of 1^-.

Dark green needle- and block-shaped crystals of the sodium salt of corannulene monoanion (4) have been grown by layering the THF solution with hexanes. According to the X-ray diffraction studies, the needles were found to be [Na(18-crown-6)][1^-] (4a, Figure 14), whereas the blocks also contain two THF molecules coordinated to the sodium ion, [Na(THF)_2(18-crown-6)][1^-] (4b, Figure 15). Two [Na(18-crown-6)]^+ moieties in 4a are linked together through intermolecular Na···O interactions with the formation of the centrosymmetric dicationic dimer. The Na···O interatomic separations within the dimer (2.461(1)−2.651(2) Å) are close to those observed for the solvated Na^+ ions. In contrast to 4a, the [Na(18-crown-6)]^+ moiety in 4b coordinates two THF molecules in apical positions. The resulting Na···O_{THF} bond lengths (2.307(3) Å and 2.309(2) Å) are significantly shorter than equatorial Na···O_{crown} separations (2.547(5)−2.776(6) Å).
In both 4a and 4b, full encapsulation of Na\(^{+}\) ions by O-donor ligands precludes any metal-\(\pi\) interactions with the bowl, affording “naked” C\(_{20}\)H\(_{10}\)\(^{-}\). The hub and flank C–C bond lengths of C\(_{20}\)H\(_{10}\)\(^{-}\) (av. 1.413(3) Å and 1.441(3) Å) remain essentially unchanged in 4a compared to the parent bowl (av. 1.415(2) Å and 1.446(2) Å) (Table 3).\(^7\)
However, the spoke and rim C–C bonds (av. 1.396(3) Å and 1.398(3) Å) are slightly elongated compared with those in neutral corannulene (av. 1.379(2) Å and 1.383(2) Å).

Table 3. Key distances (in Å) for neutral C_{20}H_{10} and C_{20}H_{10}− in 4a, 4b, 5, 6, and 7.

<table>
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</tbody>
</table>

Some differences in geometrical parameters of C_{20}H_{10}− in 4a and 4b (Table 3) can be explained by the engagement of monoanions, being free of any interaction with the sodium cations, in various C–H⋯π interactions.\textsuperscript{8b,12} The corannulene bowls in 4a are linked together into a 1D polymeric chain \textit{via} the T-contacts between the hydrogen atoms of C_{20}H_{10}− and the convex face of the neighboring anions (Figure 16, left). The
corresponding shortest H···C and H···C$_6$(centroid) distances (2.80 Å and 2.60 Å, respectively) are close to the related C–H···π contacts, observed in corannulene (2.66 Å (H···C) and 2.59 Å (H···C$_6$(centroid))). In addition, the cations are weakly bound to the resulting layers of bowl-shaped anions to form a 2D network based on interactions of hydrogen atoms of 18-crown-6 ether with the concave and convex faces of C$_{20}$H$_{10}$$^–$. Similar anion-cation contacts can also be found in 4b (Figure 16, right).

**Figure 16.** Space-filling depictions of polymeric networks in 4a (left) and 4b (right). Black and gray colours represent corannulene monoanions and counter-ions, respectively.

2.2.2.2 [Na(15-crown-5)(diglyme)][C$_{20}$H$_{10}$$^–$]

We continued to explore how the structure and size variations of macrocyclic crown ethers can be further used for tuning the alkali metal binding in such systems. Crystals of the new sodium adduct, [Na(15-crown-5)(diglyme)][1$^–$] (5), were grown by layering the diglyme solution with hexanes. Similar to 4a and 4b, an X-ray diffraction
study revealed the presence of the solvent-separated C$_{20}$H$_{10}$\textsuperscript{−} anions and sodium cations, [Na(15-crown-5)(diglyme)]\textsuperscript{+} (Figure 17).

**Figure 17.** Molecular structure (left) and solid state packing (right) of 5.

In 5, the Na\textsuperscript{+} ion is bearing one 15-crown-5 moiety and one diglyme molecule with the corresponding Na···O bond length distances ranging from 2.377(3)–2.569(3) Å. It should be noted that only two oxygen atoms of diglyme are bound to the sodium ion (the third Na···O separation is 4.606(3) Å). In general, the resulting Na···O$_{\text{diglyme}}$ bond lengths (2.377(3) Å and 2.434(3) Å) are shorter than the Na···O$_{15\text{-crown-5}}$ separations (2.413(3)–2.569(3) Å). This full encapsulation of Na\textsuperscript{+} centers precludes any interactions between the alkali metal ions and the curved surface of 1\textsuperscript{−}.

In general, the geometrical parameters of C$_{20}$H$_{10}$\textsuperscript{−} in 5 (Table 3) show only minor deviations from other lithium and sodium salts containing corannulene monoanions. The hub and flank C–C bond lengths of C$_{20}$H$_{10}$\textsuperscript{−} remain essentially unchanged in 5 compared to the parent bowl (Table 3).\textsuperscript{7} However, the spoke and rim C–C bonds are slightly elongated compared with those in neutral corannulene. Moreover, the bowl depth of the
“naked” $\text{C}_{20}\text{H}_{10}^-$ in 5 (0.85 Å) is similar to other corannulene monoanions with solvent-separated counterions. They all show that the acquisition of one electron only slightly reduces the corannulene bowl depth (Table 3). Furthermore, the concave and convex surfaces of corannulene in 5 are engaged in C–H···π interactions (2.68 and 2.81 Å, respectively); similar behavior was observed for salts 2–4.

2.2.2.3 $[\text{Na(DME)}_3][\text{C}_{20}\text{H}_{10}^-]$ and $[\text{Na(THF)}_3][\text{C}_{20}\text{H}_{10}^-]$

Solvents showed a considerable effect on the outcome of the coordination of sodium cations to planar perylene, $\text{C}_{20}\text{H}_{12}$. Single crystal X-ray diffraction studies demonstrated three different binding modes when perylene was reduced with Na to the dianions in the presence of different coordinating solvents (Figure 18). When monoglyme is used as a solvent, $\eta^6$-coordination of Na$^+$ is exhibited, whereas, the use of tetruglyme resulted in an $\eta^2$-coordination of the metal center to perylene dianion. The use of diglyme resulted in the formation of solvent-separated ion pairs.
We set out to use different coordinating solvents as an additional controlling factor for switching on/off interactions between metals and buckybowl anions. Dark green prisms of $[\text{Na(DME)}_3][\text{C}_{20}\text{H}_{10}^-$], 6, were isolated from DME in moderate yield. Similar to 4 and 5, the $\text{C}_{20}\text{H}_{10}^-$ anions in 6 were solvent-separated from $[\text{Na(DME)}_3]^+$ cations (Figure 19). The hexacoordinated Na$^+$ ions are fully encapsulated by six oxygen atoms of three DME molecules with Na···O separations of (2.365(3)–2.432(3) Å).
Figure 19. Molecular structure of 6 (left) and 7 (right).

Unlike all prior sodium-generated corannulene monoanions, the reduction of corannulene to the monoanion stage in THF resulted in a contact-ion pair, [Na(THF)_3][C_{20}H_{10}^–] (7). The Na⁺ ion is coordinated to the exo surface of the corannulene moiety in an η⁶-fashion (Figure 19). The corresponding Na···C distances are 2.751(5)–3.510(6) Å. The sodium ion in 7 is additionally bound to three THF molecules with the corresponding Na···O distances of 2.242(4)–2.268(4) Å. These Na···O separations are notably shorter than those observed in 6.

Despite different overall structures of 6 and 7, the changes in the geometry of monoreduced corannulene are rather similar (Table 3). The hub and flank C–C bond lengths of C_{20}H_{10}^– in both cases are close to those measured in neutral corannulene, whereas in 7, the spoke C–C bonds are notably elongated. The rim C–C bonds are longer
in 6 when compared to the neutral ligand. The corannulene monoanion with the Na\(^+\) ion coordinated to the curved surface is slightly flatter than the “naked” 1\(^-\) in sodium salts 4–6 (0.83 Å vs. 0.85 Å). Overall, the presence of a single negative charge does not significantly affect the depth of corannulene bowl, similar to the lithium-generated C\(_{20}\)H\(_{10}\)\(^-\).

Both the convex and concave face of C\(_{20}\)H\(_{10}\)\(^-\) in 6 are involved in intermolecular interactions with hydrogen atoms of the crown ether moieties (2.670 Å and 2.722 Å, respectively). Moreover, additional C–H···π interactions with the adjacent DME molecules were observed in the crystal lattice with the shortest corresponding distance (2.689 Å). The open concave cavities of the monoreduced corannulene bowls in 7 are occupied by hydrogen atoms of the THF molecules. The corresponding shortest interatomic H···C separations (2.814 Å to 2.893 Å) are indicative of these C–H···π interactions.

### 2.2.3 Potassium Salts

#### 2.2.3.1 [K(18-crown-6)][C\(_{20}\)H\(_{10}\)\(^-\)]

After evaluating the binding trends towards C\(_{20}\)H\(_{10}\)\(^-\) for the light alkali metals Li\(^+\) and Na\(^+\), we moved to their heavier Group 1 congener, potassium. It should be mentioned that unlike the lithium- and sodium-generated corannulene monoanions, there has been no solution data for the potassium analog previously reported.

Crystals of the only potassium adduct isolated, [K(18-crown-6)][C\(_{20}\)H\(_{10}\)\(^-\)] (8), were grown by layering the DME solution with hexanes. In contrast to 2–6, the potassium analog exists as a contact-ion pair according to an X-ray diffraction study.
The potassium ions in 8 coordinate to the exo surface of two neighboring bowl-shaped anions in an \( \eta^2 \)-rim binding mode. In addition, each bowl serves as a bridge between two \([\text{K}(18\text{-crown-6})]^+\) moieties. The steric repulsion of 18-crown-6 ether moieties most likely causes the potassium ions to shift to the edges of \( C_{20}H_{10}^- \) in 8. The K···C contacts (3.142(3)−3.289(2) Å) responsible for the formation of polymeric chains in the crystal lattice of 8 are comparable with the corresponding separations in the \( \pi \)-adduct of planar coronene monoanion (3.133(4)−3.548(4) Å). \(^{14}\)

Figure 20. Fragment of the 1D chain in 8.

The potassium cation is coordinated by six oxygen atoms of 18-crown-6 ether with the K···O bond length distances (2.736(2)−2.811(2) Å) being close to those previously reported for some \([\text{K}(18\text{-crown-6})]^+\) containing salts. \(^{15}\)

The two rim C−C bonds of \( C_{20}H_{10}^- \) engaged in metal binding (bond lengths 1.384(4) Å and 1.400(4) Å) are slightly elongated compared to the rim bonds free of such interactions (1.364(4)−1.374(4) Å). \(^7\) Overall, the geometrical parameters of \( C_{20}H_{10}^- \) in 8 (Table 4) show only slight deviations from those in corannulene monoanions with lighter alkali metals (Tables 2 and 3). It should be mentioned that the “free” concave face of
corannulene monoanion in 8, is involved in interacting with hydrogen atoms of the adjacent 18-crown-6 ether (the shortest H···C separation measures at 2.73 Å).

Table 4. Key distances (in Å) for neutral C$_{20}$H$_{10}$ and C$_{20}$H$_{10}^-$ in 8.

<table>
<thead>
<tr>
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<th>C$<em>{20}$H$</em>{10}^0$</th>
<th>8</th>
</tr>
</thead>
<tbody>
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<td>hub</td>
<td>1.411(2)–1.417(2)</td>
<td>1.384(4)–1.398(3)</td>
</tr>
<tr>
<td>spoke</td>
<td>1.376(2)–1.381(2)</td>
<td>1.365(4)–1.384(4)</td>
</tr>
<tr>
<td>flank</td>
<td>1.441(2)–1.450(2)</td>
<td>1.390(4)–1.434(4)</td>
</tr>
<tr>
<td>rim</td>
<td>1.377(2)–1.387(2)</td>
<td>1.364(4)–1.400(4)</td>
</tr>
<tr>
<td>bowl</td>
<td>0.875(2)</td>
<td>0.846(4)</td>
</tr>
<tr>
<td>depth</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.2.4 Rubidium Salts

2.2.4.1 [Rb(18-crown-6)]|C$_{20}$H$_{10}^-$

As we continued to explore the effect of alkali metal ion size on binding to the C$_{20}$H$_{10}^-$ bowl, we began to notice that in order to saturate the coordination sphere of heavier Group 1 metals, their binding to C$_{20}$H$_{10}^-$ was necessary. Specifically, to tune the binding preferences of rubidium, we adjusted a variety of factors, such as solvents and/or the presence of crown ethers. As a result, several rubidium salts of C$_{20}$H$_{10}^-$ have been successfully isolated and structurally characterized.
From the reaction solution in DME containing 18-crown-6 ether upon layering with hexanes at 10 °C, products of the composition \([\text{Rb}(18\text{-crown-6})][\text{C}_{20}\text{H}_{10}^-]\) 9 crystallize as dark green long needles (major) and blocks (minor).\(^{16}\) According to the X-ray diffraction studies, the main crystallization product is the monomeric modification of 9 (9a), whereas the minor product shows the 1D polymeric structure in the solid state (9b) (Figure 21).

![Molecular structure for 9a (top) and the fragment of a 1D polymeric chain for 9b (bottom).](image)

**Figure 21.** Molecular structure for 9a (top) and the fragment of a 1D polymeric chain for 9b (bottom).

The rubidium center in 9a is arranged above the six-membered ring of the corannulene moiety. A related \(\eta^6\)-coordination mode was previously observed for some complexes of corannulene with some transition metals (Chapter 1).\(^{17}\) The Rb···C bond
lengths (3.273(3)–3.479(3) Å) and the distance of the Rb atom to the center of the benzene ring of the anion (3.04 Å) are indicative of the strong binding of the metal to the π-bowl.

In both 9a and 9b, the Rb⁺ ion is coordinated to six oxygen atoms of the 18-crown-6 ether with the corresponding Rb···O distances, 2.849(3)–2.940(3) Å and 2.794(4)–2.893(4) Å, respectively. Overall, the Rb···O interatomic distances are close to those observed in related compounds.¹⁸

The hub and flank C−C bonds lengths of C₂₀H₁₀⁻ (av. 1.413(3) Å and 1.440(3) Å, respectively) remain almost unchanged in 9a compared to neutral C₂₀H₁₀ (1.415(2) Å and 1.446(2) Å), whereas the spoke and rim C−C interatomic separations are slightly elongated (av. 1.397 Å and 1.395 Å vs. 1.379(2) Å and 1.383(2) Å). The bowl depth of C₂₀H₁₀⁻ in 9a is 0.86 Å.

Table 5. Key distances (in Å) for neutral C₂₀H₁₀ and C₂₀H₁₀⁻ in 9a.

<table>
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<th>C₂₀H₁₀⁰</th>
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<td>1.411(2)–1.417(2)</td>
<td>1.387(4)–1.407(4)</td>
</tr>
<tr>
<td>spoke</td>
<td>1.376(2)–1.381(2)</td>
<td>1.405(3)–1.424(3)</td>
</tr>
<tr>
<td>flank</td>
<td>1.441(2)–1.450(2)</td>
<td>1.390(3)–1.404(3)</td>
</tr>
<tr>
<td>rim</td>
<td>1.377(2)–1.387(2)</td>
<td>1.427(3)–1.451(4)</td>
</tr>
<tr>
<td>bowl depth</td>
<td>0.875(2)</td>
<td>0.861(4)</td>
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</tbody>
</table>
In the polymorph 9b, the corannulene monoanions are linked together by the [Rb(18-crown-6)]⁺ ions into 1D polymeric chains. The solid state structure of 9b is close to that previously observed for the corresponding potassium salt, [K(18-crown-6)][C₂₀H₁₀⁻] (8). The steric repulsion of the crown ether fragments most probably precludes the η⁶-coordination of the Rb ions, moving both [Rb(18-crown-6)]⁺ moieties to the edge of the corannulene monoanion in the crystal lattice of 9b. The positional disorder of corannulene in 9b precludes the precise inspection of its geometrical parameters.

2.2.4.2 [Rb(15-crown-5)₂][C₂₀H₁₀⁻] and [Rb(dicyclohexano-18-crown-6)][C₂₀H₁₀⁻]

When estimating the energetics of the above systems, our DFT calculations revealed a very small preference (ca. 1.55 kcal mol⁻¹) for Rb⁺ ions in selecting between the six- (η⁶) or five-membered ring (η⁵) sites on the convex surface of C₂₀H₁₀⁻. This predicted flexibility in binding was also seen experimentally (Section 2.2.4.1) when we crystallized two polymorphs (9a and 9b) of the rubidium salt, [Rb(18-crown-6)][C₂₀H₁₀⁻], under the same experimental conditions. Thus we continued to explore how the structure and size variations of macrocyclic crown ethers can be further used for tuning the alkali metal binding in such systems.¹⁹

Single crystals of [Rb(15-crown-5)₂][C₂₀H₁₀⁻] 0.5C₆H₁₄, (10·0.5C₆H₁₄), were grown from the DME solution containing 15-crown-5 ether by layering with hexanes. An X-ray diffraction study of 10·0.5C₆H₁₄ (Figure 22) showed the presence of the solvent-separated C₂₀H₁₀⁻ anions and [Rb(15-crown-5)₂]⁺ cations, with hexane molecules filling
the cavities in the crystal lattice. In contrast to 9, the bowl-shaped \( \text{C}_{20}\text{H}_{10}^- \) does not exhibit any direct metal binding in this case.

Figure 22. Molecular structure (left) and solid state packing (right) of 10.

In 10, the \( \text{Rb}^+ \) ion is coordinated by two 15-crown-5 molecules with the corresponding \( \text{Rb} \cdots \text{O} \) bond length distances ranging broadly from 2.835(3) to 3.172(3) Å. Overall, the \( \text{Rb} \cdots \text{O} \) interatomic distances are close to those observed in related compounds.\(^{20}\) Importantly, this full encapsulation of \( \text{Rb}^+ \) centers prevents any interactions between the alkali metal ions and \( \pi \)-surface of \( \text{C}_{20}\text{H}_{10}^- \). As shown above, “naked” corannulene monoanions have been seen only with the light alkali metal ions such as lithium and sodium.

Crystals of \( [\text{Rb(dicyclohexano-18-crown-6)}][\text{C}_{20}\text{H}_{10}^-] \) (11) were grown from THF containing dicyclohexano-18-crown-6 ether upon layering with hexanes. In contrast to 10, an X-ray diffraction study revealed the formation of a contact-ion pair in this case (Figure 23).
In 11, the Rb$^+$ ion is bound to the convex side of the monoanion in an $\eta^6$-fashion (Rb···C 3.245(3)−3.571(3) Å). The distance of the Rb atom to the benzene ring center (3.15 Å) is indicative of rather strong metal binding to the π-bowl. The coordination is similar to that observed in the rubidium analog with 18-crown-6 ether. However, no polymeric product based on the $\eta^2$: $\eta^2$-bridging mode of C$_{20}$H$_{10}$\textsuperscript{−} has been found in this case. The use of bulkier crown ether blocks the access to the bowl surface for the second metal center and thus prevents the formation of a 1D chain.

Regardless of different overall structures of 10 and 11, the changes in the geometry of monoreduced corannulene are similar. The hub C−C bonds lengths of C$_{20}$H$_{10}$\textsuperscript{−} in both cases are close to those measured in neutral corannulene, whereas the spoke and rim C−C bonds are notably elongated. The flank C−C bond lengths of the monoreduced bowl are significantly shortened compared to the parent molecule. The bowl depths of C$_{20}$H$_{10}$\textsuperscript{−} in 10 and 11 of 0.853(5) and 0.834(4) Å, respectively, are similar to the values seen for the series of corannulene monoanions isolated previously. They all show that the acquisition of one electron only slightly reduces the corannulene bowl depth (Table 6).
Table 6. Key distances (in Å) for neutral C_{20}H_{10} and C_{20}H_{10}^{-} in 10 and 11.

<table>
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<th>C_{20}H_{10}^0</th>
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<th>11</th>
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<td>hub</td>
<td>1.411(2)−1.417(2)</td>
<td>1.395(5)−1.422(5)</td>
<td>1.404(4)−1.409(4)</td>
</tr>
<tr>
<td>spoke</td>
<td>1.376(2)−1.381(2)</td>
<td>1.398(5)−1.412(5)</td>
<td>1.401(4)−1.411(4)</td>
</tr>
<tr>
<td>flank</td>
<td>1.441(2)−1.450(2)</td>
<td>1.410(5)−1.435(5)</td>
<td>1.409(5)−1.442(5)</td>
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<td>rim</td>
<td>1.377(2)−1.387(2)</td>
<td>1.409(5)−1.433(6)</td>
<td>1.402(4)−1.430(4)</td>
</tr>
<tr>
<td>bowl</td>
<td>0.875(2)</td>
<td>0.853(5)</td>
<td>0.834(4)</td>
</tr>
<tr>
<td>depth</td>
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</table>

It should be mentioned that the concave and convex faces of C_{20}H_{10}^{-} in 10 are engaged in intermolecular C−H···π interactions with the crown moiety of [Rb(15-crown-5)$_2$]$^+$, with the shortest contacts being 2.62 and 2.80 Å. In 11, the interactions are seen between the H-atoms of crown ether and the endo surface of the bowl (2.695(3) Å). In addition, the corannulene monoanions in 11 are involved in interactions with the hydrogen atoms of the neighboring dicyclohexano-18-crown-6 ether (2.859(3) Å). The shortest π−π distances between the neighboring monoanions in 10 and 11 (2.846(3) Å and 2.700(3) Å, respectively) can be mentioned here; they are close to the π−π contacts observed in the neutral ligand.
2.2.5 Cesium Salts

A remarkable development was achieved by Hirao and coworkers who discovered the first selective endo coordination of a buckybowl by binding the FeCp unit to the inside of the sumanene (C_{21}H_{12}) bowl both in solution and in solid state.\textsuperscript{21} Interestingly, the heavier RuCp unit exhibits both exo and endo coordination to sumanene in solution, while it forms the endo bound complex in the solid state.

In contrast, no endo bound complexes have been observed for corannulene. In order to shed more light on the strength of binding and preferable coordination modes of alkali metals to corannulene, we carried out calculations, at the DFT and MP2 levels of theory, for K, Rb, and Cs complexes (Table 7).

Table 7. Relative energies\[^{[a]}\] at PBE0 and MP2\[^{[b]}\] levels of theory.

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<td>(+12.80)</td>
<td>(+6.59)</td>
<td>(0.00)</td>
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</table>

\[^{[a]}\] The energy estimations are related to the lowest isomer for each metal. All energies are in kcal/mol. \[^{[b]}\] in brackets.
Our calculations demonstrated an energy preference of \textit{endo} binding for Cs only due to a perfect size fit between the cesium cation and \textit{endo} cavity of the corannulene bowl (Figure 24). The stability of \textit{endo} coordination decreases from Cs to K, since there is no “ideal match” between the size of K$^+$ and Rb$^+$ ions and concave surface of the corannulene monoanion. Thus, we considered Cs as a perfect candidate for concave binding and targeted the cesium corannulene products experimentally.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure24.png}
\caption{Schematic representation for the arrangement of an alkali metal inside C$_{20}$H$_{10}$.}
\end{figure}

\textbf{2.2.5.1 $[\text{Cs(18-crown-6)}][\text{C}_2\text{H}_{10}^{-}]$}

Single crystals of complex \textbf{12}, $[\text{Cs(18-crown-6)}][\text{C}_2\text{H}_{10}^{-}]$, were grown from the diglyme solution by layering with hexanes.$^{16}$ The X-ray diffraction study of \textbf{12} revealed the unprecedented \textit{endo} binding of the metal to the concave face of corannulene (Figure 25). The cesium cation, bearing 18-crown-6, sits almost exactly above the center of the five-membered ring, thus representing the first example of $\eta^5$-binding of a metal center to
the corannulene bowl. The corresponding Cs···C_{hub} distances (3.424(3)–3.573(3) Å) are comparable with those measured in the π-adducts having η^6- or η^5-bound cesium with planar polyaromatic hydrocarbons, Cs-intercalated C_{60}-fullerene, and fullerene nanopeapods. The distance between the bottom of the anionic “dish” and the Cs^+ ion is 3.28 Å. The additional Cs···C contacts with interior walls of a corannulene bowl fall in the range of 3.616(3)–3.899(3) Å, while the separations with rim C-atoms are much longer (3.900(3)–4.230(3) Å).

![Molecular structure for 12: side (left) and bottom (right) views.](image)

**Figure 25.** Molecular structure for 12: side (left) and bottom (right) views.

Owing to its large size, Cs^+ is pulled out of the coordinated 18-crown-6 molecule in 12, with the Cs···O bond length distances (3.139(2)–3.216(2) Å) being close to those previously reported for some [Cs(18-crown-6)]^+ containing salts.

For the corannulene anion, the slight shortening of the hub C–C bonds lengths (av. 1.403(4) Å) leads to the shrinking of the central five-membered ring compared to the parent bowl (av. 1.415(2) Å). The spoke C–C bonds are longer in the monoanion than in corannulene (av. 1.412(4) Å vs. 1.379(2) Å). Notably, the shortened flank C–C bonds (av. 1.423(4) Å vs. 1.446(2) Å) and significantly elongated rim bonds (av. 1.410(4) Å vs.
1.383(2) Å) are indicative of the stronger delocalization of the π-electrons in the outer 15-membered ring of the monoanion compared to the neutral bowl species.

The space filling model indicates that the cesium cation is perfectly “dished-up” in the monoanionic corannulene bowl (Figure 26). The steric complementarity of the diameters of 18-crown-6 molecule bearing Cs⁺ (9.1 Å) and the corannulene anion (8.3 Å) provides a very compact packing in the solid state structure of 12 (Figure 26).

![Space filling model of Cs⁺ with corannulene anion and solid state packing of 12.](image)

**Figure 26.** Space filling models for Cs⁺ with corannulene anion (left) and the solid state packing (right) of 12.

### 2.2.5.2 [Cs(diglyme)][C_{20}H_{10}⁻]

A different cesium product was isolated from diglyme in the absence of crown ethers. The structural investigation of the adduct of [Cs(diglyme)][C_{20}H_{10}⁻] (13) revealed the formation of a 1D polymer built on simultaneous η⁵-endo and η⁶-exo binding of the large cesium ion to the convex and concave surfaces of the adjacent C_{20}H_{10}⁻ anions (Figure 27).²⁵ Each bowl serves as an η⁵:η⁶-bridge connecting two [Cs(diglyme)]⁺ ions. Notably, the Cs⋯C₅ distances (3.349(3)–3.463(3) Å) are shorter than the Cs⋯C₆ separations (3.397(3)–3.899(3) Å). The distances of the cesium ion to the centers of the five- and six-membered rings (3.156(3) and 3.431(3) Å, respectively) are indicative of
the strong binding to the π-bowl. It should be noted that the Cs\(^+\) ion is asymmetrically bound to the benzene rings of corannulene and symmetrically coordinated to the central 5-membered ring.

Figure 27. 1D polymeric chain of 13.

The coordination environment of Cs\(^+\) ion is completed by one bound diglyme molecule with the corresponding Cs···O bond distances (3.026(2)–3.069(2) Å). The latter are shorter than the Cs···O\(_{\text{crown}}\) bond length separations observed in adduct 12.

Although the rotational disorder of the corannulene monoanion in 13 prevents accurate measurements of its geometrical parameters, it is clearly seen that the convex faces of C\(_{20}\)H\(_{10}\)\(^-\) are involved in intermolecular interactions with hydrogen atoms of the diglyme molecules (2.751 Å).

It should be mentioned that the concave cavities of charged corannulene bowls are occupied by cesium ions in both crystallographically characterized salts 12–13. This is in full agreement with our calculations which revealed the most ideal geometrical match.
between the *endo* surface of the corannulene moiety ("the lock and key" model) is with cesium cations (Figure 24).

### 2.2.6 Solution Studies of Corannulene Monoanion Radical

#### 2.2.6.1 ESR Studies

Crystals of 3, 4, 8, 9, and 12 can be redissolved in THF to allow the investigation of solution behavior of these compounds. The ESR spectra of \([\{\text{Li}(15\text{-crown-5})\}_2]\text{C}_{20}\text{H}_{10}^-\) (3) and \([\text{Na}(18\text{-crown-6})]\text{C}_{20}\text{H}_{10}^-\) (4) have 11 equally spaced peaks with hyperfine coupling constants (Figure 28). This is in full agreement with the previous ESR data at room temperature of the \(\text{C}_{20}\text{H}_{10}^-\) anions with solvent-separated \(\text{Li}^+\) and \(\text{Na}^+\) cations.\(^{26}\)

![Figure 28. ESR spectra of 3 (top) and 4 (bottom).](image)

\(^{26}\)
The complexity of the ESR signals at room temperature for the solutions of [K(18-crown-6)][C_{20}H_{10}^-] (8), [Rb(18-crown-6)][C_{20}H_{10}^-] (9), and [Cs(18-crown-6)][C_{20}H_{10}^-] (12) (Figure 29), in comparison with the above, is most probably attributed to the coordination of larger [K(18-crown-6)]^+, [Rb(18-crown-6)]^+, and [Cs(18-crown-6)]^+ ions to the C_{20}H_{10}^- bowl.

![ESR spectra of 8 (top), 9 (middle), and 12 (bottom).](image)

**Figure 29.** ESR spectra of 8 (top), 9 (middle), and 12 (bottom).

### 2.2.6.2 \(^1\)H NMR Investigations

In general, the \(^1\)H NMR study of the redissolved crystals of the corannulene monoanion-radicals in THF-\(d_8\) revealed the presence of broad singlets of crown protons for [M(18-crown-6)][C_{20}H_{10}^-] products, where M = Na, K, Rb, and Cs (See Experimental Section). A similar low-field shift of crown protons was seen for [M(15-crown-5)][C_{20}H_{10}^-], where M = Li and Na. Such significantly low shifted resonances,
compared to the NMR data of diamagnetic salts containing [M(18-crown-6)]$^+$ (ca. 3.6 ppm)$^{16,20}$ and [M(15-crown-5)]$^+$ (ca. 3.6 ppm)$^{27}$ are attributed to the paramagnetic shielding of the crown protons from the corannulene radical anion. This illustrates that the binding of the [M(18-crown-6)]$^+$ and [M(15-crown-5)]$^+$ moieties to the C$_{20}$H$_{10}$$^{−}$ anion persists in the solution.

2.2.6.3 UV-vis Data

Crystals of 4, 7–9, and 12 were redissolved in THF to allow their UV-vis spectroscopic investigation. The UV-vis data for 4, 7–9, and 12 are listed in Table 8 along with absorption maxima previously assigned to the C$_{20}$H$_{10}$$^{−}$ anions generated by lithium, rubidium, or cesium reduction in THF.

Table 8. The UV-vis data (in nm) for salts of corannulene monoanions with Group 1 metals with or without 18-crown-6 ether (in THF, the most intense band is bold).

<table>
<thead>
<tr>
<th>C$<em>{20}$H$</em>{10}$$^{−}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td><strong>No crown</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Li</td>
</tr>
<tr>
<td>443, 648, 805, 904$^{[a]}$</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>440, 660,804, 902$^{[c]}$</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>449, 651, 810, 905$^{[b]}$</td>
</tr>
<tr>
<td>Rb</td>
</tr>
<tr>
<td>444, 647, 809, 903$^{[b]}$</td>
</tr>
<tr>
<td>Cs</td>
</tr>
<tr>
<td>438, 644, 812, 912$^{[b]}$</td>
</tr>
<tr>
<td><strong>18-crown-6</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Li</td>
</tr>
<tr>
<td>440, 662, 810, 904$^{[c]}$</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>440, 662, 810, 904$^{[c]}$</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>455, 658, 807, 897$^{[c]}$</td>
</tr>
<tr>
<td>Rb</td>
</tr>
<tr>
<td>445, 655, 805, 900$^{[c]}$</td>
</tr>
<tr>
<td>Cs</td>
</tr>
<tr>
<td>440, 652, 796, 894$^{[c]}$</td>
</tr>
</tbody>
</table>

[a] from the literature; [c] $^{[c]}$ in-situ measurement, solid material was not isolated; [c] redissolved crystals.
The maximum of the most intense band in the UV-vis spectrum of 4 is observed at 662 nm. The corresponding maximum is hypsochromically shifted by approximately 3 nm in the related K–Cs adducts of C_{20}H_{10}−, when going from lighter to heavier Group 1 metals. The presence of crown ether in solutions results in a shift (up to 8 nm) of the most intense absorbance maxima of corannulene monoanions. This can be explained by association of the crown ether moieties with corannulene anions via C–H(crown)···π interactions and/or alkali metal binding. The small difference (2 nm) detected in the UV-vis spectra of 4 and the C_{20}H_{10}− anion generated by the in-situ Na-reduction in the presence or absence of 18-crown-6 ether, may indicate the existence of the naked corannulene anion in solution in these cases.

2.3 Conclusions

The controlled preparation and isolation of corannulene monoanions has been achieved in our laboratory with a series of alkali metal ions ranging from Li to Cs. Structures of their salts with alkali metal counterions have been investigated in the solid state and solution revealing the first trends in binding preferences and geometry perturbation of a bowl-shaped corannulene core upon charging with one electron. The first “naked” C_{20}H_{10}− monoanion has been found with the alkali metal ions Li^+, Na^+, and Rb^+, when solvents or crown ethers provide full encapsulation of metal centers (Scheme 5).
In contrast, when the coordination sphere of the alkali metals is incomplete, different binding modes to the corannulene bowl can be seen in the solid state products. Generally, we observed that lithium and sodium often form solvent-separated products with “naked” $\text{C}_{20}\text{H}_{10}^-$, whereas heavier metals tend to bind to the surface of the corannulene monoanion. Coordination depends on a variety of factors, such as solvents,
other strong donors present in the system, experimental conditions, etc. In all cases, coordination is to the exo surface of corannulene with lighter metals. In contrast, the largest alkali metal, cesium, shows preferential endo binding in an $\eta^5$-fashion, rendering the first example of the concave complex of corannulene. Importantly, the acquisition of one electron by C$_{20}$H$_{10}$ does not significantly perturb the bowl core.
2.4 Experimental Details

**Materials and Methods.** All manipulations were carried out using break-and-seal\textsuperscript{28} and glove-box techniques under an atmosphere of argon. Solvents (THF and hexanes) were dried over Na/benzophenone and distilled prior to use. DME, THF-\textit{d}_8, and diglyme were dried over NaK\textsubscript{2} alloy and vacuum-transferred. Crown ethers, 15-crown-5, 18-crown-6, and dicyclohexano-18-crown-6, were purchased from Strem Chemicals and dried over P\textsubscript{2}O\textsubscript{5} \textit{in vacuo} for 24 h. Alkali metals were purchased from Strem Chemicals and used as received. Corannulene was prepared as described previously\textsuperscript{29} and sublimed at 175 °C prior to use. NMR spectra were measured on a Bruker AC-400 spectrometer at 400 MHz for \textsuperscript{1}H and 155.5 MHz for \textsuperscript{7}Li and were referenced to the solvent used or external standard (0.1 M LiCl in THF-\textit{d}_8). The UV-vis spectra were recorded on a PerkinElmer Lambda 35 spectrometer. The ESR spectra were recorded on a Bruker ER-200 D-SRC X-band spectrometer that is interfaced to a Compaq 386 PC equipped with the IBM analog-to-digital converter and Scientific Software Services Systems (Bloomington, IL). The probe for the ESR studies were prepared by dissolving crystals of 3, 4, 8, 9, and 12 and transferring the resulting solution (\(\approx 2\times10^{-5}\) M) into a quartz capillary (\(\Phi 0.6\) mm), which was then sealed. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

\[
[\text{Li(DME)}_3][\text{C}_{20}\text{H}_{10}^-] (2)
\]

DME (2 mL) was added to a flask containing excess Li metal and corannulene (5 mg, 0.02 mmol). The resulting deep green solution was stirred at room temperature for 8 h to give a deep brown color characteristic of the corannulene tetraanion. The mixture was
filtered and combined with the solution of neutral corannulene (15 mg, 0.06 mmol) in DME (2 mL). The resulting green solution was layered with hexanes (3 mL) and kept at 10 °C. The X-ray quality green needles of 2 were collected in 30 h, washed several times with hexanes and dried in vacuo. Yield: 65%. UV-vis (DME, nm): $\lambda_{\text{max}} = 660$. The ESR spectrum of 2 is consistent with the previously reported.\textsuperscript{22} \textsuperscript{1}H NMR (400 MHz, THF-$d_8$, 15 mM, −80 °C, ppm): $\delta = 3.28, 3.43$. \textsuperscript{7}Li NMR (155.5 MHz, THF-$d_8$, 15 mM, −80 °C, ppm): $\delta = 2.8, 1.0$.

\textsuperscript{7}Li NMR of 2

\[
\text{[Li(15-crown-5)]}_2[C_{20}H_{10}]_2 (3)
\]

THF (3 mL) was added to a flask containing excess Li metal, 15-crown-5 (4.5 mg, 0.02 mmol), and corannulene (5 mg, 0.02 mmol). The resulting deep green solution was stirred at room temperature for 12 h to give a deep brown color of the corannulene tetraanion. The mixture was filtered and combined with the solution of neutral corannulene (15 mg, 0.06 mmol) in THF (2 mL). The resulting green solution was
layered with hexanes (3 mL) and kept at 10 °C to afford green blocks of 3 in 27 h. They were collected, washed several times with hexanes and dried in vacuo. Yield: 60%. UV-vis (THF, nm): \( \lambda_{\text{max}} = 660 \). \(^1\text{H} \) NMR (400 MHz, THF-\(d_8\), 15 mM, −80 °C, ppm): \( \delta = 8.79, 3.73 \). \(^7\text{Li} \) NMR (155.5 MHz, THF-\(d_8\), 15 mM, −60 °C, ppm): \( \delta = 2.1 \). Anal. Calcd for C\(_{30}\)H\(_{30}\)LiO\(_5\): C, 75.38; H, 6.29. Found: C, 75.46; H, 6.33.

\(^1\text{H} \) NMR of 3

\[ \text{\( \lambda_{\text{max}} = 660 \) THF, } \text{\( \delta = 8.79, 3.73 \) ppm, } \text{\( \delta = 2.1 \) ppm, } \text{\( \delta = 75.38 \) ppm, } \text{\( \delta = 6.29 \) ppm, } \text{\( \delta = 75.46 \) ppm, } \text{\( \delta = 6.33 \) ppm} \]
[Na(18-crown-6)][C_{20}H_{10}^-] (4)

THF (3 mL) is added to a flask containing an excess Na, corannulene (15 mg, 0.06 mmol), and 18-crown-6 ether (0.07 mmol). The resulting deep green solution is stirred at room temperature for 12 h to give a bright purple solution of the corannulene dianion. It is filtered and combined with the solution of neutral corannulene (15 mg, 0.06 mmol) in THF (2 mL). The resulting green solution is layered with hexanes (3 mL) and kept at 10 °C. Green crystals were collected in 36 h, washed several times with hexanes, and dried in vacuo. Yield: 80%; $^1$H NMR (400 MHz, THF-$d_8$, 15 mM, 25 °C, ppm): $\delta = 6.2$; $^1$H NMR (400 MHz, THF-$d_8$, 15 mM, −80 °C, ppm): $\delta = 7.8$; UV-vis (THF, nm): $\lambda_{\text{max}} = 440, 662, 810$. 
[Na(15-crown-5)(diglyme)][C_{20}H_{10}]^- (5)

Diglyme (3 mL) is added to a flask containing an excess of Na, corannulene (15 mg, 0.06 mmol), and 15-crown-5 ether (0.07 mmol). The resulting deep green solution is stirred at room temperature for 12 h to give a bright purple solution of the corannulene dianion. It is filtered and combined with the solution of neutral corannulene (15 mg, 0.06 mmol) in diglyme (2 mL). The resulting green solution is layered with hexanes (3 mL) and kept at 10 °C. Green crystalline solid was collected in 48 h, washed several times with hexanes, and dried in vacuo. Yield: 65%. Anal. Caled for C_{36}H_{44}NaO_{8}: C, 68.88; H, 7.07; Found: C, 68.77; H, 6.99. \(^1\)H NMR (400 MHz, THF-\(d_8\), 20 mM, 25 °C, ppm): \(\delta = 7.5\); \(^1\)H NMR (400 MHz, THF-\(d_8\), 20 mM, −60 °C, ppm): \(\delta = 8.8\). UV-vis (diglyme, nm): \(\lambda_{\text{max}} = 445, 661, 810\)
$^1$H NMR of 5

[Dime (Na)(DME)$_3$][C$_{20}$H$_{10}^-$] (6)

DME (2 mL) was added to a flask containing an excess of Na metal and corannulene (10 mg, 0.04 mmol). The green solution was stirred at room temperature for 8 h to give a deep purple mixture (corannulene-dianion) which was then filtered and combined with a solution of neutral corannulene (10 mg, 0.04 mmol) in DME (2 mL). The resulting green solution was layered with hexanes (3 mL) and kept at 10 °C. Green crystalline solid was collected in 30 h, washed several times with hexanes and dried in vacuo. Yield: 75%. Anal. Calcd for C$_{32}$H$_{40}$NaO$_6$: C, 70.70; H, 7.42; Found: C, 70.73; H, 7.44. UV-vis (DME, nm): $\lambda_{\text{max}} = 450, 658, 800$.

[Na(THF)$_3$][C$_{20}$H$_{10}^-$] (7)

THF (2 mL) was added to a flask containing an excess of Na metal and corannulene (10 mg, 0.04 mmol). The green solution was stirred at room temperature for 16 h to give a deep purple mixture (corannulene dianion) which was then filtered and combined with a solution of neutral corannulene (10 mg, 0.04 mmol) in THF (2 mL). The resulting green solution was layered with hexanes (3 mL) and kept at 10 °C. A green crystalline solid
was collected in 56 h, washed several times with hexanes and dried in vacuo. Yield: 65%.

UV-vis (THF, nm): \( \lambda_{\text{max}} = 450, 659, 803 \).

\([\text{K(18-crown-6)}][\text{C}_{20}\text{H}_{10}^-] \) (8)

DME (3 mL) was added to a flask containing an excess of K, corannulene (15 mg, 0.06 mmol), and 18-crown-6 ether (18 mg, 0.07 mmol). The resulting deep green solution was stirred at room temperature for 12 h to give a bright purple solution of the corannulene-dianion. It is filtered and combined with the solution of neutral corannulene (15 mg, 0.06 mmol) in DME (2 mL). The resulting green solution was layered with hexanes (3 mL) and kept at 10 °C. A green crystalline solid was collected in 36 h, washed several times with hexanes, and dried in vacuo. Yield: 70%; \(^1\)H NMR (400 MHz, THF-\(d_8\), 7 mM, 25 °C, ppm): \( \delta = 4.9 \); \(^1\)H NMR (400 MHz, THF-\(d_8\), 7 mM, −80 °C, ppm): \( \delta = 6.6 \) and 3.6; UV-vis (THF, nm): \( \lambda_{\text{max}} = 455, 658, 807, 897 \); Anal. Calcd for C\(_{32}\)H\(_{34}\)O\(_6\)K: C, 69.41; H, 6.19; Found: C, 69.39; H, 6.12.
$^1$H NMR of 8

$[\text{Rb}(18\text{-crown-6})][\text{C}_{20}\text{H}_{10}^{-}]$ (9)

DME (3 mL) was added to a flask containing Rb metal (10 mg, 0.12 mmol), corannulene (10 mg, 0.04 mmol), and 18-crown-6 (22 mg, 0.083 mmol). The resulting deep green solution was stirred at room temperature for 12 h to give a bright purple solution of the corannulene-dianion. The mixture was filtered and combined with the solution of neutral corannulene (10 mg, 0.04 mmol) in DME (2 mL). The resulting green solution was layered with hexanes (3 mL) and kept at 10 °C. The crystalline solid was deposited in a
few days. The X-ray quality crystals were obtained by layering the DME solution with hexanes at 10 °C. Yield: 75%. Anal. Calcd for C_{32}H_{34}RbO_6: C, 64.05; H, 5.71; Found: C, 63.97; H, 5.65. ^1H NMR (400 MHz, THF-d_8, 7 mM, 25 °C, ppm): δ = 4.9. UV-vis (THF, nm): λ_{max} = 401, 445, 655, 805, 900.

**^1H NMR of 9**

![^1H NMR of 9](image)

[Rb(15-crown-5)\_2][C\_20H\_10\^-] (10)

DME (3 mL) was added to a flask containing Rb metal (10 mg, 0.12 mmol), corannulene (10 mg, 0.04 mmol), and 15-crown-5 ether (44 mg, 0.200 mmol). The resulting deep green solution was stirred at room temperature for 12 h to give a bright purple solution of the corannulene dianion. The mixture was filtered and combined with the solution of neutral corannulene (10 mg, 0.04 mmol) in DME (2 mL). The resulting green solution was layered with hexanes (3 mL) and kept at 10 °C. The X-ray quality crystals of 10·0.5C_6H_{14} were collected in 48 h, washed several times with hexanes, and dried. Yield:
75 %. $^1$H NMR (400 MHz, THF-$d_8$, 8 mM, 25 °C, ppm): $\delta = 4.51$. UV-vis (DME, nm):

$\lambda_{\text{max}} = 373, 455, 662, 805$.

$^1$H NMR of 10

[Image]

$\text{[Rb(dicyclohexano-18-crown-6)][C}_2\text{O}_{10}^{-} \text{]}$ (11)

THF (3 mL) was added to a flask containing Rb metal (10 mg, 0.12 mmol), corannulene (10 mg, 0.04 mmol), and dicylcohexano-18-crown-6 ether (0.083 mmol). The resulting deep green solution was stirred at room temperature for 12 h to give a bright purple solution of the corannulene dianion. The mixture was filtered and combined with the solution of neutral corannulene (10 mg, 0.04 mmol) in THF (2 mL). The resulting green solution was layered with hexanes (3 mL) and kept at 10 °C. The X-ray quality crystals of 11 were collected in 56 h, washed several times with hexanes, and dried in vacuo.

Yield: 60 %. Anal. Calcd for C$_{40}$H$_{46}$RbO$_6$: C, 67.83; H, 6.55; Found: C, 67.36; H, 6.19. UV-vis (THF, nm): $\lambda_{\text{max}} = 391, 452, 661, 804$. 

65
[Cs(18-crown-6)][C_{20}H_{10}^-] (12)

THF (3 mL) was added to a flask containing Cs metal (11 mg, 0.08 mmol), corannulene (15 mg, 0.06 mmol), and 18-crown-6 (18 mg, 0.07 mmol). The resulting deep green solution was stirred at room temperature for 2 h, then filtered, layered with hexanes (3 mL) and kept at 10 °C. Green crystalline solid was collected in 36 h, washed several times with hexanes and dried in vacuo. The X-ray quality crystals were grown by layering the diglyme solution with hexanes at 10 °C. Yield: 85%. Anal. Calcd for C_{32}H_{34}CsO_{6}: C, 59.36; H, 5.29; Found: C, 59.21; H, 5.29. $^1$H NMR (400 MHz, THF-$d_8$, 15 mM, 25 °C, ppm): $\delta = 4.2$. UV-vis (THF, nm): $\lambda_{\text{max}} = 396, 440, 652, 796, 894$.

$^1$H NMR of 12
Diglyme (3 mL) was added to a flask containing Cs metal (8 mg, 0.06 mmol, 1.5 eq.) and corannulene (10 mg, 0.04 mmol). The resulting deep green solution was stirred at room temperature for 15 h. The resulting green solution was filtered then layered with hexanes (3 mL) and kept at 10 °C. A green crystalline solid was collected after 48 h, washed several times with hexanes, and dried in vacuo. The X-ray quality crystals were obtained by layering the diglyme solution with hexanes at 10 °C. Yield: 60%. UV-vis (diglyme, nm): \( \lambda_{\text{max}} = 442, 658, 810 \). Anal. Calcd for C\(_{26}\)H\(_{24}\)CsO\(_3\): C, 60.36; H, 4.68; Found: C, 60.44; H, 4.69. \(^1\)H NMR (400 MHz, THF-\(d_8\), 25 °C, ppm): \( \delta = 3.32, 3.49, 3.57 \). \(^1\)H NMR (400 MHz, THF-\(d_8\), –60 °C, ppm): \( \delta = 3.29, 3.40, 3.67 \).
2.5 References


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3. Corannulene Dianions

3.1. Lithium Salts

After we were able to isolate the series of corannulene monoanions, we looked into controlled preparation of corannulene dianion in order to follow up on the alkali metal ion binding trends by studying the interactions of \( \text{C}_{20}\text{H}_{10}^{2-} \) with Group 1 metals. It should be noted that evidence of corannulene dianion \( 1^{2-} \) has only been observed in solution by \(^1\text{H} \text{NMR} \) and UV-vis investigations.

3.1.1 \([\{\text{Li(DME)}\}\{\text{Li(DME)}\}_{1.5}\}]_{2}[\text{C}_{20}\text{H}_{10}^{2-}]_{2}\)

The corannulene dianion has been crystallized for the first time in our group, under different experimental conditions as both solvent-separated and contact-ion pairs.\(^{1}\) The X-ray diffraction study of the product crystallized from DME reveals the formation of \([\text{Li(DME)}]_{2}[1^{2-}]\) moieties having two \( \text{Li}^+ \) cations bound to the \textit{exo}-surface of the corannulene core (Figure 30a). These species are further linked into dimers by a DME molecule \textit{via} the \( \text{Li} \cdots \text{O} \) contact of 1.986(7) Å to give the product of the overall formula \([\{\text{Li(DME)}\}\{\text{Li(DME)}\}_{1.5}\}]_{2}[\text{C}_{20}\text{H}_{10}^{2-}]_{2} \) (14). The Li1 ion coordinates to the \textit{exo} side of the dianion in an \( \eta^4 \)-fashion (Li\cdots C 2.313(7)–2.814(8) Å). The Li2 ion is bound to either 5- (Li2x, \textit{exo}-\( \eta^5 \)) or 6-membered (Li2y, \textit{exo}-\( \eta^6 \)) rings of \( \text{C}_{20}\text{H}_{10}^{2-} \) with the related occupancies of 0.65:0.35 (Figure 30b,c). An additional O-contact available for coordination to Li2\(^+\) (Figure 30b) slightly favors \( \eta^5 \)-coordination over \( \eta^6 \).
Figure 30. Molecular structure of 14 (a, Li atoms and DME molecules with the occupancies of 0.35 are not indicated), and the coordination environments of the corannulene dianion with the $\eta^5$ (b), and $\eta^6$ (c) binding modes for Li2.

The interatomic Li2x···C distances lie in the range of 2.335(11)−2.512(11) Å (Li···C5(centroid) 2.105(11) Å), which is similar to the Li···C distances generally observed for anions of planar and non-planar polyarenes.\(^2\) This demonstrates rather strong binding of alkali metal ions to the exo surface of corannulene dianions. The Li2y···C distances are noticeably longer (2.56(2)−2.85(2) Å, Li···C6(centroid) 2.29(2) Å). The hub C−C bond length distances of C$_{20}$H$_{10}^{2−}$ in 14 are close to those measured in neutral corannulene;\(^3\) whereas its spoke bonds are noticeably elongated in comparison to C$_{20}$H$_{10}$. The flank and rim C−C bond length distances of C$_{20}$H$_{10}^{2−}$ show their significant equalization (Table 9). Unlike the corannulene monoanions, the acquisition of two electrons by corannulene in
14 leads to a noticeable flattening of its curved carbon core (0.796(4) Å vs. 0.875(2) Å for C$_{20}$H$_{10}$).

<table>
<thead>
<tr>
<th></th>
<th>C$<em>{20}$H$</em>{10}^0$</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>hub</td>
<td>1.411(2)–1.417(2)</td>
<td>1.398(4)–1.427(4)</td>
<td>1.390(3)–1.427(3)</td>
</tr>
<tr>
<td>spoke</td>
<td>1.376(2)–1.381(2)</td>
<td>1.392(4)–1.413(4)</td>
<td>1.400(3)–1.418(3)</td>
</tr>
<tr>
<td>flank</td>
<td>1.441(2)–1.450(2)</td>
<td>1.391(4)–1.464(4)</td>
<td>1.404(3)–1.475(3)</td>
</tr>
<tr>
<td>rim</td>
<td>1.377(2)–1.387(2)</td>
<td>1.374(4)–1.451(4)</td>
<td>1.375(3)–1.435(3)</td>
</tr>
<tr>
<td>bowl</td>
<td>0.875(2)</td>
<td>0.796(4)</td>
<td>0.811(3)</td>
</tr>
</tbody>
</table>

Table 9. Key distances (in Å) for neutral C$_{20}$H$_{10}$ and C$_{20}$H$_{10}^{2-}$ in 14 and 15.

3.1.2 [Li(diglyme)$_2$]$_2$[C$_{20}$H$_{10}^{2-}$]

The X-ray diffraction study of the product crystallized from diglyme solution reveals the formation of [Li(diglyme)$_2$]$_2$[I$_2^-$] (15). In contrast to 14, it contains corannulene dianions free from metal ion interactions (Figure 31a). In the crystal structure of 15, the hexacoordinated lithium ion is fully encapsulated by two diglyme molecules (Figure 31b) and this precludes any direct binding of metal ions to the polyarene surface.
The first example of the “naked” $\text{C}_{20}\text{H}_{10}^{2-}$ dianion, in which the geometry is not affected by metal ion coordination, allows us to clearly evaluate the effect of adding two electrons to the bowl core. The hub C–C bond length distances of $\text{C}_{20}\text{H}_{10}^{2-}$ (av. 1.410 Å) are close to those measured in the parent coronulene (av. 1.415 Å), whereas its spoke bonds (av. 1.408 Å) are noticeably elongated in comparison to $\text{C}_{20}\text{H}_{10}$ (av. 1.379 Å). The flank and rim C–C bond length distances of $\text{C}_{20}\text{H}_{10}^{2-}$ show their significant equalization (Table 9). The observed structural changes in the coronulene dianion may be generally explained by the formation of a central five-membered aromatic ring inside an anti-aromatic 16-membered rim upon reduction (Scheme 6).
The flattening of the curved carbon surface is slightly smaller for the “naked” dianion in 15 compared to that in 14 (0.811(3) Å vs. 0.796(4) Å, respectively). In both cases, the bowl depth of C\textsubscript{20}H\textsubscript{10}\textsuperscript{2−} is much greater than the calculated value of 0.57 Å,\textsuperscript{4} clearly confirming that experimental structural studies are needed to evaluate the reliability and accuracy of modern theoretical methods applied to curved π-systems.

3.2 Sodium Salts

3.2.1 \([\text{Na(THF)}\textsubscript{2}(18\text{-crown-6})]\textsubscript{2}[\text{Na}_2(18\text{-crown-6})(\text{C}_{20}\text{H}_{10}\textsubscript{2−})\textsubscript{2}]^{2−}\cdot2\text{THF}\) and \([\text{Na(THF)}\textsubscript{2}(18\text{-crown-6})][\text{Na}(18\text{-crown-6})(\text{C}_{20}\text{H}_{10}\textsubscript{2−})]\textsuperscript{−}\)

Numerous crystallization techniques were applied and lead to the successful isolation of several new sodium salts of 1\textsuperscript{2−}. The corannulene dianion, generated by the reduction with sodium in the presence of 18-crown-6 ether, has been crystallized from the THF solution by layering with hexanes.\textsuperscript{5} The overall formula of the resulting major product can be written as \([\text{Na(THF)}\textsubscript{2}(18\text{-crown-6})]\textsubscript{2}[\text{Na}_2(18\text{-crown-6})(\text{C}_{20}\text{H}_{10}\textsubscript{2−})\textsubscript{2}]^{2−}\cdot2\text{THF}\) (16a\textsuperscript{−}2THF). An X-ray diffraction study revealed the presence of two separate [Na(THF)\textsubscript{2}(18-crown-6)]\textsuperscript{+} cations along with the supramolecular dimer formed by two 1\textsuperscript{2−} dianions and the dicationic [Na\textsubscript{2}(18-crown-6)]\textsuperscript{2+} moiety residing on a crystallographic inversion center (Figure 32). The sodium ions of the latter exhibit \textit{exo} η\textsuperscript{6-…}
binding to the benzene rings of \( \text{C}_{20}\text{H}_{10}^{2-} \). The interatomic Na···C separations (2.732(2)−2.910(2) Å) and the distance to the benzene ring centroid (2.412(2) Å) are indicative of a strong binding of Na\(^+\) ions to the carbon surface of \( \text{I}^{2-} \).

![Molecular structure of \( \text{16a} \).](image)

**Figure 32.** Molecular structure of \( \text{16a} \).

The hub C–C bond lengths of \( \text{C}_{20}\text{H}_{10}^{2-} \) in \( \text{16a} \) are close to those measured in neutral corannulene, whereas the spoke bonds are slightly elongated (Table 10). The flank and rim C–C bond distances demonstrate a significant equalization. Similar to the lithium-generated corannulene dianions, this perturbation of C–C bond lengths in the \( \text{C}_{20}\text{H}_{10}^{2-} \) may be explained by the presence of the central five-membered aromatic (6\(\pi\)) ring inside the antiaromatic 15-membered ring (16\(\pi\)). As seen from adducts 14 and 15, the acquisition of two electrons by corannulene leads to a noticeable flattening of the curved carbon surface (0.795(3) Å in \( \text{16a} \) vs. 0.875(2) Å in \( \text{C}_{20}\text{H}_{10} \)).
Table 10. Key distances (in Å) for C_{20}H_{10}^{2−} in 16a, 16b, and 17.

<table>
<thead>
<tr>
<th></th>
<th>16a</th>
<th>16b</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>hub</td>
<td>1.390(3)−1.428(2)</td>
<td>1.402(5)−1.421(5)</td>
<td>1.393(5)−1.422(4)</td>
</tr>
<tr>
<td>spoke</td>
<td>1.404(3)−1.419(3)</td>
<td>1.405(5)−1.413(5)</td>
<td>1.395(4)−1.422(4)</td>
</tr>
<tr>
<td>flank</td>
<td>1.405(3)−1.460(3)</td>
<td>1.420(5)−1.445(6)</td>
<td>1.394(5)−1.475(5)</td>
</tr>
<tr>
<td>rim</td>
<td>1.390(3)−1.445(3)</td>
<td>1.399(6)−1.420(6)</td>
<td>1.369(6)−1.429(6)</td>
</tr>
<tr>
<td>bowl</td>
<td>0.795(3)</td>
<td>0.799(6)</td>
<td>0.792(5)</td>
</tr>
</tbody>
</table>

The open concave bowl cavity of the [Na_2(18-crown-6)(C_{20}H_{10}^{2−})_2]^{2−} anionic aggregate in 16a is occupied by hydrogen atoms of the crown ether moiety from the adjacent cations (Figure 33, left). The corresponding shortest interatomic H···C separation (2.54 Å) is indicative of C−H···π interactions. The packing of anionic and cationic products in the crystal of 16a results in the formation of cavities that are filled by non-coordinating THF molecules (Figure 33, right).

Figure 33. Space-filling depictions of the cation insertion into the bowl (left) and of the solid state packing in 16a (right). Black, gray, and white colors are attributed to the
corannulene dianion aggregates, counterions, and non-coordinating THF molecules, respectively (right).

Upon crystallization of 16, the formation of a few small cubic crystals of [Na(THF)2(18-crown-6)][Na(18-crown-6)(C_{20}H_{10}^{2−})] (16b) is observed. An X-ray diffraction study of this minor product revealed an unprecedented \textit{exo}-coordination of Na\textsuperscript{+} to the five-membered ring of the corannulene bowl (Figure 34, left). The isolation of two isomers in 16 reveals that there is a small difference in energies between the \(\eta^5\)- and \(\eta^6\)-binding modes.

The corresponding Na···C bond lengths (2.717(4)–2.996(4) Å) in 16b are comparable to those measured in 16a, whereas the Na···C_{5(centroid)} separation is significantly elongated in comparison with the Na···C_{6(centroid)} distance in 16a (2.608(4) Å vs. 2.412(2) Å). Despite the difference in coordination environment of corannulene dianions in 16a and 16b, their geometrical parameters are very close (Table 10). Only four oxygen atoms of 18-crown-6 ether coordinate to the sodium ion in the anionic fragment of 16b. The open concave face of corannulene dianion in 16b is occupied by hydrogen atoms of crown ether of the [Na(THF)2(18-crown-6)]\textsuperscript{+} cation in a fashion, similar to that observed in 16a (Figure 34, left).
3.2.2 \([\text{Na}_2(\text{DME})_3][\text{C}_{20}\text{H}_{10}^{2-}]\)

The X-ray diffraction study of the corannulene dianion generated by excess Na metal in DME revealed the formation of \([\text{Na}_2(\text{DME})_3][\text{C}_{20}\text{H}_{10}^{2-}]\) (17, Figure 35). Both Na\(^+\) ions are coordinated to the exo surface of corannulene dianion in an \(\eta^6\) mode. A similar binding mode was observed in the \([\text{Na(THF)}_2(18\text{-crown-6})]_2[\text{Na}_2(18\text{-crown-6})(\text{C}_{20}\text{H}_{10}^{2-})]_2^{2-}\cdot2\text{THF}\) product. The Na···C separations (2.672(4)–2.990(3) and 2.694(4)–3.016(4) Å) and the distance to the benzene ring centroid (2.391(4) and 2.543(4) Å, respectively) are indicative of the strong binding of Na\(^+\) ions to the curved carbon surface of \(1^{2-}\).
The Na···O interatomic separations for the tri- and tetracoordinated sodium ions (2.310(3)−2.404(3) Å and 2.358(3)−2.490(3) Å, respectively) are close to those observed for the solvated Na⁺ ions. It is worth mentioning, one DME molecule is bridging two Na⁺ ions in 17. The corresponding Na···Na separation (3.74 Å) is shorter than that observed in elemental sodium (3.82 Å).

Regarding the geometry of the corannulene dianion, a similar trend was observed for the C–C bond distances in 17 as that in 14–16. Specifically, the hub C–C bond lengths of C₂₀H₁₀²⁻ in 17 are close to those measured in neutral corannulene, whereas the spoke bonds are slightly elongated (Table 10). The flank and rim C–C bond distances demonstrate a significant equalization. The open concave surface of C₂₀H₁₀²⁻ is engaged in C–H···π interactions with the neighboring DME molecule with the shortest distance being 2.730 Å (Figure 35).
3.3 Potassium Salts

3.3.1 [K(18-crown-6)]_2[C_{20}H_{10}^{2-}]

Based on our previous data, we clearly observed that a variety of factors can affect the outcome of coordination of alkali metal cations to the anionic bowl of corannulene. To tune metal coordination, we used several different crystallization methods in order to obtain various adducts of potassium generated C_{20}H_{10}^{2-}.

Two isomers of the potassium adduct, [K(18-crown-6)]_2[C_{20}H_{10}^{2-}] (18a and 18b) with different metal binding modes (Figure 36), have been isolated and structurally characterized. The contact-ion pair 18a, with the $\eta^6$-binding of K$^+$ ion, is isolated as the main product when 18 is crystallized from the THF solution by layering with a hexanes/diglyme (v:v 10:1) mixture at 10 °C. Under similar crystallization conditions, the use of hexanes only leads to the precipitation of 18b having one of the potassium ions bound to the central five-membered ring of C_{20}H_{10}^{2-}.

Figure 36. Molecular structures of 18a (left) and 18b (right).
The isomer 18a demonstrates the metal ion binding to the center of the six-membered ring (Figure 36, left), similar to that observed in the sodium adduct 18a and several transition metal complexes of coronulene. The corresponding interatomic K···C distances lie in the range of 3.052(4)−3.378(4) Å. These distances, along with the K···C_{6(centroid)} separation of 2.881(4) Å, indicate a strong binding of the K$^+$ ion to the exo face of C$_{20}$H$_{10}^{2-}$. The adduct 18a also shows the endo $\eta^2$-binding of another K$^+$ ion to the rim C−C bond. The resulting K···C separations (3.068(4) Å and 3.269(4) Å) are shorter than those in the potassium monoanion adduct 8 (3.142(3)−3.289(2) Å). In general, the geometry perturbation trends for the coronulene dianion in 18a are close to those found with lighter alkali metals (Table 11). The C−H···π interactions between the crown ether moieties and both faces of coronulene dianions were observed in the crystal lattice of 18a.

### Table 11. Key distances (in Å) for neutral C$_{20}$H$_{10}$ and C$_{20}$H$_{10}^{2-}$ in 18a.

<table>
<thead>
<tr>
<th></th>
<th>C$<em>{20}$H$</em>{10}^{0}$</th>
<th>18a</th>
</tr>
</thead>
<tbody>
<tr>
<td>hub</td>
<td>1.411(2)−1.417(2)</td>
<td>1.400(5)−1.422(5)</td>
</tr>
<tr>
<td>spoke</td>
<td>1.376(2)−1.381(2)</td>
<td>1.400(5)−1.423(5)</td>
</tr>
<tr>
<td>flank</td>
<td>1.441(2)−1.450(2)</td>
<td>1.415(5)−1.460(5)</td>
</tr>
<tr>
<td>rim</td>
<td>1.377(2)−1.387(2)</td>
<td>1.391(6)−1.437(6)</td>
</tr>
<tr>
<td>bowl depth</td>
<td>0.875(2)</td>
<td>0.785(6)</td>
</tr>
</tbody>
</table>
In contrast to 18a, the adduct 18b shows symmetric η⁵-binding of the potassium ion to the exo surface of C₂₀H₁₀²⁻ (Figure 36, right). The K···C and K···C₅(centroid) separations (3.05(2)–3.29(1) Å and 2.96(2) Å, respectively) are close to the related K···C distances in 18a. Another K⁺ ion binds to the concave face of the bowl in an η³-fashion (K···C, 3.15(1)–3.43(2) Å). The rotational disorder of corannulene dianion in 18b precludes the accurate measurement of its geometrical parameters. The isolation of two isomers of 18 indicates a small difference in energies between the η⁵- and η⁶-binding modes.

3.4 Cesium Salts

3.4.1 [Cs₂(dicyclohexano-18-crown-6)₁.₅][C₂₀H₁₀²⁻]·THF

In order to crystallize the cesium generated corannulene dianion, we needed to resolve several issues. Our major problem was the very limited solubility of Cs-produced C₂₀H₁₀²⁻ in the solvents commonly used for reduction reactions, such as THF, DME, or diglyme. After several adaptions to our procedure, we were able to find the ideal conditions for the crystallization of this product.

The X-ray diffraction study of the corannulene dianion generated by Cs (2.2 eq.) reduction in the presence of dicyclohexano-18-crown-6 revealed the formation of [Cs₂(dicyclohexano-18-crown-6)₁.₅][C₂₀H₁₀²⁻]·THF (19·THF).¹⁰ Notably, THF molecules fill the cavities in the crystal lattice of 19.
The salt of corannulene dianion is crystallized as a linear tetranuclear product. The structure is built by aggregation of two terminal \textit{exo}-bound \([\text{Cs}(\text{dicyclohexano-18-crown-6})(\text{C}_{20}\text{H}_{10}^{2-})]^{-}\) moieties with the central \([\text{Cs}_2(\text{dicyclohexano-18-crown-6})]^{2+}\) cationic gluing block. The Cs···O distances in \([\text{Cs}_2(\text{dicyclohexano-18-crown-6})]^{2+}\) range broadly (3.147(11)−3.627(11) Å), whereas the Cs···O separations in \([\text{Cs}(\text{dicyclohexano-18-crown-6})]^{+}\) are much shorter (3.028(2)−3.129(2) Å). The cesium ions of \([\text{Cs}_2(\text{dicyclohexano-18-crown-6})]^{2+}\) share one crown molecule and occupy the concave cavities of the doubly-charged corannulene bowls. The Cs\textsuperscript{+} ions are coordinated to both the \textit{exo} and \textit{endo} surface of corannulene in an \(\eta^5\)-fashion. The corresponding Cs···C distances are 3.317(12)−3.445(12) Å and 3.203(10)−3.321(10) Å, respectively. The distance of the cesium ions to the center of the five membered ring are indicative of the strong metal binding to the convex and concave faces of corannulene (3.185(12) Å and 3.025(10) Å, respectively). It should be noted that the Cs\textsuperscript{+} ion coordinated to the convex
face of $\text{C}_{20}\text{H}_{10}^{2-}$ is asymmetrically bound, whereas the cesium metal center which binds to the concave surface is symmetrically coordinated. The rotational disorder of the corannulene dianion in 19 precludes accurate measurements of its geometrical parameters.

3.5 Solution Behavior of Corannulene Dianion

3.5.1 UV-vis Data

Crystals of 16 and 19 can be redissolved in THF to allow the investigation of the solution behavior of these compounds. The UV-vis spectroscopy data for 16 and 19 are listed in Table 12 along with absorption maxima previously assigned to the $\text{C}_{20}\text{H}_{10}^{2-}$ anions generated by in-situ lithium, rubidium, or cesium reduction in THF.\textsuperscript{5,11} All show broad absorbance bands centered around 503–508 nm, in full agreement with previous observations.\textsuperscript{11}

Table 12. The UV-vis data (in nm) for salts of corannulene dianions with Group 1 metals with or without 18-crown-6 ether (in THF, the most intense band is bold).

<table>
<thead>
<tr>
<th></th>
<th>C$<em>{20}$H$</em>{10}^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no crown</td>
</tr>
<tr>
<td>Li</td>
<td>387, 503$^{[b]}$</td>
</tr>
<tr>
<td>Na</td>
<td>392, 508$^{[b]}$</td>
</tr>
<tr>
<td>K</td>
<td>380, 505$^{[b]}$</td>
</tr>
<tr>
<td>Rb</td>
<td>384, 503$^{[b]}$</td>
</tr>
<tr>
<td>Cs</td>
<td>377, 503$^{[b]}$</td>
</tr>
</tbody>
</table>

[a] from the literature;\textsuperscript{11T} [b] in-situ measurement, solid material was not isolated; [c] redissolved crystals
The presence of crown ether in solutions results in a shift (up to 15 nm) of the most intense absorbance maxima of corannulene dianions. This can be explained by association of the crown ether moieties with corannulene anions via C−H(crown)···π interactions and/or alkali metal binding.

3.5.2 1H NMR Investigations

In the 1H NMR spectra of C_{20}H_{10}^{2−}, the resonance signals of the protons of the paratropic corannulene dianions appear only at low temperatures as very broad signals.\(^{11}\) Previously, the low temperature 1H NMR spectra were investigated by Scott et al. to show the diamagnetic C_{20}H_{10}^{2−} may be viewed as a central aromatic (diatropic) cyclopentadiene anion and an antiaromatic (paratropic) 16\(\pi\) perimeter.\(^{11}\) It is the shielding effect of the outer ring current that shifts the signal, which is in full agreement with our data (Table 13).

Table 13. 1H NMR investigations (in THF-\(d_8\)) of C_{20}H_{10}^{2−} with alkali metals, Li, Na, and K (in ppm).

<table>
<thead>
<tr>
<th></th>
<th>Our data</th>
<th>Literature(^{11})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>−5.5</td>
<td>−5.6</td>
</tr>
<tr>
<td>Na</td>
<td>−6.0</td>
<td>−</td>
</tr>
<tr>
<td>K</td>
<td>−4.5</td>
<td>−5.6</td>
</tr>
</tbody>
</table>
3.6 Conclusions

The selective preparation and isolation of corannulene dianions have been achieved in our laboratory with the series of Group 1 metals, Li, Na, K, and Cs. Structures of their salts with alkali metal counterions have been investigated in the solid state and solution revealing the first trends in alkali metal binding (Scheme 7) and geometry deformations of the curved carbon surface of corannulene upon acquisition of two electrons.

Scheme 7.
The first “naked” C$_{20}$H$_{10}^{2-}$ dianion has been prepared with the lightest alkali metal lithium, whereas heavier metals tend to form contact-ion pairs. The isolation of the first naked corannulene dianion and its comparison with contact-ion pair complexes, allowed us to demonstrate that charging the bowl with two electrons prevails over alkali metal binding in perturbing the geometry of C$_{20}$H$_{10}^{2-}$. Notably, the experimental bowl depth of C$_{20}$H$_{10}^{2-}$ was found to be much greater than the calculated value (0.57 Å), revealing the importance of structural investigations.$^4$
3.7 Experimental Details

Materials and Methods. All manipulations were carried out using break-and-seal\textsuperscript{12} and glove-box techniques under an atmosphere of argon. Solvents (THF and hexanes) were dried over Na/benzophenone and distilled prior to use. DME, THF-$d_8$, and diglyme were dried over NaK\textsubscript{2} alloy and vacuum-transferred. Crown ethers, 18-crown-6 and dicyclohexano-18-crown-6, were purchased from Strem Chemicals and dried over P\textsubscript{2}O\textsubscript{5} in vacuo for 24 h. Alkali metals were purchased from Strem Chemicals and used as received. Corannulene was prepared as described previously\textsuperscript{13} and sublimed at 175 °C prior to use. The \textsuperscript{1}H NMR spectra were measured on a Bruker AC-400 spectrometer at 400 MHz for \textsuperscript{1}H and were referenced to the resonances of the corresponding solvent used. The UV-vis spectra were recorded on a PerkinElmer Lambda 35 spectrometer. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

\[ \left\{ \text{Li(DME)} \right\}_{1.5} \left\{ \text{Li(DME)}_{1.5} \right\}_2 \text{C}_{20}\text{H}_{10}^{2-} \] (14)

DME (2 mL) was added to a flask containing excess Li metal and corannulene (5 mg, 0.02 mmol). The resulting deep green solution was stirred at room temperature for 8 h to give a deep brown color characteristic of the corannulene tetraanion. The mixture was filtered and combined with the solution of neutral corannulene (5 mg, 0.02 mmol) in DME (2 mL). The resulting purple solution was layered with hexanes (3 mL) and kept at 10 °C to afford purple blocks. They were collected in 36 h, washed several times with hexanes and dried in vacuo. Yield: 60%. UV-vis (DME, nm): $\lambda_{\text{max}} = 502$. \textsuperscript{1}H NMR (400 MHz, THF-$d_8$, −70 °C, ppm): $\delta = −5.4$. \textsuperscript{7}Li NMR (155.5 MHz, THF-$d_8$, −55 °C, ppm): $\delta = 3.1$. 

90
$^1$H NMR of 14

$^7$Li NMR of 14
[Li(diglyme)$_2$][C$_{20}$H$_{10}$]$^{2-}$ (15)

Diglyme (2 mL) was added to a flask containing excess Li metal and corannulene (5 mg, 0.02 mmol). The resulting deep green solution was stirred at room temperature for 72 h to give a deep brown color of the corannulene tetraanion. The mixture was filtered and combined with the solution of neutral corannulene (5 mg, 0.02 mmol) in diglyme (2 mL). The resulting purple solution was layered with hexanes (3 mL) and kept at 10 °C to give purple blocks of 5. They were collected in 48 h, washed several times with hexanes and dried in vacuo. Yield: 80%. UV-vis (diglyme, nm): $\lambda_{\text{max}}$ = 500. $^1$H NMR (400 MHz, THF-d$_8$, −70 °C, ppm): $\delta$ = −5.6. $^7$Li NMR (155.5 MHz, THF-d$_8$, −60 °C, ppm): $\delta$ = 2.85. Anal. Calcd for C$_{44}$H$_{66}$Li$_2$O$_{12}$: C, 65.99; H, 8.31; Found: C, 65.80; H, 8.32.

$^1$H NMR of 15
[Na(THF)$_2$(18-crown-6)]$_2$[Na$_2$(18-crown-6)(C$_{20}$H$_{10}^{2-}$)$_2$]$_2$·2THF and [Na(THF)$_2$(18-crown-6)]$^-$ (16)

THF (3 mL) was added to a flask containing excess of sodium, corannulene (15 mg, 0.06 mmol), and 18-crown-6 (18 mg, 0.07 mmol). The resulting green solution was stirred at room temperature for 12 h to give a bright purple solution of the corannulene-dianion. The resulting purple solution was layered with hexanes (3 mL) and kept at 10 °C. Purple crystalline solid was collected in 48 h, washed several times with hexanes and dried in vacuo. Yield: 85%; $^1$H NMR (400 MHz, THF-$d_8$, 15 mM, 25 °C, ppm): $\delta$ = 7.9; $^1$H NMR (400 MHz, THF-$d_8$, 15 mM, 25 °C, ppm): $\delta$ = 9.9 (OCH$_2$), 6.2 (OCH$_2$), −6.0 (C$_{20}$H$_{10}^{2-}$); UV-vis (THF, nm): $\lambda_{\text{max}}$ = 398, 522.
[Na$_2$(DME)$_3$][C$_{20}$H$_{10}^{2-}$] (17)

DME (3 mL) was added to a flask containing an excess of Na metal and corannulene (10 mg, 0.04 mmol). The green solution was stirred at room temperature for 16 h to give a deep purple mixture. The purple mixture was filtered, layered with hexanes (3 mL) and kept at 10 °C. Purple crystalline material was collected in 70 h. The purple solution was decanted, and the crystals were washed several times with hexanes, and dried in vacuo. Yield: 60%. Anal. Calcd for C$_{32}$H$_{40}$Na$_2$O$_6$: C, 67.81; H, 7.12. Found: C, 67.93; H, 7.02;

$^1$H NMR (400 MHz, THF-$d_8$, 15 mM, 25 °C, ppm): $\delta = 3.57$ (CH$_3$), 3.84 (CH$_2$); $^1$H NMR (400 MHz, THF-$d_8$, 15 mM, -60 °C, ppm): $\delta = 5.20$ (CH$_3$), 7.201 (CH$_2$), -4.88 (C$_{20}$H$_{10}^{2-}$); UV-vis (DME, nm): $\lambda_{max} = 387$ (sh), 500.
THF (3 mL) is added to a flask containing excess K, corannulene (15 mg, 0.06 mmol), and 18-crown-6 ether (18 mg, 0.07 mmol). The resulting green solution is stirred at room temperature for 12 h to give a bright purple solution of the corannulene dianion. It is filtered, layered with hexanes (3 mL) and kept at 10 °C. Layering with hexanes leads to the precipitation of 19b as the major product; for the crystallization of 19a a hexanes/diglyme (v:v 10:1) mixture has been used as a solute. Yield: 85%; $^1$H NMR (400 MHz, THF-$d_8$, 15 mM, 25 °C, ppm): $\delta = 6.2$ (OCH$_2$); $^1$H NMR (400 MHz, THF-$d_8$, 15 mM, −80 °C, ppm): $\delta = 7.2$ (OCH$_2$), −4.5 (C$_{20}$H$_{10}^{2-}$); UV-vis (THF, nm): $\lambda_{\text{max}} = 386, 517$; Anal. Calcd for C$_{44}$H$_{58}$O$_{12}$K$_2$ ($M_W = 857.12$): C, 61.66; H, 6.82; Found: C, 61.67; H, 6.60.
\[ \text{[Cs}_2(\text{dicyclohexano-18-crown-6})_{1.5}]\text{[C}_{20}\text{H}_{10}^2^-]\text{-THF (19·THF)} \]

Diglyme (3 mL) was added to a flask containing Cs metal (11.8 mg, 0.088 mmol, 2.2 eq.), dicyclohexano-18-crown-6 (30 mg, 0.08 mmol), and corannulene (10 mg, 0.04 mmol). The resulting deep green solution was stirred at room temperature for 24 h to give a bright purple solution of the corannulene dianion. The resulting purple solution was filtered, layered with THF:hexanes (1:10, 3 mL) and kept at 10 °C. Purple crystals (plates) of 19 were collected in 56 h. The crystals were separated from the purple solution, washed several times with hexanes, and dried in vacuo. Yield: 30 mg, 65\%.

UV-vis (diglyme, nm): \( \lambda_{\text{max}} = 504, 664 \).
[\text{Cs}_2(\text{dicyclohexano-18-crown-6})_{1.5}]\text{[C}_{20}\text{H}_{10}^{2-}] \ (19)

Diglyme (3 mL) was added to a flask containing Cs metal (11.8 mg, 0.088 mmol, 2.2 eq.), dicyclohexano-18-crown-6 (30 mg, 0.08 mmol), and corannulene (10 mg, 0.04 mmol). The resulting deep green mixture was stirred at room temperature for 24 h to give a bright purple mixture of the corannulene dianion. The resulting purple mixture was filtered, crashed out with hexanes (3 mL), and the precipitate was allowed to settle overnight at room temperature. The following day, the solution was decanted. The purple powder was washed several times with hexanes and dried \textit{in vacuo}. Yield: 32 mg, 75%.

Anal. Calcd C_{50}H_{64}Cs_{2}O_{9}: C; 55.87, H; 6.00; Found: C; 55.82; H; 5.83.
3.8 References


4. Corannulene Trianions

4.1 Introduction

Trianions of polycyclic arenes are extremely rare. They have been structurally characterized for bisanthryl,\(^{1}\) decacyclene,\(^{2}\) and the \(\text{C}_{60}\)-fullerene\(^{3}\) only. Previously, the paramagnetic \(\text{C}_{20}\text{H}_{10}\)\(^{3-}\) radical was detected by ESR spectroscopy by \textit{in-situ} reduction of corannulene with lithium metal in THF.\(^{4}\) It provided the only evidence of existence of this transient species in solution, as the initially reported UV-vis spectroscopic data for the \(\text{C}_{20}\text{H}_{10}\)\(^{3-}\) trianion were later re-assigned to the tetrareduced state of corannulene.\(^{5}\) We therefore decided to focus on the controlled preparation of corannulene trianions and their full characterization. Although our numerous attempts to isolate transient trianions from reduction reactions of corannulene with light alkali metals have been unsuccessful so far, the use of cesium resulted in the preparation of the first two products containing \(\text{C}_{20}\text{H}_{10}\)\(^{3-}\) anions. These products were fully characterized to reveal a number of unique features, as detailed below.

4.2 \([\text{Cs}_3(\text{diglyme})_2][\text{C}_{20}\text{H}_{10}\)\(^{3-}\])

Several attempts to crystallize corannulene trianion, upon reduction of \(\text{C}_{20}\text{H}_{10}\) with cesium metal (3.5 eq.), led to the precipitation of oily or amorphous powders. Ultimately, we found that addition of dicyclohexano-18-crown-6 to the reaction mixture followed by its layering with hexanes resulted in the formation of several brown-red crystals of \([\text{Cs}_3(\text{diglyme})_2][\text{C}_{20}\text{H}_{10}\)\(^{3-}\]) (20).\(^{6}\) Surprisingly, crown ether is not found in the final crystalline product although its presence in the reaction mixture somehow facilitates crystallization. For the next step, the product yield was significantly improved (from 10%
up to 50%) when a mixture of cesium and lithium metals (in a 3.5:2 ratio with respect to corannulene) was used for the reduction. Such cooperative effects of two metals leading to their enhanced reactivity was recently described. Notably, no crown ether was used in that optimized procedure, providing reproducibly bulk crystals of 20 in good yield. These crystals are soluble in diglyme and very sparingly soluble in THF.

The X-ray crystallographic study revealed that the asymmetric unit of 20 consists of one corannulene trianion, three cesium ions, and two diglyme molecules (Figure 38). In the molecular structure, four cesium ions form an unprecedented tetranuclear alkali metal cluster that is sandwiched between two triply reduced corannulene bowls to yield a novel type of supramolecular assembly, \([\text{C}_{20}\text{H}_{10}^{3-}/\text{Cs}_4/\text{C}_{20}\text{H}_{10}^{3-}]^{2-}\) (Figure 38b).

**Figure 38.** Asymmetric unit (a), sandwich view (b), and depiction of the solvated Cs\(^+\) ions within the sandwich, superimposed with the space filling model (c) of 20.

In the above sandwich, a convex-to-convex arrangement of two bowls is found with their shortest separation of 4.952(5) Å (Figure 39a). The \([\text{C}_{20}\text{H}_{10}^{3-}/\text{Cs}_4/\text{C}_{20}\text{H}_{10}^{3-}]^{2-}\)
aggregate demonstrates a staggered conformation of two C$_{20}$H$_{10}^3^-$ anions that are slipped in respect to each other by 1.843(5) Å (Figure 39b).

![Figure 39. Side (a) and top (b) view of the sandwich [C$_{20}$H$_{10}^3^-$/Cs$_4$/C$_{20}$H$_{10}^3^-]^2^-$ in 20.](image)

The sandwiched Cs$_2$, Cs$_2'$, Cs$_3$, and Cs$_3'$ ions form a rectangle with the Cs···Cs separations (4.181(4) and 4.995(4) Å) being notably shorter than that in the parent metal (5.318(7) Å)$^8$ or twice the van-der-Waals radius of cesium (3.43 Å)$^9$. The Cs$_2$ ions are bound to both anionic bowls in an $\eta^6$-mode (Figure 38b) with the Cs$_2$···C interatomic distances of 3.275(5)−3.740(5) Å (Cs$_2$···C$_6$(centroid) 3.229(5) and 3.265(5) Å). In contrast, the Cs$_3$ ions are $\eta^3$- and $\eta^6$-bound to the bowls with the Cs$_3$···C distances of 3.314(6)−3.601(5) Å and 3.231(5)−3.775(5) Å (Cs$_3$···C$_6$(centroid) is 3.188(5) Å), respectively. The coordination spheres of the encapsulated Cs$_2$ and Cs$_3$ ions are completed by chelating diglyme molecules (Figure 38c). The corresponding Cs···O bond lengths (3.069(4)−3.466(4) Å) are close to those previously reported for the salts of aromatic ligands with Cs$^+$ ions solvated by O-donors.$^{10}$
Interestingly, the extraneous Cs1 cation is bound to the concave face of the anionic dish and located above its five-membered ring with the Cs···C_{hub} distances measured at 3.116(5)–3.328(5) Å (Figure 38b). The concave placement of metals into the corannulene bowl is very rare and was only recently discovered. The endo Cs···C_{hub} contacts with a triply charged bowl are much shorter than those in [Cs(18-crown-6)][C_{20}H_{10}^-] (12), 3.424(3)–3.573(3) Å. In contrast to a very symmetrical cesium coordination in [Cs(18-crown-6)][C_{20}H_{10}^-], the Cs1 ion in 20 is shifted toward the benzene rings of the trianion. The resulting intramolecular contacts between Cs1 and peripheral C atoms of C_{20}H_{10}^{3-} range from 3.275(5) Å to 3.662(5) Å. The Cs1 ion is also η^3-bound (Cs···C 3.542(5)–3.638(5) Å) to the exterior of C_{20}H_{10}^{3-} from the neighboring dimer and shares a diglyme molecule with the sandwiched Cs2 cation. The resulting Cs1···C and Cs1(2)···O interactions lead to the formation of a 2D polymeric network in the solid state (Figure 40).

Figure 40. Fragment of a 2D polymeric network in 20. Corannulene trianions and cesium cations are depicted using the space-filling model.
Interestingly, the acquisition of three electrons by \( \text{C}_{20}\text{H}_{10} \) and subsequent aggregation with multiple cesium ions does not induce any significant flattening of the resulting trianion. The bowl depth of \( \text{C}_{20}\text{H}_{10}^{3-} \) in 20 (0.850(7) Å) remains almost unchanged compared to that in \( \text{C}_{20}\text{H}_{10}^{0} \) (0.875(2) Å).\(^{11}\) The addition of the first and second electrons to \( \text{C}_{20}\text{H}_{10} \) is known to cause minor core flattening (to 0.850(3) and 0.811(3) Å, respectively) (Chapters 2 and 3). Thus, the carbon framework of \( \text{C}_{20}\text{H}_{10}^{3-} \), being more curved than that of the dianion of corannulene, stands out from the previously expected general trend of a step-wise bowl depth decrease upon consecutive electron addition. The theoretically predicted bowl depth of uncoordinated \( \text{C}_{20}\text{H}_{10}^{3-} \) (0.41 Å) is much smaller than the experimental value.\(^{12}\) This again illustrates the need for structural studies to provide the experimental benchmarks for validation of theoretical methods.

The central hub C–C bond lengths in the trianion (1.401(7)–1.429(7) Å) are comparable to those measured in \( \text{C}_{20}\text{H}_{10} \) (Table 14).\(^{11}\) The spoke and rim C–C bond lengths in corannulene trianion are elongated when compared to the neutral ligand. In general, all C–C bonds of \( \text{C}_{20}\text{H}_{10}^{3-} \) demonstrate a stronger equalization of the bond lengths compared to \( \text{C}_{20}\text{H}_{10}^{0} \), \( \text{C}_{20}\text{H}_{10}^{-} \), and \( \text{C}_{20}\text{H}_{10}^{2-} \).
Table 14. Key distances (in Å) for corannulene and C_{20}H_{10}^{3−} in 20 and 21.

<table>
<thead>
<tr>
<th></th>
<th>C_{20}H_{10}^{0}</th>
<th>20</th>
<th>21</th>
</tr>
</thead>
<tbody>
<tr>
<td>hub</td>
<td>1.411(2)−1.417(2)</td>
<td>1.401(7)−1.429(7)</td>
<td>1.401(5)−1.418(5)</td>
</tr>
<tr>
<td>spoke</td>
<td>1.376(2)−1.381(2)</td>
<td>1.418(8)−1.443(7)</td>
<td>1.423(5)−1.430(5)</td>
</tr>
<tr>
<td>flank</td>
<td>1.441(2)−1.450(2)</td>
<td>1.421(7)−1.439(7)</td>
<td>1.416(5)−1.488(5)</td>
</tr>
<tr>
<td>rim</td>
<td>1.377(2)−1.387(2)</td>
<td>1.416(7)−1.438(8)</td>
<td>1.411(5)−1.455(5)</td>
</tr>
<tr>
<td>bowl depth</td>
<td>0.875(2)</td>
<td>0.850(7)</td>
<td>0.808(5)</td>
</tr>
</tbody>
</table>

4.3 [K_{2}Cs(diglyme)_{2}][C_{20}H_{10}^{3−}]

The isolation of 20 prompted us to investigate if other alkali metals were capable of reducing corannulene to the trianion stage. After numerous attempts, we found that when a mixture of cesium (3.5 eq.) and excess potassium, with respect to corannulene, was used for the reduction, the formation of [K_{2}Cs(diglyme)_{2}][C_{20}H_{10}^{3−}], 21, can be achieved. The dark red blocks of 21 were successfully crystallized by slow diffusion of hexane vapors into a diglyme solution of the product kept at 10 °C. According to an X-ray diffraction study, the asymmetric unit of 21 consists of one corannulene trianion, two potassium ions, one cesium ion, and two diglyme molecules (Figure 41a). In the molecular structure, four potassium ions are bound between the two triply reduced corannulene bowls to yield the supramolecular sandwich [C_{20}H_{10}^{3−}/K_{4}/C_{20}H_{10}^{3−}]^{2−} (Figure 41b). This triple-decker structure is similar to that found in 20. However, four potassium ions are now sandwiched between two C_{20}H_{10}^{3−} anions. As observed in 20, a convex-to-convex arrangement of two bowls is also found in 21. The
[C$_{20}$H$_{10}$$^{3-}$/K$_4$/C$_{20}$H$_{10}$$^{3-}$]$^{2-}$ aggregate demonstrates a staggered conformation of two C$_{20}$H$_{10}$$^{3-}$ anions that are slipped in respect to each other by 1.838(4) Å.

**Figure 41.** Asymmetric unit (a) and sandwich view (b) of 21.

The sandwiched K1, K2, K1’, and K2’ ions form a rectangle with the K···K separations of 4.212(4) Å and 5.185(4) Å (compared to those in elemental potassium of 4.54 Å). These distances are comparable to the Cs$_4$ rectangle in 20 (Figure 39). The K1 ions are bound to both anionic bowls in an $\eta^6$-mode with the K1···C interatomic distances of 2.975(4)–3.634(4) Å (K1···C$_{6\text{centroid}}$): 2.791(4) and 3.041(4) Å. In contrast, the K2 ions are $\eta^3$- and $\eta^6$-bound to the bowls with the K2···C distances of 3.129(4)–3.440(4) Å and 2.977(4)–3.335(4) Å (K2···C$_{6\text{centroid}}$) is 2.810(4) Å. The coordination sphere of the encapsulated K2 ion is completed by chelating diglyme (Figure 41). The corresponding K···O distances are 2.691(3)–2.859(3) Å.
As observed with cesium-generated C\textsubscript{20}H\textsubscript{10}\textsuperscript{−} and C\textsubscript{20}H\textsubscript{10}\textsuperscript{2−},\textsuperscript{10b,14} the concave cavities of the charged corannulene are occupied by large Cs\textsuperscript{+} ions in 21, confirming the remarkable selectivity of this ion towards endo-binding to C\textsubscript{20}H\textsubscript{10}-bowl. The cesium ions are coordinated to the \textit{endo} surface of this bowl-shaped polyarene in an \(\eta^5\)-fashion (Cs···C 3.125(3)–3.313(3) Å). The separation of the Cs\textsuperscript{+} ion to the center of the five membered ring (2.98 Å) verifies the strong metal binding to the \(\pi\)-bowl. In order to satisfy the coordination sphere of cesium, the ion is also bound to three oxygen atoms of diglyme (Cs···O 3.110(3)–3.467(3) Å) and one oxygen atom of a neighboring diglyme molecule (3.400(3) Å). As a result, the [Cs(diglyme)]\textsuperscript{+} cations serve as building blocks for the formation of a 1D polymeric chain in the solid state (Figure 42).

\textbf{Figure 42.} Polymeric chain of 21.

It should be mentioned that additional contacts between K1 and the adjacent C\textsubscript{20}H\textsubscript{10}\textsuperscript{3−} moieties are observed in the crystal lattice of 21 (3.284(4)–3.428(4) Å, Figure 43).
In general, the geometric perturbations of $C_{20}H_{10}^{3-}$ in 21 are quite similar to those in 20. In both cases, the hub C–C bond lengths of $C_{20}H_{10}^{3-}$ are comparable to those in neutral $C_{20}H_{10}$ (Table 14), whereas the spoke and rim C–C bond distances are elongated. The acquisition of three electrons by $C_{20}H_{10}$ and subsequent aggregation with multiple potassium and cesium ions does not induce any significant flattening of the resulting trianion. The bowl depth of $C_{20}H_{10}^{3-}$ in 21 is 0.808(5) Å. It should be mentioned that the bowl of the mixed-metal corannulene trianion in 21 is more flattened than that in 20 (0.81 vs. 0.85 Å).

4.4 Solution Behavior of Corannulene Trianion

4.4.1 UV-vis Data

The study of the in-situ generated products 20 and 21 (in diglyme) by UV-vis spectroscopy shows relatively similar data (Figure 44). In both cases, a broad absorbance band at approximately $\lambda = 500$ nm is observed, along with the most intense band at $\lambda_{\text{max}} = 388$ nm, which is characteristic of the $C_{20}H_{10}^{3-}$ anion.
The absorbance maximum in the optical spectra of $\text{C}_{20}\text{H}_{10}^{3-}$ are hypsochromically shifted compared to the most intense band of $\text{C}_{20}\text{H}_{10}^{4-}$ ($\lambda_{\text{max}} = 460$ nm in diglyme\textsuperscript{15} and 429 nm in THF, Chapter 5).\textsuperscript{16}

It should be noted that further reduction of $\text{C}_{20}\text{H}_{10}^{3-}$ to the $\text{C}_{20}\text{H}_{10}^{4-}$ state was not detected upon corannulene reaction with cesium (3.5 eq.) in diglyme, even when an excess of lithium metal was added to the mixture (Figure 45). The reaction time was limited to less than 24 h.
**Figure 45.** UV-vis spectra of *in-situ* generated products in diglyme (a) excess Cs and (b) excess Li and Cs (3.5 eq.).

### 4.5 Conclusions

The first crystallographic characterization of $C_{20}H_{10}^{3−}$ revealed that corannulene trianions show preference for self-assembly and form novel and unique supramolecular aggregates with four alkali metal ions, Cs₄ or K₄, sandwiched between two bowls (Figure 46). The double negative charge of the resulting sandwiches is compensated by two extraneous Cs⁺ cations placed inside the concave cavities of the triply-reduced corannulene bowls. In this case, NMR could not be used for predicting the self-aggregation pattern of corannulene trianion-radicals, leaving X-ray crystallography as the only source of structural information. The revealed new aggregation type may serve as a model for various intercalated carbonaceous materials, fabricated from carbon allotropes with non-planar carbon surfaces.
Figure 46. Space filling model of $[\text{C}_{20}\text{H}_{10}^3^-/\text{Cs}_4/\text{C}_{20}\text{H}_{10}^3^-]^{2-}$ (left) and $[\text{C}_{20}\text{H}_{10}^3^-/\text{K}_4/\text{C}_{20}\text{H}_{10}^3^-]^{2-}$ (right) in 20 and 21, respectively.
### 4.6 Experimental Details

**Materials and Methods.** All manipulations were carried out using break-and-seal\(^{17}\) and glove-box techniques under an atmosphere of argon, as previously described.

\[
[\text{Cs}_3(\text{diglyme})_2][\text{C}_{20}\text{H}_{10}^{3-}] \ (20)
\]

**Direct Cs reduction**

Diglyme (3 mL) was added to a flask containing Cs metal (28 mg, 0.21 mmol, 3.5 eq.), corannulene (15 mg, 0.06 mmol), and dicyclohexano-18-crown-6 (22 mg, 0.06 mmol). The resulting green mixture was stirred at room temperature for 60 h to give a bright purple-red solution. This solution was filtered, layered with hexanes (3 mL), and kept at 10 \(^\circ\)C. A few X-ray quality crystals of 20 were collected in four weeks. Yield: ca. 10%.

**Cs/Li reduction**

Diglyme (3 mL) was added to a flask containing Cs metal (28 mg, 0.21 mmol, 3.5 eq.), Li (0.85 mg, 0.12 mmol), and corannulene (15 mg, 0.06 mmol). The resulting green solution was stirred at room temperature for 16 h to give a bright purple-red solution. The resulting purple-red solution was filtered, layered with hexanes (3 mL), and kept at 10 \(^\circ\)C. X-ray quality crystals (prisms) of 20 were present in 72 h. Yield: up to 50%. UV-vis (diglyme, nm): \(\lambda_{\text{max}} = 388, 495\). UV-vis (THF, nm): \(\lambda_{\text{max}} = 386\). Anal. Calcd for \(\text{C}_{32}\text{H}_{38}\text{Cs}_3\text{O}_6\): C, 41.90; H, 4.18; Found: C, 41.78; H, 4.14.

\[
[\text{K}_2\text{Cs}(\text{diglyme})_2][\text{C}_{20}\text{H}_{10}^{3-}] \ (21)
\]

Diglyme (3 mL) was added to a flask containing Cs (19 mg, 0.14 mmol), excess K, and corannulene (10 mg, 0.04 mmol). The deep green solution was stirred at room
temperature for 15 h resulting in a deep red mixture. The red mixture was filtered, layered with hexanes (2.5 mL), and kept at 10 °C. Dark red blocks of 21 were present in 90 h. The red solution was decanted, and the crystals were washed several times with hexanes and dried in vacuo. Yield: 32 mg, 60%. UV-vis (diglyme, nm): $\lambda_{\text{max}} = 388, 514$. Anal. Calcd for C$_{32}$H$_{38}$K$_2$CsO$_6$: C, 52.67; H, 5.25; Found: C, 52.78 ; H, 5.24. $^1$H NMR (400 MHz, THF-$d_8$, 20 °C, ppm): $\delta = 3.32, 3.48, \text{ and } 3.58$. $^1$H NMR (400 MHz, THF-$d_8$, −60 °C, ppm): $\delta = 3.35 (\text{OCH}_3), 3.51 (\text{CH}_2), \text{ and } 3.59 (\text{CH}_2)$. 
4.7 References


5. Corannulene Tetraanions

5.1 Introduction

The $\text{C}_{20}\text{H}_{10}^{4−} (1^4)$ anion, the highest reduction state of corannulene, bears one electron per five carbon atoms and as such is more electron-rich than the fullerene hexaanion, $\text{C}_{60}^{6−}$. On the basis of NMR studies, earlier investigators concluded that the tetraanions of corannulene and its derivatives aggregate into supramolecular dimers charge-compensated by coordinated $\text{Li}^+$ cations. Two tetraanions, $1^4$, in the dimer were described as “glued” together by four lithium ions to form a “stable high-order molecular sandwich” in solution (Chapter 1, Figure 8). The residual four $\text{Li}^+$ ions were suggested to bind to the dimer exterior: two on the top and two on the bottom of the sandwich. Although the original NMR data were inconclusive about the locations of the $\text{Li}^+$ ions and the depths and relative orientations of the two bowls, this proposed model has been largely accepted as a paradigm for the assembly of reduced buckybowls and fullerenes with $\text{Li}^+$ ions ever since. Since direct structural characterization of the resulting self-assembled product was missing, we decided to focus on its crystallization followed by the first X-ray crystallographic study.

5.2 Reduction in THF

The addition of electrons to corannulene initially results in generation of an intense green solution (monoanion), which subsequently endures higher reduction and transforms to a deep purple solution (dianion). Finally, the furthest reduction stage of corannulene with Li metal can be detected by the appearance of a brown solution of
corannulene tetraanions. In THF, the reduction of corannulene to the tetraanion stage occurs rather quickly (within 12 h).

After multiple attempts, the lithium salt of $1^{4-}$ was successfully crystallized by slow diffusion of hexanes vapors into a THF solution of the product kept at 15 °C under strictly anaerobic conditions. Our X-ray structural analysis confirmed a sandwich-type assembly for $1^{4-}$ (Scheme 8).

**Scheme 8.**

However, in contrast to the previously proposed model, five lithium ions were found to be sandwiched between the two tetraanionic corannulene decks in the solid state (Figure 47). Two more Li$^+$ ions are bound to the external surface of this supercharged sandwich, one on the top and one on the bottom, while the remaining Li$^+$ cation is solvent-separated. The overall product can be formulated as $[\text{Li(THF)}_4] \{[\text{Li(THF)}_2]/[\text{Li}_5(\text{C}_{20}\text{H}_{10}^{4-})_2]^3-/[\text{Li(THF)}_3]\}$ (22).
Figure 47. Molecular structure of the salt 22 with the sandwich being in anionic form and [Li(THF)$_4$]$^+$ as a counterion (a). Space-filling drawings of the side view of the sandwich (b).

The corannulene bowls of the dimer are almost ideally eclipsed, as was correctly proposed in the previous study.$^1$ In contrast to the model proposed by Scott et al.$^1$ which suggested a “stacked-bowl” (convex-to-concave) geometry, a convex-to-convex bowl arrangement in [1$^4$/Li$_5$/1$^4$]$^{3-}$ is evident from our X-ray crystallographic analysis.

All five adjacent six-membered rings of corannulene in 22 are involved in interactions with Li$^+$. In particular, each Li$^+$ center is sandwiched between the benzene rings of two corannulene decks with a slight shift to the outer edges of the aromatic framework. The Li···Li distances within an almost planar Li$_5$-cluster (3.048(4)–3.100(4) Å) are slightly elongated in comparison with lithium metal (3.04 Å). The Li···C and Li···C$_6$ (centroid) distances within the sandwich fall in the ranges of 2.226(3)–2.718(4) Å and 1.924(3)–2.094(3) Å, respectively.
In 22, two exterior lithium ions are coordinated to the sandwich in an \( \eta^3 \)- and \( \eta^6 \)-fashion with the corresponding Li···C separations (2.316(3)−2.704(3) Å and 2.203(3)−2.735(3) Å, respectively). The external lithium ion bound to the sandwich in an \( \eta^3 \)-mode is coordinated to three THF molecules (Li···O 1.962(3)−2.024(3) Å). It should be mentioned that the Li\(^+\) ion bound to the bowl in an \( \eta^6 \)-manner is coordinated to two THF molecules with much shorter Li···O separations (1.918(3)−1.933(3) Å).

The bowl depth of corannulene in 22 is reduced to 0.288(2) Å from 0.875(2) Å in the parent polyarene.\(^3\) The acquisition of four electrons by corannulene also strongly affects the C−C bond length distribution in the tetraanion (Table 15). The interior 5-membered ring of 22 slightly shrinks, while all exterior C−C bonds become essentially equalized compared to a clearly alternating double and single bond pattern in neutral corannulene. These perturbations indicate the formation of the predicted “annulene-within-an-annulene” electronic structure,\(^1\) where an aromatic cyclopentadienyl anion (6\(\varepsilon\)/5C) is suspended by five radial bonds within the hole of an aromatic 18\(\varepsilon\)/15C annulenylin.
Table 15. Key distances (in Å) for neutral C$_{20}$H$_{10}$ and C$_{20}$H$_{10}$$^{4-}$ in 22, 23, and 24.

<table>
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<tr>
<th></th>
<th>C$<em>{20}$H$</em>{10}$</th>
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<td>1.429(5)</td>
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<td>0.259(2)</td>
<td>0.283(5), 0.214(3),</td>
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<td>0.404(3)</td>
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<td>2.718(4)</td>
<td>2.662(7)</td>
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<td>Li···C$_{\text{inter}}$</td>
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<tr>
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<td>2.316(3)</td>
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<tr>
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<td>2.203(3)</td>
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<td>Li···Li</td>
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<td>3.100(4)</td>
<td>3.083(7)</td>
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120
Having elucidated the structure formed by the highly charged corannulene anion, we re-investigated its solution behavior, using variable-temperature $^7$Li NMR spectroscopy.$^2$ First, the sample for the NMR study was prepared by redissolving the pure crystalline salt of 22 in THF-$d_8$ (Figure 48).

![Variable-temperature $^7$Li NMR spectra of 22 (redissolved in THF-$d_8$).]

**Figure 48.** Variable-temperature $^7$Li NMR spectra of 22 (redissolved in THF-$d_8$).

Second, the direct reduction of corannulene with excess lithium in an NMR tube was also carried out; reproducing the experimental conditions reported by Scott *et al.*$^1$ In both cases, identical $^7$Li NMR spectra were obtained. Each displays a broad resonance at $-4.3$ ppm and a sharp signal at $-11.7$ ppm ($-80$ °C, Figure 49), which were assigned to exterior and interior lithium ions, respectively.
In contrast to the previous account, the relative peak intensities are integrated with a ratio of 3:5, which is consistent with X-ray data and the presence of stacked aggregates having five interior lithium cations. This clearly verifies that the \([\text{Li}_5(\text{C}_{20}\text{H}_{10}^{4^-})_2]^{3^-}\) sandwich adopts the same form in solution and that its structure is not induced by crystallization conditions. Concerning the previous results, we can speculate that some excess of extraneous lithium ions might appear due to partial oxidation or hydrolysis processes. The latter could have resulted in the formation of \(^1\text{H}\) and \(^{13}\text{C}\) NMR silent species, such as corannulene mono- and dianions, that affected the overall peak
integration for unsandwiched lithium ions and given the overestimated ratio of 4:4. A broad $^7\text{Li}$ NMR resonance signal at $-4.3$ ppm demonstrates the fluxional behavior of the more loosely bound exterior lithium ions and their fast exchange with the solvent-separated $[\text{Li(THF)}_4]^+$ cations.

### 5.3 Crystallization in the Presence of Crown Ether

The remarkable stability of the $[\text{I}^{4-}/\text{Li}_5/\text{I}^{4-}]^{3-}$ dimer has been further demonstrated by crystallization of the sandwich from a THF solution containing a strong chelating agent, 12-crown-4 ether. From this system, the new crystalline product, $[\text{Li(THF)}_4][\text{Li(THF)(12-crown-4)}]_2[\text{Li}_5(\text{C}_{20}\text{H}_{10}^{4-})_2]^{3-}$ (23, Figure 50) was obtained.$^2$

![Figure 50](image)

**Figure 50.** Molecular structure of 23 (left) along with space filling model for the sandwich core (right).
Each sandwiched Li\(^+\) ion in 23 sits between the benzene rings of two corannulene decks with a slight shift to the outer edge of C\(_{20}\)H\(_{10}\)\(^{4-}\). The Li···Li distances within the Li\(_5\)-cluster (3.044(4)–3.083(4) Å) are comparable to those observed in 22 (Table 15). The Li···C distances within the sandwich fall in the ranges of 2.240(6)–2.662(7). These distances are very similar to those in 22.

In 23, two different coordination environments around the solvent-separated lithium ions are observed in the crystal lattice. In the first, lithium is bound to four THF molecules with the corresponding Li···O distances 1.919(3)–1.963(3) Å (Figure 50). In the second, lithium is coordinated to one THF molecule and four oxygen atoms of 12-crown-4 (Figure 50). Notably, the Li···O\(_{\text{crown}}\) separations are elongated 1.908(3)–2.149(3) Å compared to the Li···O\(_{\text{THF}}\), 1.919(3) and 1.946(3) Å.

The \(^7\)Li NMR spectrum of 23 shows three peaks at −80 °C (0.2, −3.8, and −11.7 ppm) with an integration ratio of 1:2:5 (Figure 51) fully consistent with the two types of solvent-separated lithium cations observed in the crystal structure. The overall ratio of external to internal lithium ions of 3:5 verifies that the [\(\text{I}^+\)/Li\(_5\)/\(\text{I}^+\)]\(^3-\) sandwich adopts the same form in solution and that its structure is not induced by crystallization conditions.
Importantly, the $[\text{I}^{4-}/\text{Li}_5/\text{I}^{4-}]^{3-}$ dimer remains intact even when lithium cations are stripped from its exterior surface and captured by crown ether cavities. This allows crystallization of a naked trianionic sandwich, in which overall charge is not reduced by direct coordination of counter cations. The exterior lithium ions do not have a substantial effect on the geometry of the $[\text{I}^{4-}/\text{Li}_5/\text{I}^{4-}]^{3-}$ dimer because its geometric parameters are very similar to that in 22 (Table 15). This result illustrates that the two tetrreduced corannulene decks remain tightly bound in solution and do not dissociate even in the presence of strongly coordinating oxygen-donor ligands.
5.4 Reduction in Diglyme

After the formation of the supramolecular [Li₅(C₂₀H₁₀⁺⁺)₂]³⁻ sandwiches shown above, in which five Li⁺ ions are jammed between two tetrareduced corannulene decks, it remained unclear whether the preparation of the above supramolecular dimer could be accomplished in coordinating solvents other than THF. Therefore, we set up an investigation of reduction and self-assembly processes of highly reduced corannulene in the presence of the strong chelating O-donor, diglyme.⁴

Upon reduction of C₂₀H₁₀ with lithium metal in diglyme at least three distinctive reduction steps can be recognized. The formation of green monoanion is followed by purple dianion, and finally, by the appearance of the brown corannulene tetraanion. These color changes closely follow the transformations observed during stepwise lithium reduction of C₂₀H₁₀ in THF. However, in contrast to a rather fast (up to 12 hours) reduction in THF, the fully reduced C₂₀H₁₀⁴⁻ anions are formed in diglyme after prolonged reaction times (up to 4 days). The reaction progress can be monitored by UV-vis spectroscopy, as the tetrareduced corannulene exhibits absorption maxima at 460, 605, and 714 nm in diglyme. These values are bathochromically shifted (30 nm) compared to the absorption maxima of C₂₀H₁₀⁴⁻ generated in THF (429, 575, and 710 nm). Such differences in optical parameters may indicate different aggregation of the highly charged C₂₀H₁₀⁴⁻ species in diglyme and THF, which can be related to the strong chelating properties of the former.

Notably, the ⁷Li NMR spectrum of the mixture of C₂₀H₁₀ with an excess of lithium metal in diglyme (Figure 52, blue line, −40 °C) does not show resonances of the sandwiched lithium ions (δ = −10.0 ppm to −16.0 ppm). Instead, the resonance signals
are observed in the range characteristic for contact-ion pairs ($\delta = -6.0$ to $-9.0$ ppm) and solvent-separated Li\(^+\) ions ($\delta = 1.5$ ppm). This observation indicates that the presence of large amounts of diglyme prevent the sandwiching of lithium ions between the tetrareduced corannulene decks. The presence of several $^7$Li NMR signals in the range of $\delta = -6.0$ ppm to $-9.0$ ppm shows that Li\(^+\) ions bind to $C_{20}H_{10}^{4-}$ in different fashions.

**Figure 52.** $^7$Li NMR spectra (diglyme/THF-$d_8 = 40:1$, v/v, $-40$ °C) of the reaction mixture of corannulene with lithium (blue) and the solution of 22 (black).

The $^1$H NMR spectrum ($-40$ °C) of the same system demonstrates several proton resonance signals for $C_{20}H_{10}^{4-}$ in the range of 6.58–7.47 ppm, which is consistent with the $^7$Li NMR data.
To investigate the influence of a strong donor solvent on the sandwich stability, a solution of the pre-made \([\text{Li}_5(\text{C}_{20}\text{H}_{10}^4\text{O})_2]^{3-}\) dimer was monitored by \(^7\text{Li}\) NMR spectroscopy. The probe was prepared by dissolving the crystals of the freshly prepared \([\text{Li}](\text{THF})_4]\{\text{Li}(\text{THF})_2//\text{Li}_5(\text{C}_{20}\text{H}_{10}^4\text{O})_2//\{\text{Li}(\text{THF})_3\}]\) salt, 22, in diglyme. The \(^7\text{Li}\) NMR spectrum, measured at \(-40\,^\circ\text{C}\) immediately after the preparation, shows a sharp resonance signal at \(\delta = -11.7\) ppm (Figure 52, black lines). This value corresponds well to the solution of \([\text{Li}_5(\text{C}_{20}\text{H}_{10}^4\text{O})_2]^{3-}\) in THF \((\delta = -11.7\) ppm). Upon prolonged standing of this NMR probe at 25 \(^\circ\text{C}\), the intensity of this resonance for sandwiched lithium ions fades; whereas the signals of contact-ion pairs in the range from \(\delta = -6.5\) ppm to \(-9.0\) ppm increase in intensity. This NMR investigation demonstrates that the pre-formed \([\text{Li}_5(\text{C}_{20}\text{H}_{10}^4\text{O})_2]^{3-}\) sandwich completely disappears in diglyme solution in three days.

Although the inability of \(\text{C}_{20}\text{H}_{10}^4\text{O}\) to form a supramolecular dimer with \(\text{Li}^+\) ions in neat diglyme was proven, the \([\text{Li}_5(\text{C}_{20}\text{H}_{10}^4\text{O})_2]^{3-}\) sandwich can be recrystallized in the presence of diglyme by layering a THF solution with a hexanes/diglyme (v:v 10:1) mixture under strictly anaerobic conditions. Under these conditions, a new product of the overall formula \([\text{Li}(\text{THF})_2(\text{diglyme})][\text{Li}_2(\text{THF})(\text{diglyme})//\text{Li}_5(\text{C}_{20}\text{H}_{10}^4\text{O})_2]\) \((24)\) is formed, as confirmed by single-crystal X-ray diffraction (Figure 53). Importantly, the \([\text{Li}_5(\text{C}_{20}\text{H}_{10}^4\text{O})_2]^{3-}\) dimer core is preserved in 24. However, these dimers form a complex 1D assembly through exterior binding to the \([\text{Li}_2(\text{THF})(\text{diglyme})]^{2+}\) cations serving as connecting building blocks.
Figure 53. Molecular structure (a), space filling model of a 1D polymer (b), top and side views of the supramolecular sandwich (c and d) for 24.

In 24, two exterior lithium ions are coordinated to the sandwich in an η³-fashion. The corresponding Li···C separations (2.215(4)–2.679(4) Å) are close to the related contacts observed in 22, (2.316(3)–2.704(3) Å) (Table 15). The THF molecule in the [Li₂(THF)(diglyme)]²⁺ dication acts as a bidentate ligand coordinating to two Li⁺ ions. The corresponding Li···O THF distances (2.101(4) and 2.119(4) Å) are slightly elongated compared to the Li···O_diglyme bond lengths (1.992(4)–2.045(4) Å).

The supramolecular dimer in the mixed THF-diglyme salt 24 shows essentially close geometrical parameters compared to that in 22 and 23 (Table 15). Each sandwiched Li⁺ ion in 24 sits between the benzene rings of two corannulene decks with a slight shift to the outer edge of C$_{20}$H$_{10}^{4−}$, as observed beforehand. The Li···Li distances within an almost planar Li$_5$-cluster (3.037(4)–3.172(4) Å) are slightly elongated in comparison with lithium metal (3.04 Å). The Li···C and Li···C$_{6$(centroid)} distances within the sandwich fall in the ranges of 2.215(4)–2.663(4) Å and 1.937(4)–2.027(4) Å, respectively. These separations compare well to those previously measured in the polyarene adducts with sandwiched or contact Li⁺ ions.6
The corannulene bowls in 24 are found to be almost ideally eclipsed and arranged in a convex-to-convex fashion (Figure 53c,d). The acquisition of four electrons by C_{20}H_{10} results in the significant flattening of its carbon framework: the bowl depths are reduced to 0.214(3) and 0.404(3) Å in 24 compared to neutral corannulene (0.875(2) Å)\(^3\) and its mono- and dianions (0.84 Å and 0.80 Å, respectively Chapter 2 and Chapter 3). The hub C−C bond lengths of C_{20}H_{10}^{4−} (1.396(3)−1.400(3) Å) are slightly shorter than in C_{20}H_{10}^{0} (1.411(2)−1.417(2) Å). The equalization of the rim and flank C−C bond distances (Table 15) and shrinking of the central five membered ring in C_{20}H_{10}^{4−} again confirm the formation of an annulene-within-an-annulene structure, proposed by Scott et al.\(^7\)

Crystals of 24 were redissolved in THF-\(d_8\) to show that the chemical shifts of the sandwich, detected in \(^1\)H and \(^13\)C NMR spectra, are very close to those reported previously.\(^1\) The resonances of coordinated diglyme molecules appear as three sharp signals at room temperature in the \(^1\)H NMR spectrum of 24. Cooling the probe results in the significant broadening of diglyme proton resonances, whereas the signal of C_{20}H_{10}^{4−} remains almost unchanged in the range of +20 to −80 °C (Figure 54). This observation may indicate the association of [Li(diglyme)\(_n\)(THF)\(_m\)]\(^+\) cations with the sandwich through C−H(diglyme)···π contacts at low temperatures (loose ion pair).
Figure 54. Variable-temperature $^1$H NMR spectra of 24.

The variable-temperature $^7$Li NMR study for 24 shows one broad lithium resonance at $\delta = -8.4$ ppm at 20 °C. Upon cooling below −30 °C, this signal is split into two resonances at −3.8 ppm and −11.7 ppm, corresponding to the exterior and sandwiched lithium ions, respectively (Figure 55). Such temperature dependent behavior and $\delta(^7\text{Li})$ chemical shifts are close to those in 22. A slightly different value of the chemical shift for exterior Li$^+$ ions in solution of 24 ($\delta = -3.8$ ppm) compared to 22 ($\delta = -4.3$ ppm) is attributed to the coordination of diglyme molecules to lithium ions. Importantly, the intensity ratio of resonance signals for exterior and interior Li$^+$ ions of 3:5 is in full agreement with the aggregation model previously revealed by us.$^2$
5.5 Reduction in DME

As demonstrated above, the triple-decker structure \([\text{Li}_5(\text{C}_{20}\text{H}_{10}^{4-})_2]^{3-}\), is retained upon re-crystallization of 22 from THF in the presence of strong O-donors such as crown ether and diglyme. At the same time, the use of neat diglyme for reduction of \(\text{C}_{20}\text{H}_{10}\) with lithium metal prevented the high-order self-assembly of \(1^{4-}\) with \(\text{Li}^+\) ions, according to our NMR investigations. Nevertheless, it remained unclear whether the preparation of the above supramolecular dimer could be accomplished in dimethoxyethane, leading us to investigate the reduction of corannulene with lithium metal in DME and discover the formation of multilayered supramolecular aggregates of a new type, namely \([1^{4-}/\text{Li}_6/(\text{OR})_6/\text{Li}_6/1^{4-}]^{2-}\) (25–27, Scheme 9).
Scheme 9.

The low-temperature $^7$Li NMR spectrum of tetrreduced corannulene in DME, measured after the formation of a brown solution characteristic for $\bf{1}^{4-}$ (3h, 20 °C), shows the sharp resonance of $[\bf{1}^{4-}/\bf{Li}_5/\bf{1}^{4-}]^{3-}$ at $\delta = -11.3$ ppm and the broad signal of solvated Li$^+$ ions at $\delta = -1.3$ ppm (Figure 56).

Figure 56. Time-evolution of the $^7$Li NMR spectra (−40 °C) of $[\bf{1}^{4-}/\bf{Li}_5/\bf{1}^{4-}]^{3-}$ sandwich in DME in the presence of Li metal.
The $^7\text{Li}$ signal of $[\text{Li}_5(\text{C}_{20}\text{H}_{10}^4^-)_2]^{3-}$ in DME is slightly high-field shifted compared to that observed in THF ($\delta = -11.7$ ppm). The prolonged reaction time leads to a decrease of the resonance intensity of this peak. This process is accompanied by the appearance of the $^7\text{Li}$ NMR signals in the range of $\delta = -6.0$ to $\delta = -11.0$ ppm (Figure 56), illustrating the formation of new contact-ion pairs and sandwiched Li-ions. Under ambient conditions, the $^7\text{Li}$ NMR resonance signal of the sandwich completely disappears in 8 days.

The $^1\text{H}$ NMR investigation also demonstrates the disappearance of the singlet at $\delta = 6.95$ ppm, characteristic of $[\text{Li}_5(\text{C}_{20}\text{H}_{10}^4^-)_2]^{3-}$, and the appearance of multiple new resonances for aromatic protons in the range of $\delta_{\text{H}} = 7.25$–7.15 ppm (Figure 57). Moreover, the time-dependent $^1\text{H}$ NMR spectra show the formation of $\text{H}_2\text{C}=\text{CHOCH}_3$ and $\text{H}_2\text{C}=\text{CH}_2$ in the reaction mixture. It should be emphasized that $[\text{Li}_5(\text{C}_{20}\text{H}_{10}^4^-)_2]^{3-}$ is stable in THF solution in the presence of lithium metal: the NMR study does not show any noticeable changes for the probe kept at ambient conditions for two months. However, the Li- and K-induced cleavage of DME with the formation of $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}^-$ alkoxide species has been previously detected by West and co-workers.⁹
Figure 57. $^1$H NMR spectra (20 °C) of the $[1^{4-}/$Li$_{5}/1^{4-}]^{3-}$ sandwich in the presence of lithium metal in DME. Signals at 6.45 (top) 4.11 (bottom) and 3.91 ppm (bottom) are attributed to $H_2C=CHOCH_3$. The singlet at 5.32 ppm corresponds to $H_2C=CH_2$.

Various crystallization techniques were applied and lead to the successful isolation of several new supramolecular aggregates of tetrreduced corannulene with lithium ions (25–27). Based on the above NMR observations, we speculate that products 25–27 are formed upon reaction of the initially produced $[Li_5(C_{20}H_{10}^{4-})_2]^{3-}$ with the reactive ionic species resulting from the DME cleavage (Scheme 11). Compound 25 has been crystallized from a DME/THF mixture (v:v = 20:1) as black blocks with an overall formula of $[Li_2(DME)_3][1^{4-}/Li_6(THF)/(OCH_3)_6/Li_6(THF)/1^{4-}]$. Its X-ray diffraction study revealed the formation of a unique $[Li_6/(OCH_3)_6/Li_6]^{6+}$ cluster core stabilized by
two corannulene tetraanions to form a remarkable supramolecular aggregate (Figure 58a). The layered lithium alkoxo belt with the overall dimensions of 6.5 × 5.5 × 2.5 Å consists of an O₆-ring bridging two essentially planar Li₆-hexagons. The Li−O distances within the cluster are in the range of 1.942(5)−1.994(5) Å and comparable to those measured in lithium methoxide (1.94(3) Å).¹⁰

![Figure 58.](image)

**Figure 58.** The building unit (a) and the space-filling model of a fragment of a 1D polymeric chain in 25 (b, THF molecules are omitted).

The Li⋯Li distances between the two Li₆-rings in 25 (2.500(6)−2.538(6) Å) are very short. They are shorter than those found in (CH₃Li)₄ (2.591(9) Å).¹¹ The Li⋯Li interatomic separations within the Li₆-rings (2.751(7)−2.767(7) Å) are longer than the above but still remain significantly shorter than those in 22 (3.053(5)−3.104(5) Å) and in lithium metal (3.04 Å).⁵ Notably, the formation of lithium alkoxo nanobelts may
represent possible structural motifs of Li–O deposits on a carbon composite electrode in Li-ion cells.\textsuperscript{12}

Two additional lithium ions are bound to the sandwich exteriors in an $\eta^2$-binding mode (2.256(5)−2.308(5) Å) in 25. In 22, the exterior coordination of lithium ions to the concave face of C\textsubscript{20}H\textsubscript{10}\textsuperscript{4−} was of the $\eta^3$-type. The coordination of the extraneous Li\textsuperscript{+} ions in 25 is completed by a chelating DME molecule. One additional DME molecule bridges two neighboring [Li(DME)]\textsuperscript{+} cations to form [Li\textsubscript{2}(DME)\textsubscript{3}]\textsuperscript{2+} units that link the sandwiches 25 into a 1D polymer (Figure 58b).

A few crystals of 26, [Li\textsubscript{2}(DME)\textsubscript{2}]\textsuperscript{1+}/Li\textsubscript{6}/(OCH\textsubscript{3})\textsubscript{2}(OCH\textsubscript{2}CH\textsubscript{2}OCH\textsubscript{3})\textsubscript{4}/Li\textsubscript{6}/\textsuperscript{1+}], were deposited from the reaction mixture of corannulene with excess lithium metal in DME layered with hexanes and kept at 13 °C for 3 weeks. An X-ray diffraction study of 26 demonstrates the presence of the same penta-decker $\textsuperscript{1+}/\textsuperscript{1+}/\textsuperscript{1+}$\textsuperscript{2−} supramolecular aggregate. In contrast to 25, both methoxide (CH\textsubscript{3}O−) and 2-methoxyethoxide (CH\textsubscript{3}OCH\textsubscript{2}CH\textsubscript{2}O−) groups participate in the formation of lithium alkoxo nanobelt to afford [Li\textsubscript{2}(DME)\textsubscript{2}]\textsuperscript{1+}/Li\textsubscript{6}/(OCH\textsubscript{3})\textsubscript{2}(OCH\textsubscript{2}CH\textsubscript{2}OCH\textsubscript{3})\textsubscript{4}/Li\textsubscript{6}/\textsuperscript{1+}] (26). The Li–O bond lengths within the belt in 26 span a broader range (1.87(3)−2.07(2) Å) than in 25. The extraneous Li\textsuperscript{+} ions are bound to the sandwich 26 in an $\eta^3$-mode (2.250(6)−2.478(6) Å). They also have one DME molecule coordinated in a chelating fashion with additional Li⋯O contacts (2.143(6) Å) that hold two neighboring [Li(DME)]\textsuperscript{+} moieties together. As a result, the slightly different cationic building units, [Li\textsubscript{2}(DME)\textsubscript{2}]\textsuperscript{2+}, glue the anionic sandwiches together in 26 (Figure 59), but the overall 1D polymeric chains in 25 and 26 are quite similar.
Figure 59. The building unit of a 1D polymer in 26 (a), the gluing blocks between two corannulene tetraanions in 26 (b), and in 25 and 27 (c).

Crystals of 27, [Li$_2$(DME)$_3$][I$_4$/Li$_6$/[OCH$_3$)$_2$(OCH$_2$CH$_2$OCH$_3$)$_4$/Li$_6$/I$_4$], were deposited from the reaction mixture in DME kept at 20 °C for 7 days. The X-ray diffraction investigation shows four CH$_3$OCH$_2$CH$_2$O$^-$ and two CH$_3$O$^-$ equatorial groups around the nanobelt interior (Figure 60).
At the same time, the cationic building block in 27, [Li$_2$(DME)$_3$]$^{2+}$, is the same as that in 25 (Figure 59c). Importantly, all three new structures contain the same type of lithium alkoxo nanobelt showing its stability and wide occurrence under different experimental settings.

The C–C bond distances of C$_{20}$H$_{10}$$^{4-}$ in 25 and 26 are almost equidistant to those measured in 22 (Table 16). Similarly, the C–C bond length perturbations of the corannulene core upon the acquisition of four electrons are indicative of the formation of the central aromatic cyclopentadienyl 6¢/5C ring surrounded by an aromatic 18¢/15C annulenyln cycle.$^{1,7}$
Table 16. Key distances (in Å) for C_{20}H_{10}^{4−} in 22, 25, and 26.

<table>
<thead>
<tr>
<th></th>
<th>[1^{4−}/Li_{6}/1^{4−}]^{3−}</th>
<th>[1^{4−}/Li_{6}/(OR)<em>{6}/Li</em>{6}/1^{4−}]^{2−}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22</td>
<td>25</td>
</tr>
<tr>
<td>hub</td>
<td>1.390(3)−1.400(2)−</td>
<td>1.394(4)−1.406(4)−</td>
</tr>
<tr>
<td>spoke</td>
<td>1.421(2)−1.433(2)−</td>
<td>1.421(4)−1.436(4)−</td>
</tr>
<tr>
<td>flank</td>
<td>1.429(3)−1.445(2)−</td>
<td>1.431(4)−1.444(4)−</td>
</tr>
<tr>
<td>rim</td>
<td>1.449(3)−1.490(2)−</td>
<td>1.445(4)−1.484(4)−</td>
</tr>
<tr>
<td>bowl depth</td>
<td>0.241(2)−0.355(2)</td>
<td>0.354(4)−</td>
</tr>
<tr>
<td>Li_{sandwich}···C</td>
<td>η^6: 2.204(4)−2.690(4)−</td>
<td>η^6: 2.337(5)−2.600(5)</td>
</tr>
<tr>
<td></td>
<td>η^4: 2.235(5)−2.528(5)−</td>
<td></td>
</tr>
<tr>
<td></td>
<td>η^3: 2.344(5)−2.665(5)−</td>
<td></td>
</tr>
<tr>
<td>Li_{extraneous}···C</td>
<td>η^3: 2.316(4)−2.776(4)−</td>
<td>η^2: 2.256(5)−2.308(5)−</td>
</tr>
<tr>
<td></td>
<td>η^6: 2.208(4)−2.736(4)−</td>
<td></td>
</tr>
<tr>
<td>Li···Li</td>
<td>3.053(5)−3.104(5)</td>
<td>2.751(7)−</td>
</tr>
<tr>
<td></td>
<td>2.768(7)^[a]</td>
<td>2.898(8)^[a]</td>
</tr>
<tr>
<td></td>
<td>2.500(6)−2.539(6)[b]</td>
<td>2.525(6)[b]</td>
</tr>
</tbody>
</table>

[a] within the Li_{6}-ring; [b] between the two Li_{6}-rings.
The presence of the quadruple negative charge along with the binding of multiple Li\(^+\) ions to the corannulene surface lead to the significant flattening of the bowl (depth 0.354(4)−0.433(4) Å) compared to the neutral ligand (0.875(2) Å).\(^3\) Notably, relatively large bowl depth variations are observed for tetrareduced corannulene in different coordination settings. For example, ca. 0.2 Å difference is revealed for C\(_{20}H_{10}\)^{4−} in 22 and 25–26. Thus, the highly reduced corannulene bowl shows sufficient core flexibility which allows it to readily adjust for the geometry and electrostatic forces of the encapsulated positively charged Li-based clusters.

Coordination of internal lithium ions to the tetrareduced surface of corannulene in 22 and 25–27 is shown in Figure 61.

**Figure 61.** Coordination of interior Li\(^+\) ions to a corannulene tetraanion in sandwiches 22 (a), 25 (b), and 26 and 27 (c) superimposed with the space-filling models.

All sandwiched Li\(^+\) ions in 22 exhibit an asymmetric η\(^6\)-binding to five six-membered rings of the anionic surface; whereas variations in coordination are observed for 25–27. Overall, the Li···C interatomic distances are shorter in 22 than those in 25–27 (Table 16). Three different Li\(_{sandwcd}···C\) binding modes, namely η\(^3\)-, η\(^4\)-, and η\(^6\)-, are
observed for the sandwiched lithium ions in 25 (Figure 61b). Notably, strong binding of the solvated THF molecule (Li–O\textsubscript{THF} 1.933(5) Å) completes the coordination of lithium ion that falls outside the corannulene core. For 26 and 27, four internal Li\textsuperscript{+} ions are bound to the π-surface of \textit{1\textsuperscript{4−}} in the \textit{η\textsuperscript{6}}-fashion, while two others exhibit \textit{η\textsuperscript{2}}-binding (Figure 61c). Additional intermolecular Li···O interactions with the donor functionalities of the equatorial alkoxo groups (1.971(6) Å and 2.011(8) Å for 26) can be identified for these \textit{η\textsuperscript{2}}-coordinated lithium ions.

### 5.6 Mixed-Metal Reactions

After the isolation of several tetrareduced anionic products of corannulene in different solvent media\textsuperscript{2,4,8}, we began to investigate if other metals, besides lithium, were capable of reducing C\textsubscript{20}H\textsubscript{10} to the tetraanion stage. It should be noted that once very broad signals of the resulting tetraanions (with K, Rb, and Cs) have been detected in the \textsuperscript{1}H NMR spectra at low temperatures\textsuperscript{13} The results were never confirmed and we were unable to detect or isolate products of highly reduced corannulene with these metals. Inspired by the work of the Mulvey group\textsuperscript{14}, that revealed unique reactivity and synergism of mixed-metal systems in alkali metal-mediated reactions, we decided to investigate the concomitant use of two Group 1 metals for corannulene reduction.

Upon reduction of C\textsubscript{20}H\textsubscript{10} with excess lithium and M, where M = Na and/or K, at least three distinctive reduction steps can be recognized. The formation of green monoanion is followed by purple dianion and finally by the appearance of red-brown corannulene tetraanion. These color changes closely follow the transformations observed during stepwise lithium reduction of C\textsubscript{20}H\textsubscript{10} in different solvent media.
The initial reduction of corannulene with mixtures of Li and Na in THF-$d_8$ revealed the formation of the known Li$_5$-aggregate, identified by a characteristic $^7$Li NMR singlet at $-11.7$ ppm (Figure 62).\textsuperscript{1,2}

![Figure 62. $^7$Li NMR of in-situ generated product using excess Li and Na in THF-$d_8$.](image)

On the contrary, the in-situ NMR measurements of the reaction mixture with Li and K metals did not show the presence of the Li$_5$-sandwich. While the formation of tetrereduced corannulene was clearly observed, the assignment of a particular product structure in solution was problematic. Notably, a noticeably shorter reaction time was observed for the mixed Li/K system compared to the lithium-only reduction, pointing to a synergism of two metals. However, all attempts to crystallize the products from the above reaction mixtures in THF have failed. When THF was replaced by diglyme, there
were no signals in the $^7$Li NMR window opened up to $-20$ ppm. It should be mentioned that all known Li-containing organometallic compounds generally show $^7$Li NMR signals in the range from 10 to $-20$ ppm.\textsuperscript{15} For example, lithium pentamethylcyclopentadienide (LiCp\textsuperscript{*}) shows a peak at $-12.5$ ppm, while shifts of $^7$Li NMR signals up to $-16$ ppm are observed for the mixtures of corannulene and substituted fullerenes in the presence of an excess of Li metal. After numerous attempts and variations of experimental conditions, the product from a diglyme/THF solution was successfully crystallized. The single crystal X-ray diffraction analysis revealed the formation of an unprecedented mixed alkali metal LiK\textsubscript{5} cluster sandwiched between two eclipsed tetrareduced bowls in $[K_2$(diglyme)(THF)//LiK\textsubscript{5}(diglyme)\textsubscript{2}(C\textsubscript{20}H\textsubscript{10}\textsuperscript{4+})\textsubscript{2}(diglyme)\textsubscript{2}]$ (28, Figure 63).\textsuperscript{16}
Figure 63. Independent unit of 28 (a), one-dimensional crystal packing of the LiK₅ units (b), and side view of the space-filling sandwich model (c).

All lithium ions that were encapsulated between the 6-membered rings of C₂₀H₁₀⁴⁻ in the Li₅-structure have been replaced by potassium ions. Importantly, the cavity formed by two central 5-membered rings in the triple-decker sandwich is now occupied by a Li⁺ ion. As a result, the corannulene surface is fully “saturated” with alkali metals, for the first time reaching coordination limit for a polyaromatic ligand. In the LiK₅ structure, the distance between the 5-membered rings is 4.004(6) Å, which is
sufficient to accommodate an additional lithium ion in the inner space. The central Li$^+$
ion sits right between the two 5-membered rings with the centroid distance being 
approximately 2.0 Å. The K···C contacts to the six-membered rings of C$_{20}$H$_{10}$$^{4-}$ range 
from 2.898(5) to 3.569(5) Å. The K···K separations are notably shorter in 28 than those 
observed in elemental potassium (K···K 3.858(5)–4.483(5) Å).

The full substitution of lithium ions by potassium ones does not significantly 
perturb the internal bond length distribution of C$_{20}$H$_{10}$$^{4-}$ in comparison with the Li$_5$-
sandwich, but rim C–C bonds in 28 are notably shortened (Table 17). The latter is a 
consequence of the substantial curvature increase of corannulene and the subsequent 
tightening of the rim.

**Table 17.** Key distances (in Å) for C$_{20}$H$_{10}$$^{4-}$ in 22, 28, 29 and 30.

<table>
<thead>
<tr>
<th></th>
<th>Li$_5$</th>
<th>LiK$_5$</th>
<th>Li$_3$K$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>22</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hub</td>
<td>1.390(3)–</td>
<td>1.405(5)–</td>
<td>1.397(5)–</td>
</tr>
<tr>
<td></td>
<td>1.400(2)</td>
<td>1.437(6)</td>
<td>1.418(4)</td>
</tr>
<tr>
<td>spoke</td>
<td>1.421(2)–</td>
<td>1.423(7)–</td>
<td>1.432(5)–</td>
</tr>
<tr>
<td></td>
<td>1.433(2)</td>
<td>1.461(6)</td>
<td>1.438(6)</td>
</tr>
<tr>
<td>flank</td>
<td>1.429(3)–</td>
<td>1.410(6)–</td>
<td>1.423(6)–</td>
</tr>
<tr>
<td></td>
<td>1.445(2)</td>
<td>1.442(7)</td>
<td>1.436(5)</td>
</tr>
<tr>
<td>rim</td>
<td>1.449(3)–</td>
<td>1.412(6)–</td>
<td>1.436(5)–</td>
</tr>
<tr>
<td></td>
<td>1.490(2)</td>
<td>1.443(6)</td>
<td>1.454(6)</td>
</tr>
<tr>
<td>bowl</td>
<td>0.241(2)–</td>
<td>0.857(6)–</td>
<td>0.664(5)</td>
</tr>
<tr>
<td>depth</td>
<td>0.355(2)</td>
<td>0.866(6)</td>
<td></td>
</tr>
</tbody>
</table>

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The bowl depth of \( \text{C}_{20}\text{H}_{10}^{4-} \) reaches an unprecedented high value of 0.862(6) Å, which is \( \text{ca.} \) 3 times greater than that in the Li-only triple-decker supramolecular aggregates (0.241(2)–0.355(2) Å) and comparable to neutral corannulene (0.875(2) Å).\(^3\) This curvature increase results from the synergism of pushing effects of five large potassium ions located around the perimeter and pulling effect of the lithium ion squeezed in between the central hub rings of corannulene. It illustrates remarkable flexibility of the tetrareduced corannulene bowls in adapting to different coordination environments, making it an exceptionally versatile \( \pi \)-ligand.

In the solid state, two additional \( \text{K}^+ \) ions occupy the concave bowl cavities at the outside of the \( \text{LiK}_5 \)-sandwich with \( \text{K} \cdots \text{C} \) contacts spanning from 2.802(5)–3.223(5) Å. Interactions of these ions with bridging diglyme and THF molecules result in the formation of a string-like 1D polymeric chain in the solid state (Figure 63b). The coordination sphere of potassium is completed by binding of one oxygen of THF and three oxygen atoms of diglyme (\( \text{K} \cdots \text{O}_{\text{THF}}: 2.729(4) \) Å and \( \text{K} \cdots \text{O}_{\text{diglyme}}: 2.679(4)–3.385(4) \) Å). It should be noted that the bulk crystalline material can be obtained on a 100 mg scale with a satisfactory elemental analysis.

After we crystallographically confirmed the presence of the hub-bound lithium cation in the \( \text{LiK}_5 \)-sandwich, the \( ^7\text{Li} \) NMR data were carefully re-measured using an extended window. Gratifyingly, a single peak (for the \text{in-situ} generated product and re-dissolved crystals) appeared at the previously concealed high negative value of \( -22.4 \) ppm (Figure 64). This previously unseen record low-field shift shows a need to reconsider the width of a \( ^7\text{Li} \) NMR window for investigation of Li-containing organometallic compounds. This observation is especially important for studies of
lithium-doped extended carbon-based materials, such as graphite or graphene, for use in Li-ion batteries.

![Figure 64. $^7$Li NMR spectra of 28.](image)

Re-investigation of the *in-situ* monitored reaction of corannulene with an excess of Li and K in THF-$d_8$ revealed the formation of LiK$_5$ ($\approx-22.4$ ppm) along with the broad signal shifted even more to the right end of the spectrum ($ca. -24.4$ ppm). This implied the existence of another mixed-metal sandwich having greater lithium content than that in 28. As crystal growth from THF was problematic due to poor product solubility and formation of unwanted oils, we turned to DME as a potential solvent. As demonstrated previously (Section 5.4), Li-induced reduction of corannulene in DME is accompanied by side-reactions affording lithium alkoxo-clusters. To avoid these complications, the
reaction time should be minimized. However even with the short reaction times, \textit{in-situ} \textsuperscript{7}Li NMR measurements for the mixed Li/K systems in DME showed a variety of peaks due to the above intrinsic problems (Figure 65).

\textbf{Figure 65.} Variable-temperature \textsuperscript{7}Li NMR spectra of the \textit{in-situ} generated product using excess Li and K in DME.

Importantly, a broad new peak appeared where a centrally coordinated lithium cation could be expected. This peak indicated the formation of a new sandwich-type product, which was successfully crystallized by layering the reaction mixture in DME with 12-crown-4 ether in hexanes.\textsuperscript{16} The single crystal X-ray diffraction analysis revealed a unique supramolecular structure having the Li\textsubscript{3}K\textsubscript{3} cluster core squeezed between two tetrareduced corannulene decks crystallized along with two [Li(12-crown-4)(DME)]\textsuperscript{+}
ations in 29, $[\text{Li}_3\text{K}_3(\text{DME})(\text{C}_{20}\text{H}_{10}^{4-})_2]/[\text{Li}(12\text{-crown-4})(\text{DME})]_2$. The separation between the two bowls in $[(\text{C}_{20}\text{H}_{10}^{4-})/(\text{Li}_3\text{K}_3)/(\text{C}_{20}\text{H}_{10}^{4-})]^{2-}$ is slightly smaller than in the LiK$_5$-sandwich (3.826(5) vs. 4.004(6) Å). Again, all coordination sites of $\text{C}_{20}\text{H}_{10}^{4-}$ are engaged in alkali metal ion binding, with one lithium ion occupying the central hub ring. Two remaining Li$^+$ ions are bound to the neighboring 6-membered rings of $\text{C}_{20}\text{H}_{10}^{4-}$ forming a Li$_3$-triangle within the Li$_3$K$_3$ cluster. In the solid state, the Li$_3$K$_3$-sandwiches form a zigzag 1D chain through the K···O interactions with a coordinated DME molecule (3.079(4) Å, Figure 66a). Notably, the latter chelates one and simultaneously coordinates two other potassium ions of the neighboring aggregates, thus exhibiting an unprecedented chelating-double-bridging mode.
Figure 66. X-ray crystal structures of 29 and 30 with the Li₃K₃ metal cluster core. Zigzag one-dimensional polymeric chain in 29 (a), ball-and-stick representation of the molecular structure of the Li₃K₃ sandwich in 30 (b), side (c), and top (d) views of the space-filling model of the Li₃K₃ sandwich in 30. Note: external solvent-separated Li⁺ ions are omitted for both 29 and 30.
The sandwiched Li\(^+\) ions are bound to the convex surface of corannulene in an \(\eta^5\)- and \(\eta^6\)-mode. The corresponding Li···C distances 2.263(4)–2.280(4) Å (Li···C\(_{\text{centroid}}\) 1.928(4) Å) and 2.266(4)–2.736(4) Å (Li···C\(_{\text{centroid}}\) 2.109(4)–2.130(4) Å) are indicative of the strong coordination of the Li atom to the curved carbon surface. Notably, the Li···Li separations (3.047(4) and 3.461(5) Å) in 29 are comparable to those found in the \([\text{Li}_{5}(\text{C}_{20}\text{H}_{10}^4\text{)})_2\]\(^3^-\) dimers. Moreover, several Li···K contacts were observed in 29 (3.482(4)–3.836(4) Å).

The sandwiched K\(^+\) ions are bound to the convex surface of the corannulene moiety in an \(\eta^3\)- and \(\eta^6\)-fashion. The K···C distances are 3.185(4)–3.523(4) Å and 2.900(4)–3.317(4) Å, respectively. The distance of the K\(^+\) ion to the center of the six-membered ring is 2.812(4)–2.835(4) Å. It should be mentioned, the potassium atom coordinated to the bowl-shaped polyarene in an \(\eta^3\)-mode is pulled out from the sandwich. This potassium ion is bound to two oxygen atoms of DME with the corresponding K···O separations 2.830(4) Å and 2.913(4) Å. The K···K distance (4.310(4) Å) of the sandwiched potassium ions is shorter than those observed in elemental potassium (4.54 Å),\(^{17}\) however, the K···K separation is elongated compared to the K···K distance between two neighboring \([\text{Li}_{3}\text{K}_{3}(\text{C}_{20}\text{H}_{10}^4\text{)})_2\]\(^2^-\) sandwiches (3.938(4) Å, Figure 66a).

In the outside \([\text{Li}(12\text{-crown}-4)(\text{DME})]^+\) moiety, the Li\(^+\) ions are bound to four oxygen atoms of 12-crown-4 (Li···O 1.962(4)–2.279(4) Å) and two oxygen atoms of DME (Li···O 2.064(4) Å and 2.296(4) Å).

The \(^7\text{Li}\) NMR investigation of Li\(_3\)K\(_3\) crystals dissolved in DME revealed that the supramolecular aggregate is stable (single peak at −23.94 ppm) without any signs of product decomposition of metal ion redistribution (Figure 67).
Moreover, these crystals can be dissolved and then crystallized from THF providing the new structure with an essentially unchanged Li\textsubscript{3}K\textsubscript{3}-core where all DME molecules in both cationic and anionic parts are replaced by THF (30, Figure 66b, c).\textsuperscript{16} The overall formula of 30 can be written as [Li\textsubscript{3}K\textsubscript{3}(THF)\textsubscript{7}(C\textsubscript{20}H\textsubscript{10}\textsuperscript{4−})\textsubscript{2}]/[Li(12-crown-4)(THF)]\textsubscript{2}. Importantly, the triple-decker [(C\textsubscript{20}H\textsubscript{10}\textsuperscript{4−})/Li\textsubscript{3}K\textsubscript{3}/(C\textsubscript{20}H\textsubscript{10}\textsuperscript{4−})]\textsuperscript{2−} aggregates crystallize as separate molecular moieties (along with two [Li(12-crown-4)(THF)]\textsuperscript{+} cations) in contrast to an extended 1D structure of 29. This fact denotes that the formation of Li/K sandwiches is not induced by crystal packing and the specific mixed-metal core can exist in various coordination environments.

The separation between the two bowls in 30 is almost the same as that in 29 (3.865(2) vs. 3.826(5) Å). One Li\textsuperscript{+} ion is bound to the central five membered rings in an
\( \eta^5 \)-mode with the Li⋯C separations of 2.274(3)–2.292(3) Å. The distance from the center of the five-membered ring to the Li ion (1.941(3) Å) is indicative of rather strong metal binding to the \( \pi \)-bowl. Another lithium ion is bound to the \( \text{exo} \) surface of corannulene in an \( \eta^6 \)-fashion. Notably, these Li⋯C distances are elongated compared to the former (2.250(3)–2.677(3) Å and Li⋯C_{centroid} 2.079(3) Å). The Li⋯Li separation (2.970(4) Å) is shorter than those observed in all \([\text{Li}_5(\text{C}_{20}\text{H}_{10})_2]^{3-}\) dimers (22–24); however, it is elongated compared to the products 25–27 having a pentadecker sandwich core, \([1^4/\text{Li}_6/(\text{OR})_6/\text{Li}_6/1^4]^2-\). For comparison, the Li⋯Li distance in elemental lithium is 3.04 Å.5

Two potassium ions are bound to the convex surface of corannulene in an assymmetric \( \eta^6 \)-fashion. The corresponding K⋯C distances are 2.889(5)–3.351(5) Å and 3.169(5)–3.586(5) Å. The distances from the center of the benzene ring to the potassium atom are 2.696(5) Å and 3.117(5) Å, respectively. The K⋯K separation in 30 (3.912(5) Å) is shorter compared to those observed in 29. It should be mentioned that one potassium ion is coordinated to two THF molecules (2.718(3) and 2.793 (3) Å); whereas, the other K\(^+\) ion is bound to three THF molecules (2.768(3)–2.918(3) Å).

The hub C–C bond lengths of \( \text{C}_{20}\text{H}_{10}^{4-} \) (1.408(2)–1.413(2) Å) in 30 are close to those in the \([\text{Li}_3\text{K}_3(\text{C}_{20}\text{H}_{10}^{4-})_2]^2-\) sandwich isolated from DME. The equalization of the rim and flank C–C bond distances (Table 17) and shrinking of the central five-membered ring in \( \text{C}_{20}\text{H}_{10}^{4-} \) confirm the formation of an annulene-within-an-annulene structure. As expected, the value of the bowl depth falls almost exactly in between the Li\(_5\) and LiK\(_5\) sandwiches (0.620(2) Å, Table 17).
5.6.1 Computational Studies and the Proposed Mechanism of Formation

To get further insights into the formation of unique mixed alkali metal supramolecular aggregates discovered in this work, DFT PBE0/def2-TZVPP(Li,K)\text{\textbackslash /}cc-pVDZ(C,O,H) calculations have been carried out.\textsuperscript{17} Since the X-ray diffraction analysis revealed that external solvent molecules can be exchanged without any significant influence on the internal parameters of sandwiches (29 vs. 30), we have selected the triple-decker structures without any solvent molecules for all computations. For charge balance and consistency, we considered structures with larger K\textsuperscript{+} ions occupying the outside concave bowl cavity in all cases. Good reproducibility of experimentally obtained geometric parameters and excellent precision of calculated $^7$Li NMR data ascertained that the selected model is an appropriate choice for theoretical description of these large and complex systems.

The calculated $^7$Li NMR shifts for the central Li\textsuperscript{+} ion in the Li\textsubscript{3}K\textsubscript{3} and LiK\textsubscript{5} organometallic complexes are $-26.1$ and $-23.9$ ppm, compared with the experimental values of $-23.9$ and $-22.4$ ppm, respectively. Thus, the highly negative shift values along with the overall dependence on Li/K ratio are fully reproduced by theory. Furthermore, calculations of the whole series of mixed Li/K sandwiches with variable core compositions allow us to discuss the step-by-step changes occurring upon metal exchange starting from the Li-only cluster sandwiched between two C\textsubscript{20}H\textsubscript{10}\textsuperscript{4-} ligands. The initial formation of a Li\textsubscript{5}-sandwich is warranted by the fact that the addition of excess Li metal quickly produces the tetrareduced anions, while the use of pure K metal affords less charged corannulene species.\textsuperscript{18} Starting from the Li\textsubscript{5}-cluster, the substitution
of small Li$^+$ ions by larger K$^+$ ions along the periphery should gradually lead to the sandwich opening, simulating the opening of a clamshell (Figure 68).

![Figure 68](image)

**Figure 68.** Schematic transformation of mixed-metal cores for a series of Li$_5$ to LiK$_5$ sandwiches.

Herein, the “clamshell effect” is quantified by measuring angles between the mean planes passing through the rim or hub carbon atoms of C$_{20}$H$_{10}^{4-}$ within the sandwich. The first substitution-step in the Li$_5$-structure leads to a substantial increase of the rim angle (12.8 °) in Li$_4$K, while the 5-membered rings of corannulene remain essentially parallel with the hub angle being unchanged. As a result, the space between the 5-membered rings in Li$_4$K sandwich (3.47 Å) remains small. Thus, a substitution of the Li$_5$-cluster with one K$^+$ ion does not provide a sufficient room between the corannulene decks for incorporation of an additional lithium ion in the central position. The second substitution step can afford two isomers, where two K$^+$ ions are located at either neighboring ($\alpha$-Li$_3$K$_2$) or separated ($\beta$-Li$_3$K$_2$) benzene rings. The substantial increase in both rim and hub angles is observed for this substitution step. Outstandingly, the $\beta$-Li$_3$K$_2$ isomer, having one Li$^+$ located between two K$^+$ ions, shows a substantially
lower thermodynamic stability (by \textit{ca.} 13 \text{ kcal/mol}) than the structure with the Li$^+$ ion being inserted into the space between the 5-membered rings of two C$_{20}$H$_{10}^4$− bowls. This provides a considerable driving force for the insertion process with the subsequent formation of the new type of sandwich. Thus, having two K$^+$ ions separated by one 6-membered ring and two Li$^+$ cations functioning as clamshell hinges on the other side open a clamshell sufficiently wide to provide a channel for the interior insertion of a Li$^+$ ion. After this insertion is completed, closing the channel with a potassium metal ion leads to the formation of the stable experimentally observed Li$_3$K$_3$-sandwich. The central Li$^+$ is now fully confined within the electrostatic trap of surrounding alkali metals and has no path to escape. Notably, while the Li$^+$ hub-to-ring insertion is essentially barrierless (0.7 \text{ kcal/mol}), the barrier for the reverse process is quite significant (13.9 \text{ kcal/mol}, Figure 69).

\textbf{Figure 69.} Schematic representation of the Li insertion into the space between two 5-membered ring sites.
For comparison, the Li⁺ insertion barrier for α-Li₃K₂, where Li could not move in between two K⁺ ions, is larger (14.5 kcal/mol) than in the β-Li₃K₂ sandwich, while the driving force for this process is much lower (2.4 kcal/mol). The next possible member of the class, Li₂K₄, is unstable toward further transformations. The presence of four K⁺ ions opens up a clamshell very wide. This makes the last Li⁺ ion located between 6-membered rings being very weakly bound and readily replaceable by a larger potassium cation, which fits the allocated space much better. This transformation eventually leads to the formation of experimentally observed LiK₅ motif.
5.7 Conclusions

We have proven that the triple-decker structure, \([\text{Li}_5(\text{C}_{20}\text{H}_{10}^4)^2]^{3-}\), is retained upon re-crystallization from THF in the presence of such strong O-donors, as crown ether and diglyme. At the same time, the use of neat diglyme for reduction of \(\text{C}_{20}\text{H}_{10}\) with lithium metal has prevented the high-order self-assembly of \(\text{I}^4^-\) with \(\text{Li}^+\) ions, according to our NMR investigations. The reduction of corannulene with lithium metal in DME revealed the formation of a unique \([\text{Li}_6/(\text{OR})_6/\text{Li}_6]^{6+}\) \((\text{R} = \text{CH}_3\text{ or CH}_2\text{CH}_2\text{OCH}_3)\) cluster core stabilized by two corannulene tetraanions to form a remarkable penta-decker supramolecular aggregate. Our recent work reveals the unique supramolecular assembly processes of highly charged corannulene, which is important and pertinent to the Li-induced electrolyte decomposition and Li-graphite intercalation processes.

Moreover, the first study of mixed-metal reduction reactions of corannulene has revealed the formation of a new class of organometallic sandwich compounds. The coordination record for tetrarreduced corannulene, able to bind six alkali metal ions by engaging its five benzene rings along with the central hub-site, has been shown. Notably, the sandwiching of \(\text{Li}^+\) ion between two hub-sites of two \(\text{C}_{20}\text{H}_{10}^4^-\) is accompanied by unprecedented shifts in \(^7\text{Li}\) NMR spectra. This experimental result, augmented by theoretical calculations, illustrates the need to reconsider the width of NMR window for \(^7\text{Li}\) NMR investigations of extended carbonaceous materials.

This work also offers a new approach on how to incorporate heavier alkali metals into supercharged curved carbonaceous materials. These results should provide a solid ground for the further exploration of potential applications of this new class of mixed alkali metal supramolecular aggregates. We expect that the successful crystallization of
the ionic solids reported here will stimulate further attempts to develop new supercharged materials with a variety of alkali metals for practical use.
5.8 Experimental Details

All manipulations were carried out using break-and-seal\textsuperscript{19} and glove-box techniques under an atmosphere of argon, as previously described.

\[ \text{[Li(THF)]}_4\text{[Li(THF)]}_2\text{[Li}_5\text{(C}_2\text{H}_{10}\text{)}_2\text{]}^3^-\text{[Li(THF)]}_3\] (22)

THF (3 mL) was added to corannulene (20 mg, 0.08 mmol) and freshly cut Li metal (10 mg, 1.45 mmol, excess). The resulting solution was sonicated for several seconds to initiate the reaction. The formation of a green solution was observed. Upon stirring using a glass stirring bar for 4 h, the mixture turned purple then brown. After the additional stirring for 12 h, the dark brown reaction mixture was filtered and layered with 3 mL of hexanes. Dark brown crystals were precipitated in a few days at 15 °C. Yield: 26 mg, 52%. \textsuperscript{1}H NMR (400 MHz, THF-\text{d}_8, 20 °C and \text{-80 °C}, ppm): \( \delta \) = 6.84 (s, 20H, Ar–H), 3.60 (m, 38H, THF), 1.77 (m, 38H). UV-vis (THF, nm): \( \lambda_{\text{max}} = 428, 575, 710 \).

\[ \text{[Li(THF)]}_4\text{[Li(THF)](12-crown-4)]}_2\text{[Li}_5\text{(C}_2\text{H}_{10}\text{)}_2\text{]}^3^-\] (23)

Compound 23 (0.04 mmol) was prepared from corannulene (20 mg, 0.08 mmol) and lithium metal (10 mg, 1.45 mmol, excess) in THF (3 mL) as described above. The resulting solution was combined with the solution of 12-crown-4 ether (14.1 mg, 0.08 mmol) in THF (2 mL). Dark brown crystals were precipitated in four days at 25 °C. Yield: 30 mg, 56%.

\[ \text{[Li(THF)]}_2\text{(diglyme)]}[\text{Li}_2\text{(THF)(diglyme)]/[Li}_5\text{(C}_2\text{H}_{10}\text{)}_2\text{]}^3^-\] (24)

THF (3 mL) was added to a flask containing excess Li metal and C\textsubscript{20}H\textsubscript{10} (15 mg, 0.06 mmol). The resulting deep green solution was stirred at room temperature for 12 h to
afford a dark brown color of C\textsubscript{20}H\textsubscript{10}\textsuperscript{4−}. The mixture was filtered, layered with hexanes/diglyme (10:1, 3 mL) and kept at 10 °C. Brown crystalline solid was collected in 36 hours, washed several times with hexanes and dried shortly \textit{in vacuo}. The X-ray quality crystals were obtained by layering the THF solution with hexanes/diglyme at 10 °C (80%). \textsuperscript{1}H NMR (400 MHz, THF-\textit{d}_8, 25 °C, ppm): \(\delta = 6.69\) (C\textsubscript{20}H\textsubscript{10}\textsuperscript{4−}). \textsuperscript{7}Li NMR (400 MHz, THF-\textit{d}_8, 25 °C, ppm): \(\delta = −8.4\). \textsuperscript{7}Li NMR (400 MHz, THF-\textit{d}_8, −80 °C, ppm): \(\delta = −3.8\) (3Li), −11.7 (5Li). \textsuperscript{13}C NMR (400 MHz, THF-\textit{d}_8, 25 °C, ppm): \(\delta = 112.3, 95.1, 87.3\). UV-vis (THF, nm): \(\lambda_{\text{max}} = 424, 572, 712\).

\[\text{[Li}_2(\text{DME})_3]\text{[C}_{20}\text{H}_{10}\textsuperscript{4−}/\text{Li}_6(\text{THF})/(\text{OCH}_3)_6/\text{Li}_6(\text{THF})/\text{C}_{20}\text{H}_{10}\textsuperscript{4−}]\ (25)\]

DME (1 mL) and THF (0.05 ml) were added to corannulene (5 mg, 0.02 mmol) and freshly cut Li metal (2 mg, 0.29 mmol, excess). The resulting mixture was sonicated for an hour until the brown solution of the corannulene tetraanion was formed. Black crystals started to form on the metal surface after keeping the reaction mixture at 25 °C for three days. The crystalline product (≈ 3 mg, 25%) was collected in six days.

\[\text{[Li}_2(\text{DME})_2]\text{[C}_{20}\text{H}_{10}\textsuperscript{4−}/\text{Li}_6/(\text{OCH}_3)_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4/\text{Li}_6/\text{C}_{20}\text{H}_{10}\textsuperscript{4−}]\ (26)\]

DME (3 mL) was added to corannulene (15 mg, 0.06 mmol) and Li metal (4 mg, 0.57 mmol, excess). The mixture was sonicated for an hour and stirred for 5 days at ambient conditions. The brown solution was then filtered, layered with hexanes and kept at 13 °C to yield brown oil in two days. This system was kept over DME/hexanes mixture (v:v = 1:1) at 13 °C to afford a few large crystals of 3 in three weeks.
[Li$_2$(DME)$_3$][C$_{20}$H$_{10}^4$−/Li$_6$(OCH$_3$)$_2$(OCH$_2$CH$_2$OCH$_3$)$_4$/Li$_6$/C$_{20}$H$_{10}^4$] (27)

DME (1.5 mL) was added to corannulene (10 mg, 0.04 mmol) and freshly cut Li metal (5 mg, 0.71 mmol, excess). The resulting mixture was sonicated for an hour until the brown solution of the corannulene tetraanion was formed. The formation of black crystals in the mixture was observed in 7 days at 25 °C. In two weeks the large black crystals were collected and washed with DME (1 ml) to give the final product (≈ 8 mg, 32%).

[K$_2$(diglyme)(THF)//LiK$_5$(diglyme)$_2$(C$_{20}$H$_{10}^4$)$_2$(diglyme)$_2$] (28)

Diglyme (3 mL) was added to a flask containing excess Li, excess K, and corannulene (15 mg, 0.06 mmol). The deep green solution was stirred at room temperature for 16 h resulting in a deep red-brown mixture. The red-brown mixture was filtered, layered with THF:hexanes (1:10, 5 mL), and kept at 10 °C. Dark red-brown blocks were present after 56 h, washed several times with hexanes and dried in vacuo. Yield: 106 mg, 75 %. UV-vis (diglyme, nm): $\lambda_{\text{max}} = 385, 512$. Anal. Calcd for C$_{118}$H$_{126}$K$_{14}$Li$_2$O$_{17}$: C, 59.61; H, 5.34; Found: C, 59.54 ; H, 5.29. $^1$H NMR (400 MHz, THF-$d_8$, 25 °C, ppm): $\delta = 6.65$. $^1$H NMR (400 MHz, THF-$d_8$, −60 °C, ppm): $\delta = 6.58$. $^7$Li NMR (155.5 MHz, THF-$d_8$, 25 °C, ppm): −22.4. $^7$Li NMR (155.5 MHz, THF-$d_8$, −60 °C, ppm): −22.40.

[Li$_3$K$_3$(DME)(C$_{20}$H$_{10}^4$)$_2$/[Li(12-crown-4)(DME)]$_2$ (29)

DME (3 mL) was added to a flask containing excess Li, excess K, 12-crown-4 (23 mg, 0.132 mmol), and corannulene (15 mg, 0.06 mmol). The deep green solution was stirred at room temperature for 8 h resulting in a deep red-brown mixture. The red-brown mixture was filtered, layered with hexanes (4 mL), and kept at 10 °C. Red-brown plates were collected in 48 h, washed several times with hexanes and dried in vacuo. Yield: 53
mg, 70 %. UV-vis (DME, nm): $\lambda_{\text{max}} = 479$. Anal. Calcd for $\text{C}_{64}\text{H}_{76}\text{Li}_{2}\text{O}_{12}$: C, 73.13; H, 7.29; Found: C, 73.09; H, 7.35. $^1\text{H}$ NMR (400 MHz, THF-$d_8$, 0 °C, ppm): $\delta = 6.64, 6.80$. $^7\text{Li}$ NMR (155.5 MHz, THF-$d_8$, 25 °C, ppm): $^7\text{Li}$ NMR (155.5 MHz, THF-$d_8$, −60 °C, ppm): −2.10, −7.75, −22.40, −23.95.

$[\text{Li}_3\text{K}_3(\text{THF})_7(\text{C}_{20}\text{H}_{10}^{4-})_2]/[\text{Li}(12\text{-crown-4})(\text{THF})]_2$ (30)

THF (3 mL) was added to a flask containing excess Li, excess K, 12-crown-4 (24 mg, 0.140 mmol), and corannulene (15 mg, 0.06 mmol). The deep green solution was stirred at room temperature for 16 h resulting in a deep red-brown mixture. The red-brown mixture was filtered, layered with hexanes (4 mL), and kept at 10 °C. Dark red-brown blocks were present after 56 h, washed several times with hexanes and dried in vacuo. Yield: 69 mg, 70%. UV-vis (THF, nm): $\lambda_{\text{max}} = 488$. $^1\text{H}$ NMR (400 MHz, THF-$d_8$, −40 °C, ppm): $\delta = 6.58, 6.78$. $^7\text{Li}$ NMR (155.5 MHz, THF-$d_8$, −60 °C, ppm): −2.59, −8.41, −22.40, −23.05, −24.58, −24.77.
5.9 References


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