Chemical reduction of planar and curved polyarenes: from group I to group II metals

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CHEMICAL REDUCTION OF PLANAR AND CURVED POLYARENES: FROM GROUP I TO GROUP II METALS

by

Natalie J. O’Neil

A Dissertation
Submitted to the University at Albany, State University of New York
in Partial Fulfillment of
the Requirements for the Degree of
Doctor of Philosophy

College of Arts & Sciences
Department of Chemistry

2017
ABSTRACT

To further advance energy storage materials research, the structural studies of carbonaceous compounds intercalated with alkali and alkaline earth metal ions are of great interest and importance. Structure-property relationships of electrode and superconductive materials can be better understood with the gained fundamental knowledge stemming from a synergistic use of solid state and solution studies. Due to the polymeric structures and insolubility in common solvent of intercalated carbonaceous materials, studies of structures and properties must be conducted on smaller subunits. Planar polycyclic aromatic hydrocarbons (PAHs) can serve as models for the infinite $\pi$-carbon layers of graphite or graphene, while nonplanar PAHs have been utilized to explore the reactivity of carbon allotropes with curved $\pi$-surfaces. Therefore, we have focused our work on the structural investigation of multi-charged fragments of both graphite and fullerenes, using planar and curved PAHs with different topologies.

In this work, we have accomplished the first structural characterization of monoreduced coronene ($\text{C}_{24}\text{H}_{12}^{2-}$) isolated with $\text{Na}^+$ countercation as a solvent-separated ion pair (SSIP). This has provided the first evaluation of the effect of the distribution of a negative charge over the coronene surface without the interference of metal binding. This has also allowed for the first structural evaluation of the Jahn-Teller (JT) effect in monoreduced coronene; the $D_{2h}$ symmetrical distortion was found to fit the experimental data. The first structural characterization of monoreduced coronene isolated with $\text{Rb}^+$ countercation as a contact ion pair (CIP) has revealed the role of secondary interactions, involving 18-crown-6 ether, in tuning the metal ion binding to the charged $\pi$-surface. In addition, we have conducted the first X-ray structural characterization of bicornannulenyl dianion ($\text{C}_{40}\text{H}_{18}^{2-}$) comprised of two fused coronulene bowls isolated with two alkali metal ions, $\text{Li}^+$ and $\text{Cs}^+$. The direct comparison has revealed two different binding modes,
namely the “naked” form in the SSIP with small Li$^+$ ions vs. the unique double concave metal coordination in the Cs product. Furthermore, the X-ray diffraction study of the biconorannulenyldianion salts confirms that, upon acquisition of two electrons, the large biaryl is converted into a charged overcrowded ethylene, as predicted by prior solution studies. Next, the controlled preparation of rubrene (C$_{42}$H$_{28}$) mono-, di-, and tetraanions has also been achieved in our laboratory with a series of alkali metal ions ranging from Li to Cs. The X-ray diffraction studies of the resulting products revealed the distortion of the rubrene core upon stepwise acquisition of additional electrons. In-depth structural analysis of the tetrareduced rubrene crystallized with Li$^+$ and Rb$^+$ counterions illustrated the inherent flexibility of its tetracene core, although the effect of alkali metal ion size was not straightforward. Finally, we have started developing the synthetic approaches needed to utilize the Group 2 metals as reducing agents towards curved carbon $\pi$-systems. The first reduction step has been achieved for corannulene (C$_{20}$H$_{10}$) using the lighter alkaline earth metals, such as magnesium and calcium. The resulting products have been isolated in the solid state and structurally characterized, revealing the tendency to produce SSIPs with solvated divalent countercations, similar to the previously observed trends for planar carbanions.

Overall, a diverse set of $\pi$-systems of increasing structural complexity, ranging from planar coronene to bowl-shaped corannulene, biconorannulenyld and rubrene, have been investigated in stepwise reduction processes. These studies reveal notable carbon framework transformations, new metal binding trends and the important role of both primary and secondary interactions. The first exploration of Group 2 metals as reducing agents for non-planar PAHs has also been initiated, opening this field for further investigations.
ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to my scientific advisor, Prof. Marina A. Petrukhina. I thank her for always being patient, helpful, and understanding through many ups and downs, both on a personal and professional level. She allowed me to develop as a scientist both inside the laboratory and out. I am thankful she supported me in all my extracurricular activities and additional teaching positions during my graduate studies.

I would like to thank my doctoral committee members, Prof. Evgeny V. Dikarev, Prof. Paul J. Toscano, Prof. Eric Block and Prof. Curtis Pulliam. I appreciate the time and effort they spent in revising my research proposal and dissertation.

I want to thank previous post-doctoral associates, Dr. Alexander V. Zabula and Dr. Sarah N. Spisak for helping me develop and perfect my synthetic skills. To Sarah thank you for always being an ear and a friend.

A special thanks to our past X-ray Crystallographer, Dr. Alexander S. Filatov, for always being approachable and willing to explain challenging concepts. A thank to our current X-Ray Crystallographer Dr. Zheng Wei for always being available and dedicated to running any sample, no matter how horrible it might have looked.

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 for his 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 the Petrukhina 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. A special thank you to Cristina for helping through the writing process.

To my friends Jenny and Alyssa, thank you for your unending support throughout this process. You both know how to give me strength when I need it most. To my NESSE friends, thank you for giving me an outlet and a passion for chemistry in a new light. To the Utica College (UC) chemistry department, thank you for giving me the opportunity to teach and for mentoring me along the way.

I want to thank my mother for always presenting me with opportunities and demonstrating the meaning of hard work. The values you have instilled in me were found to be priceless throughout this process. Thank you for always listening to my endless rants and reminding me that I could complete anything I put my mind too.

Last but certainly not least, a special thank you to my husband, Jay. You have the ability to motivate me when I need it the most and have been an integral part of this process. Without your support and encouragement, this degree would have not been possible.
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LIST OF PUBLISHED WORK ACCOMPLISHED DURING GRADUATE STUDIES


4. Spisak, S. N.; Sumner, N. J.; Zabula, A. V.; Filatov, A. S; Petrukhina, M. A.; Tuning Binding of Rubidium Ions to Planar and Curved Negatively Charged \(\pi\)-Surfaces, *Organometallics* 2013, 32, 3773–3779 (*Cover Art, designed by N.J.S. & S.N.S*).


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Licensed Content Title: Reshaping Rubrene by Controlled Reduction with Alkali Metals
Licensed Content Author: Alexander V. Zabula, Natalie J. Sumner, Alexander S. Filatov, Sarah N. Spisak, Vladimir M. Grigoryants, Marina A. Petrukhina
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CHAPTER 1

Curved Nanocarbon Systems: Structures, Properties and Applications

1.1 Background and Significance

Due to greenhouse gas (H₂O, CO₂, CH₄, NO₂ and O₃) levels progressively rising, 195 countries united in Paris in December 2015 to establish a worldwide strategy to avoid dangerous climate change. The agreement sets out to hold the global average temperature well below 2 °C above pre-industrial levels.¹ Carbon dioxide (CO₂) is the largest contributor to global temperature change among the greenhouse gases. Therefore, this agreement requires the transition of society away from fossil fuels due to the large emissions of carbon dioxide from burning hydrocarbons.²

In the United States in 2016, 81% of our energy is currently produced from fossil fuels, mainly coal (15%), petroleum (37%) and natural gas (29%).³ The remaining 19% is produced by nuclear power and renewable energy sources (solar, wind, water etc.), each contributing 9% and 10%, respectively (Figure 1.1).

Figure 1.1 Primary sources of energy in the United States in 2016.
From these primary energy sources electricity is produced (a secondary energy source) and
transportation is possible throughout the country. With the goal of reducing carbon dioxide
emissions, electricity production from renewable energy sources is on the rise. However,
renewable sources are intermittent; the sun is not always shining and the wind is not always
blowing, which means we cannot currently store all the available energy from the sun and wind to
support the constant energy demands of our society. Therefore, if we aim to transition fully to
renewable resources efficient energy storage technologies are needed. These systems assist in the
integration of renewable energy into our current power grids. The systems function by managing
the electric supply from renewable sources by storing excess energy when it is available and
distributing it as needed.

Unsurprisingly, 72% of the petroleum used in the production of energy in the United States
is used in transportation. The combustion engine in cars is largely responsible for the increase in
carbon emissions. Consequently, there have been many developments in electric vehicle (EV)
technologies, which produce no emissions and do not rely on fossil fuels. Energy for EVs is
produced from an onboard high density energy storage system. However, no system currently
available on the market compares to the energy produced by one tank of gasoline. As a result, the
mileage ranges of EVs are minimal in comparison to combustion engine based vehicles and have
not completely taken over the automotive market. Hybrid electric vehicles (HEVs), which run off
an energy storage system and gas mixture have extended ranges in comparison. However, some
require recharging (plug-in hybrid electric vehicle, PHEV) and many charge off the gas engine
(regenerative braking). Hydrogen fuel cells have been entering the transportation market as well.
Hydrogen is the most abundant and lightest element. As a fuel, it is the richest in energy per unit
mass, 34 kcal/g vs. petroleum 10.3–8.4 kcal/g, making it ideal for energy production. Hydrogen
Fuel cells produce zero emissions and appear to be a sustainable and “clean” energy technology for transportation. However, 95% of commercially available hydrogen gas is produced from the reformation of natural gas.\textsuperscript{11} To truly be an environmentally friendly technology, new renewable sources of hydrogen gas must be explored and become commercially available.\textsuperscript{12} Although hydrogen can be burned as a fuel directly in a combustion engine, hydrogen fuel cells in combination with energy storage systems are the most efficient emerging technology.\textsuperscript{9}

For these reasons, among others not noted here, the field of energy storage has become a topic of great interest to researchers and society as a whole. As the production of energy by combustion of fossil fuels (electricity, transportation, etc.) decreases due to its detrimental environmental impacts there will be an increased need for novel high density energy storage systems by society. Research into sustainable and environmentally compatible energy storage is necessary if we aim to circumvent the progression of climate change.

1.2 Energy Storage

1.2.1 Batteries

Batteries are electrochemical cells that supply stored chemical energy as electrical energy with zero emissions. Battery technology has developed slowly despite being a simple concept based on oxidation reduction (redox) reactions which occur at the active electrode sites. All batteries consist of three components, regardless of the electrochemical composition, namely two electrodes, an anode (negative electrode) and a cathode (positive electrode), which are connected by an ionically conductive electrolyte. There are also chemically inactive components of the battery which are needed to maintain the electrode’s electronic and mechanical reliability. Inactive components include a current collector (metal foils), separators (microporous film in which
electrolyte is inserted), conductive additives (inorganic conducting compounds or carbon derivatives) and a polymeric binder. The sluggish advancement in battery technology is due to the shortage of suitable electrode materials and electrolytes, along with the complications in understanding the interfaces between them in the complex system of the battery.13

Numerous electrochemical couples were proposed and commercialized for rechargeable batteries over the nineteenth and twentieth centuries; noteworthy are the lead-acid, nickel cadmium (Ni-Cd), nickel metal hydride (NiMH), and the lithium-ion battery (LIB). Lithium-ion batteries are the most efficient and widely used in many applications.

1.2.1.1 Lithium-Ion Batteries

Lithium-ion batteries (LIBs) fundamentally have an advantage over all other types due to lithium having the lowest reduction potential (−3.0 V vs. the standard hydrogen electrode)14 and being the third lightest element (6.941 g/mol). Lithium-ion batteries use carbon materials as the anode due to higher specific charges and low redox potentials when compared to other candidates such as metal oxides, chalcogenides, and polymers.15,16 Carbon is the fourth most abundant element and is the sixth lightest element (12.02 g/mol). Carbon is tetravalent and forms several allotropes with remarkable structural diversity resulting in distinctive physical and chemical properties. Diamond and graphite are the most common and naturally occurring allotropes of carbon. The observed differences in their properties and structures result from the difference in hybridization of the carbon atoms sp\(^3\) and sp\(^2\), respectively (Scheme 1.1).17
Scheme 1.1: Carbon allotropes, diamond (left) and graphite (right).

The name lithium-ion batteries (LIBs) comes from the fact that there is an exchange of lithium ions between the graphite (LiC₆) anode and a layered oxide cathode, as both compounds intercalate lithium. Graphite is an allotrope of carbon, consisting of sp² hybridized carbon atoms fused into hexagons to form an extended planar two-dimensional (2D) layer (Scheme 1.1, right). The un-hybridized 2pₓ orbitals of C-atoms form a delocalized orbital of π symmetry which stabilizes the in-plane σ-bonds, while weak van der Waals forces hold the 2D layers stacked 3.35 Å apart, thus forming a three-dimensional (3D) extended structure. These characteristics make graphite a great conducting material in the plane (π-p bonds and σ-sp² bonds) and a poor conductor in the stacking direction (van der Waals force between the layers). For the above LIBs, the layered oxide cathode is composed of LiTO₂, where T is a transition metal, typically cobalt, manganese, or nickel (Scheme 1.2). With contributions from several research groups the LIB technology became commercially available in 1991, followed by modifications to both anode and cathode materials to increase life cycle and energy density.

When an electrical current is applied to the battery, the anode (lithiated graphite) is reduced by the flow of electrons from the cathode (LiTO₂) through an external circuit. During this process, the cathode material is oxidized. The lithium ions are transported through an electrolyte which maintains the charge balance in the cell. When the current is removed and the battery is in use...
(discharging), the electrons flow from the negative electrode (anode) to the positive electrode (cathode) (Scheme 1.2). The flow of electrons is caused by the difference in electrochemical potential of the redox pair.\textsuperscript{25}

**Scheme 1.2:** General components of a lithium-ion battery.

The biggest challenges facing LIBs are low abundance and inherent instability of lithium metal.\textsuperscript{4,26} Lithium-ion batteries, to date, have been the mainstay for electronics and are now widely used in electric vehicles. With the increase in renewable energy, LIBs are also now used for stationary energy storage for the current power grid. However, as the demand for energy storage increases along with a decrease in consumption of fossil fuels, lithium-ion batteries will not be able to support this growth. It is predicted that our mineable supply of lithium could be sustained for approximately 65 years.\textsuperscript{27} Of course, as the demand increases the price of lithium will increase making large scale applications of LIBs costly. Some demand could be alleviated by recycling the lithium in LIBs or sourcing lithium from seawater which is a much greener process than mining.\textsuperscript{28}
However, even if recycling and sourcing problems are resolved, the lithium-ion battery is nearing its energy limit. It has been predicted that improvements on the most modern LIB can only expect to lead to 30% more energy by weight.\textsuperscript{26} For these reasons alternatives to LIBs are being explored, known as post-lithium-ion batteries (PLIBs). Some emerging technologies are lithium-air, lithium-sulfur, lithium-metal, and solid state batteries.\textsuperscript{29} Nevertheless, due to the future cost associated with lithium and other drawbacks discussed above, some technologies are looking past lithium all together. Researchers are considering other metals with higher abundance and similar electrochemical properties to lithium.\textsuperscript{30} Sodium is discussed here; alkaline earth metals are discussed in Chapter 5.

1.2.1.2 Sodium-Ion Batteries

Due to the future need for large scale applications of energy storage systems, alternatives to LIBs are being explored based on abundant and inexpensive elements. Sodium is the fourth most abundant element on earth\textsuperscript{31} and also has a similar reduction potential (\textasciitilde2.7 V vs. standard electrode potential (SHE)) compared to lithium (\textasciitilde3.0 V vs. SHE).\textsuperscript{14} Sodium-ion batteries (SIBs) function similarly to LIBs in terms of the components of the battery; the only variation is the ion carrier. In the cathode material intercalation of sodium is very similar to that of lithium despite having a larger ionic radius (0.95 Å vs. 0.60 Å, 6 coordinate, respectively).\textsuperscript{32} However, transport properties and stability of sodium ions do vary.\textsuperscript{33} One major difference between sodium and lithium includes the intercalation into graphite as sodium is not correctly intercalated due to the mismatch between the graphite structure and the size of the sodium ion.\textsuperscript{34} Therefore, non-graphitic carbon materials, such as carbon black\textsuperscript{35}, carbon-fibers\textsuperscript{36} and hard carbons,\textsuperscript{37} are the only option for efficient SIB anodes. The economic initiative for switching from lithium-ion batteries to a
technology based on sodium is significant. However, the chemistry involved in making a SIB with the same energy density has yet to be elucidated and higher capacity anode materials need to be explored.\textsuperscript{38}

1.2.2 Superconductors

Unlike batteries which store energy in a chemical reaction, superconducting coils store energy \textit{via} a magnetic field and consequently they are much more efficient. Batteries provide high energy over extended periods of time, whereas superconductors can provide high power rapidly. Therefore, each is needed to support future energy storage of renewably sourced electricity.\textsuperscript{39}

Superconductors are materials which have no electrical resistance below a critical temperature ($T_c$) and become diamagnetic materials.\textsuperscript{40} There are two types of superconductors, type I (soft) and type II (hard). At a critical magnetic field ($H_c$) a material can abruptly transition from superconductivity to normal material (type I) or can slowly transition from superconductor to normal conductor (type II) (Scheme 1.3).

\textbf{Scheme 1.3:} Plot of magnetic field vs. temperature to compare type I and type II superconductors.
Type II superconductors can be used in energy storage due to the fact that high field electromagnets can be made out of superconducting wires. These materials are of high interest in conducting electricity due to the instantaneous energy discharge and infinite number of recharge cycles (theoretically) with little power loss (a charge-discharge efficiency over 95%). However, one major drawback is the low temperatures needed for the material to exhibit superconductivity.

Researchers continue searching for materials with higher transition temperatures for practical applications. Two recent developments are noteworthy in the field of superconductor materials research. In 2001, An and Pickett reported on the superconductivity of magnesium diboride (MgB$_2$), which interestingly is isoelectric to graphite. The $T_c$ reported for MgB$_2$ is 40 K and the authors conclude that strong covalent bonding is responsible for this higher $T_c$. For comparison, alkali metal (Na, K) intercalated graphite has been reported to have a $T_c$ of 5 K. In 2015, Drozdov et al. reported on the superconductivity of sulfur hydride (H$_2$S), which at 90 GPa has a $T_c$ of 200 K. The authors conclude that structure and strong covalent bonding in the material can be attributed to the high $T_c$ found experimentally. Therefore, these two reports, among others, have sparked great interest in hydrogen containing materials with strong covalent bonds. Organic compounds fit these criteria well. Although organic compounds are commonly insulators, compounds can be tuned to a metallic state by metal intercalation or doping. One repeating sentiment from the literature is that investigation into molecular structure is needed to advance the discovery of superconductive materials with higher $T_c$ for energy storage applications.
1.2.2.1 Carbonaceous Superconductor Materials

Carbon-based superconductor materials are of great interest due to the high abundance of carbon, low cost, and nonexistence of health hazards. Therefore, carbon-based superconductor materials are important for future applications of superconductivity in energy storage. There has been significant exploration into both planar and curved carbon systems for superconductive materials.\(^{45}\)

1.2.2.1.1 Planar Polyaromatic Hydrocarbons

As mentioned above, graphite becomes a superconductive material when intercalated with alkali metal ions. This was first discovered by Hannay \textit{et al.} in 1965; the authors established a critical temperature for the potassium-graphite compound, KC\(_8\), to be 0.14 K.\(^ {46}\) By increasing the metal concentration and conducting the synthesis at high-pressure, an increase in T\(_c\) was observed for LiC\(_2\), NaC\(_2\) and KC\(_2\) measured at 1.9 K and 5 K, respectively. Each alkali metal graphite compound (MC\(_8\)) (M = K, Rb, Cs) exhibits a hexagonal structure and has been assigned to the P6\(_3/mmc\) space group, except for LiC\(_6\) which is assigned to the space group P6/mmm (Figure 1.2, left).

\[\]

\textbf{Figure 1.2} A representation of LiC\(_6\) (left) and CaC\(_6\) (right).
The highest temperature superconducting compound of graphite, which was produced at ambient pressures, is calcium intercalated graphite, CaC$_6$, with a transition at 11.5 K.$^{49}$ By increasing the pressure to 7.5 GPa, the $T_c$ reached a maximum of 15.1 K.$^{50}$ This is the highest transition temperature recorded for graphite intercalated compounds to date.$^{51}$ The crystal of CaC$_6$ was reported by Emery et al. in 2005 to be rhombohedral and belongs to the $R3m$ space group (Figure 1.2, right).$^{52}$

Some small polycyclic aromatic hydrocarbons (PAHs) have been explored for superconductivity properties upon metal doping. The intercalation of metal atoms into solid-phase picene (C$_{22}$H$_{14}$) (Figure 1.3, top left) was studied in 2010 by Mitsuhashi et al.$^{53}$ The authors report the superconductive material, K$_3$picene, to have a $T_c$ of 18 K. The superconductivity of potassium doped coronene (C$_{24}$H$_{12}$) (Figure 1.3, bottom left) was studied by Kubozono et al. in 2011, reporting the synthesis and transition temperature for K$_3$coronene ranging from 3.5 to 15 K.$^{45,54}$

![Figure 1.3](image)

*Figure 1.3* Picene (C$_{22}$H$_{14}$) (top left), coronene (C$_{24}$H$_{12}$) (bottom left), phenanthrene (C$_{14}$H$_{10}$) (top right), and 1,2:8,9-dibenzopentacene (C$_{30}$H$_{18}$) (bottom right).
Phenanthrene (C<sub>14</sub>H<sub>10</sub>) (Figure 1.3, top right) doped with potassium or rubidium was synthesized by Wang et al. in 2011 and showed superconductivity at 5 K.<sup>55</sup> In comparison to the reported K<sub>3.3</sub>picene this transition temperature is significantly lower. The authors speculate that organic hydrocarbons with longer chains of benzene rings are potential candidates for higher T<sub>c</sub> superconductors. A report in literature of a compound containing 7 benzene rings in a chain, 1,2:8,9-dibenzopentacene (C<sub>30</sub>H<sub>18</sub>) (Figure 1.3, bottom right), helps to support this hypothesis.<sup>56</sup> The potassium doped hydrocarbon exhibits superconductivity up to 33.1 K; this is the highest T<sub>c</sub> reported for an organic superconductor at ambient pressure. It should be noted here that, until a recent study investigated the solid-solid insertion of potassium into picene, no crystallographic information was known for any of these systems. In 2017 Romero et al. reported the synthesis of the K<sub>2</sub>picene product and studied its structure by high-resolution synchrotron powder X-ray diffraction.<sup>57</sup>

To date, these are the only planar polyaromatic hydrocarbon alkali metal doped superconductor materials reported. However, with such high transition temperatures exploration into similar systems with higher transition temperatures is currently underway.

1.2.2.1.2 Curved Polyaromatic Hydrocarbons

The new carbon allotrope, C<sub>60</sub>-fullerene was discovered in 1985 in the products of graphite vaporization (Figure 1.4).<sup>58</sup> C<sub>60</sub>-fullerene consists of 60 sp<sup>2</sup> hybridized carbon atoms which are fused into 20 hexagons and 12 pentagons forming a hollow sphere that is zero-dimensional (0D) (Figure 1.4, right). This discovery by Kroto, Heath, and Smalley would later win the 1996 Nobel Prize in Chemistry. Since its discovery, the intercalation and doping of fullerene has been broadly explored. The lowest unoccupied molecular orbitals (LUMOs) of C<sub>60</sub> are nonbonding and triply
degenerate, meaning that the C$_{60}$ molecule can accept up to 6 additional electrons. The “LUMO +1” level is also chemically accessible and is triply degenerate as well, so the possibility of accepting a total of 12 electrons is feasible for C$_{60}$. The pure solid has a face-centered cubic (fcc) packing in the solid state. The octahedral and tetrahedral sites in the fcc structure can be occupied by alkali metal cations resulting in the formation of the fullerene trianion, C$_{60}^{3-}$.

![Figure 1.4 Structure of C$_{60}$ fullerene (left) and 3D depiction (right).](image)

In 1991, Hebard *et al.* reported the discovery of superconductivity in potassium doped fulleride, K$_3$C$_{60}$, with a transition temperature of 18 K at ambient pressure.$^{60}$ This initial report sparked investigation into other alkali metal doped fullerides, as well as mixed alkali metal systems. In the same year, many alkali metal doped fullerides were reported in the literature. Two reports were published by Rosseinsky *et al.*$^{61}$ and Holczer *et al.*$^{62}$ on the increased transition temperature to 28 K and 30 K, respectively, when rubidium was used in place of potassium. The increased transition temperature is hypothetically a result of increased density of states at the Fermi level, due to the larger lattice constant produced by the larger alkali metal. This was further supported by a report from Fleming *et al.* which explored the structures of A$_3$C$_{60}$ (A = K, Rb, Cs or a mixture).$^{63}$ The authors reported the face-centered cubic (fcc) structure of A$_3$C$_{60}$ and observed the increase in T$_c$ with increased size of the unit cell (Figure 1.5). It should be noted here that alkali
metal cations occupy octahedral (Figure 1.5, orange metal cations) and tetrahedral (Figure 1.5, blue metal cations) sites in the fcc unit cell.

![Diagram of fcc structure]

**Figure 1.5** A representation of the face-centered cubic (fcc) structure of A₃C₆₀ (A = K, Rb, Cs or a mixture).

The authors concluded that all A₃C₆₀ compounds have the same structure and that Tₑ changes are due to the alterations on the Fermi level.⁶³ Shortly after, Tanigaki *et al.* reported the synthesis and superconductivity properties of the mixed metal fulleride, Cs₂RbC₆₀, Tₑ = 33 K at ambient pressure.⁶⁴ To expand the crystal lattice further cesium is the clear choice for fullerides doping; however, it wasn’t until 1995 that Cs₃C₆₀ was successful synthesized and characterized. The authors report the Cs₃C₆₀ product to have a Tₑ = 40 K under 15 kbar. However, it should be noted that the structure was not fcc.⁶⁵ The X-ray diffraction studies reported by Palstra *et al.* reveal two non-fcc phases: at 1 bar the compound has a body centered tetragonal phase (bct), whereas at 26 kbar the structure is body centered cubic (bcc).⁶⁵ The cesium doped fulleride, Cs₃C₆₀, still has the highest Tₑ to date for alkali metal fulleride compounds and has a unique body-centered anion packing which allows for more spacious sites for the large cesium cation (Figure 1.6).⁶⁶
Figure 1.6 A representation of the body centered cubic (bcc) structure of Cs$_3$C$_{60}$.

It should be noted here that only one alkali metal intercalation product of fullerene has been studied by single crystal X-ray diffraction. In 2010, Hoffmann and co-workers isolated single crystals of Rb$_4$C$_{60}$ and found that the compound exhibits a tetragonal bcc structure that has been assigned to the I$_4/mmm$ space group (Figure 1.7).$^{67}$

Figure 1.7 A representation of the tetragonal body centered cubic (bcc) structure of Rb$_4$C$_{60}$. $^{67}$

In the structure, the C$_{60}^{4-}$ is rotationally disordered and has the shape of a distorted truncated icosahedron ($D_{2h}$). The authors conclude that the structural data and density functional
theory (DFT) calculations reveal a metallic ground state for Rb₄C₆₀; this is in contrary to the insulating state observed experimentally.⁶⁸

Recently, Schon et al. reported a Tc of 52 K for a hole-doped C₆₀ compound, in which gate-induced doping was used to introduce significant densities of holes into C₆₀.⁶⁹ Interestingly, carbon nanotubes (CNTs), another carbon allotrope with unique properties and structures, have also been reported to have superconductive properties.⁷⁰ Carbon nanotubes are comprised of graphene sheets (sp² hybridized carbon atoms) rolled up to form a one-dimensional (1D) tube. The tube diameter is measured on the nanometer scale. The most frequently observed CNTs exhibit a diameter of at least 14 Å; however, the smallest conceivable nanotube is 3 Å.⁷¹ The lengths of CNTs can vary from hundreds of microns to decimeters. Ultralong CNTs measure on the centimeter to decimeter scale and are grown on flat substrates parallel with each other. Ultralong CNTs are known for their perfect structures and excellent properties (mechanical, intershell superlubricious, electrical and thermal).⁷² Depending on how many sheets are rolled up, carbon nanotubes are either described as single (SWCNT)⁷³ or multi-walled (MWCNT) (Figure 1.8).⁷⁴

![Figure 1.8 Single (left) and multi-walled (right) carbon nanotubes.](image)

In 2001, Tang et al. revealed that 4 Å SWCNTs embedded on zeolite exhibit superconductivity at Tc = 15 K.⁷⁴ However, the authors report zero resistance was only reached at
Also in 2001, Kociak et al. investigated ropes of single walled carbon nanotubes, reporting intrinsic superconductivity below 0.55 K.76

The transition temperatures observed for carbon nanotubes are comparable to those experimentally determined for graphite intercalated with alkali metals. Fullerides are the most promising carbon-based superconductors as the transition temperatures are in the range of liquid hydrogen, making these materials useful for future energy storage.

1.3 Carbonaceous Anode Materials

The intercalation of alkali metal ions into polycyclic aromatic hydrocarbons (PAHs) is of great interest in materials science due to the increased need for stable anode materials with high capacity for energy storage.77 Carbonaceous materials have been used as the sole anode for lithium-ion batteries since 1991 when the lithium-ion technology was first developed.78 Graphite is currently used as the anode material for lithium-ion batteries due to its features, such as layered extended planar structure (Scheme 1.1), excellent stability and low cost due to the high abundance of carbon. However, lithiated graphite, LiC₆, has a low theoretical charge capacity of 372 mAh/g.79 Although advancements in natural and artificial graphite have been achieved by optimizing particle and pore structure, the overall processing is still energy-intensive.80 Therefore, exploration into novel carbon anode materials with desirable properties has increased with the demand for more efficient batteries for advancing technologies.81

1.3.1 Advancing Anode Materials: Disordered Carbons

The next generation of carbon-based anode materials must have a high capacity for lithium and exhibit fast lithium insertion/extraction with low volume changes during these processes.82
Recently, there has been investigations into disordered carbon systems for anode materials due to their high lithium intercalation (Li$_2$C$_6$ or Li$_3$C$_6$). Disordered carbons are prepared from pyrolysis of pitch, complex organic molecules and polymers. The resulting structure of the carbon anode prepared depends on the precursor and the temperature of pyrolysis. Products are deemed either soft or hard carbon depending on their tendency to graphitization at high temperatures. Hard carbons do not demonstrate graphitization. The distance between layers in soft and hard carbons is smaller than in graphite and the carbon atoms are irregularly placed. Pores, cavities and vacancies are increased in disordered carbons and these defects in the carbon network result in improved capacity. For instance, a soft carbon anode prepared from petroleum pitch experimentally shows a capacity of ~900 mAh/g and a hard carbon anode prepared from resin exhibits a capacity of ~560 mAh/g. The mechanism of intercalation into disordered carbons is proposed to be different from graphite intercalation. In 1994, Sato et al. suggested based on high-resolution electron microscopy and lithium NMR ($^7$Li) that Li$_2$ covalent molecules in the carbon material act as capacity reservoirs during discharging. In 1995, Dahn et al. put forth three different routes for lithium insertion into carbonaceous materials based on their overall composition. In graphitic carbon, intercalation occurs but lithium cannot be caught between adjacent layers that show misalignment of the basal planes. In carbons in which the hydrogen to carbon ratio is high, lithiums bind close to the hydrogen atoms. Finally, in materials which consist of one atom thick layers, lithium can be absorbed by both sides of the carbon layers.

The first lithium insertion into a hard carbon anode was reported in 2003 by Letellier et al. using $^7$Li NMR spectroscopy. The authors report that 81% disorder was observed by transmission electron microscopy (TEM) in the anode material. The resulting capacity of the disordered hard
carbon anode is 1.5 times greater than that of graphite. One major drawback is that the precise site of lithium intercalation was not established in situ in this study.

### 1.3.2 Graphene and Nanographene

Graphene is a two-dimensional (2D) carbon-based material consisting of a single layer of graphite and was thought to be unstable until 2004. Novoselov et al. reported the preparation of graphitic sheets, including graphene, which opened the doors to the exploration of the electronic properties of graphene (Scheme 1.4).  

**Scheme 1.4:** Production of graphene from graphite through mechanical exfoliation.

In 2015, Raccichini et al. conducted the first study of lithium intercalation into multilayered graphene. The authors report a specific capacity of 265 mAh/g at low temperatures (< 0 °C). Sun et al. explored if the performance of the anode would improve based on variation in the graphene flakes thickness, few-layer graphene vs. multi-layer graphene. On the first cycle, the former provided higher specific capacity values; however, the intercalation showed low reversibility. The authors conclude that graphene (in any thickness) may be part of the ultimate anode material, but it cannot be sole main character based on the low specific capacity observed thus far.
Graphene sheets can be reassembled into graphene nanosheets (GNSs) consisting of 2D layers of one atom thickness (Scheme 1.5). In reassembling there is structural control which allows for tuning of the interlayer spacing.

**Scheme 1.5**: Production of graphene nanosheets from graphene through a reassembling process.

An interesting report on the specific capacity of GNSs was published by Yoo et al., who investigated the capacity of pure GNSs and GNSs with macromolecules incorporated, namely carbon nanotubes (CNTs) and C₆₀. The authors report that the specific capacity of pure GNS is 540 mAh/g, which is greater than that of graphite. They found that even higher capacities were exhibited when macromolecules, CNT and C₆₀, were incorporated, resulting in capacities of 730 mAh/g and 784 mAh/g, respectively. The authors conclude that the presence of the π-electron system of the macromolecules must be responsible for the observed increase in the distance between nanosheets. This report, among others, supports the evolution towards the use of curved carbon systems in anode materials.
1.3.3 Curved Carbons

Carbon nanotubes (Figure 1.8) have been used as anode materials due to their structure which allows for lithium ion intercalation both on the interior and exterior of the CNT.\textsuperscript{92} Defects which occur naturally or are artificially added, along with shorter CNT lengths increase the capacity.\textsuperscript{93} Theoretically, the reversible capacity for SWCNTs is calculated to be 1116 mAh/g, LiC\textsubscript{2}.\textsuperscript{94} However, anodes composed of pure CNTs have not shown much promise, therefore, other avenues have been explored such as doping, carbonaceous composites and composites with group IVA or transition metal oxides.\textsuperscript{93} Although composite CNTs have exhibited higher specific capacities than graphite and are proposed to play an important role in the enhancement of capacity for LIBs, there are drawbacks to CNTs such as cost and toxicity which need to be overcome.\textsuperscript{95}

In 2016, Sato \textit{et al.} used [6]cyclo-2,7-napththylene ([6]CNAP) (Figure 1.9), a non-planar aromatic hydrocarbon macrocycle, as an anode material in a solid state lithium battery. The studies revealed a high capacity (727 mAh/g)\textsuperscript{96} and Li\textsubscript{2.3}C\textsubscript{6} intercalation pattern. The authors propose that nanopores observed by X-ray diffraction analysis allow for larger than predicted lithium storage.

![Molecular structure of [6]CNAP, top view (left) and side view (right).](image)

\textbf{Figure 1.9} Molecular structure of [6]CNAP, top view (left) and side view (right).\textsuperscript{97}
However, the lithium ion intercalation pattern for [6]CNAP was calculated using structural information from two different X-ray diffraction studies. The coordination of lithium to the [6]CNAP was based on the lithium naphthalene dianion salt crystallized from tetramethylethylenediamine (TMEDA), ([Li(TMEDA)_2][C_{10}H_8]). Additionally, the lithium ions proposed to be located in the central opening of the macrocycle were based on the X-ray diffraction report of a hexameric lithium cluster in (LiC_6H_3-3,5-t-Bu_2)_6. Therefore, the lithium intercalation into [6]CNAP has only been modeled based on calculations and intercalation patterns observed for subunits of the molecule.

In 2000, Sandi and Gerald et al. investigated the use of curved carbon systems as anode materials selecting corannulene for experimental manipulations. The bowl-shaped corannulene (C_{20}H_{10}), the 1/3 subunit of the C_{60}-fullerene, shares with fullerenes the convex three-dimensional unsaturated carbon surface (Figure 1.10) but also has its concave face open and accessible.

Figure 1.10 Corannulene (C_{20}H_{10}) (left), corannulene highlighted as the 1/3 subunit of the C_{60}-fullerene (center) and side view of corannulene (right, H-atoms removed).

For the first investigation, the electrodes were composed of corannulene and C_{60}; the authors used ^7Li NMR and molecular orbital calculations to reveal a reversible capacity of 464
mAgh\textsuperscript{g}.\textsuperscript{100a} A purely corannulene-based anode was studied by Gerald \textit{et al.} using the Coin Cell Battery Imager, which recorded wide line \textsuperscript{7}Li NMR spectra of the lithium ions that were intercalated between the curved carbon surfaces. This study revealed a reversible lithium ion insertion capacity of 602 mAgh\textsuperscript{g}. When compared to the currently used graphite anode, it has a 1.6 times greater lithium capacity.\textsuperscript{100b} Moreover, the charge transfer from lithium ions to the C\textsubscript{20}H\textsubscript{10} ring system was found to be minimal. These results infer that high reversible lithium intercalation capacities are enabled by lithium cluster formation within cavities formed by bowl-shaped corannulene.\textsuperscript{105} These finding prompted special interest into the investigation of Li intercalation patterns within bowl-shaped carbon-rich arenes.

\textbf{1.4 Reduction of Corannulene with Alkali Metals: Solution Studies}

Corannulene is known to serve as a very convenient model of curved \textit{\pi}-surfaces in a variety of theoretical and experimental studies. This small buckybowl was first prepared by a tedious seventeen-step synthesis in 1966 by Barth and Lawton in a very small yield.\textsuperscript{106} However now its preparation is well developed.\textsuperscript{107,108,109,110} Corannulene can be visualized as an “annulene-within-annulene”; in other words, C\textsubscript{20}H\textsubscript{10} consists of a cyclopentadienyl ([5]-annulene) anion (6e\textsuperscript{−}/5C) and [15]annulene cation (14e\textsuperscript{−}/15C).\textsuperscript{111} Corannulene is known to exhibit very interesting redox behavior. Over the past few decades, considerable research into multiple reduction stages of corannulene has been underway using optical absorption, ESR, and nuclear magnetic spectroscopy.\textsuperscript{112,113,114,115,116,117} The existence of several reduced forms, C\textsubscript{20}H\textsubscript{10}\textsuperscript{−}, C\textsubscript{20}H\textsubscript{10}\textsuperscript{2−}, C\textsubscript{20}H\textsubscript{10}\textsuperscript{3−}, and C\textsubscript{20}H\textsubscript{10}\textsuperscript{4−}, has been proven in solution using different alkali metals (Li, Na, K, Rb, Cs) as the reducing agents (Scheme 1.6).
In 1994, Scott et al. reported that corannulene could be reduced \textit{in situ} to the tetraanion using lithium metal in the O-donor solvent tetrahydrofuran (THF). The authors proposed that the corannulene tetraanion exists as a complex supramolecular dimer based on $^1$H and $^{13}$C NMR data.\textsuperscript{118} In the $^1$H NMR spectrum only a single peak was observed, exhibiting equivalence of all hydrogens. In $^{13}$C NMR spectrum three signals with a chemical shift indicating the delocalization of the four additional electrons over all 20 carbons of the corannulene tetraanion was observed. The authors proposed that the corannulene tetraanions serve as “decks” of the dimer with eight lithium ions spread above, below, and between (Scheme 1.7).\textsuperscript{118}

The authors assigned the location of the lithium cations in their proposed model using $^7$Li NMR spectroscopy. In the $^7$Li NMR spectrum two peaks of equal intensity were observed at −4.5 (broad) and −11.7 ppm (narrow), revealing only two different lithium ion environments in solution.
The unusually high field shift is a result of shielding by the diamagnetic ring currents of the aromatic corannulene tetraanion, proving that the ions were located above or below the \( \pi \)-delocalized ring. To assign the peaks to “interior” (between the decks) or “exterior” (above or below supramolecular dimer) lithium ions, a common ion (LiBr) was introduced to the system. During the experiment, the peak at \(-4.5 \text{ ppm}\) disappeared and new peak appeared at \(-2.5 \text{ ppm}\). At the same time, the peak at \(-11.7 \text{ ppm}\) was unaffected. The authors concluded that the peak at \(-11.7 \text{ ppm}\) must consist of lithium ions which are bound to the corannulene tetraanion, constituting contact ion pairs (CIPs). The peak at \(-4.5 \text{ ppm}\) was assigned to exterior ions as solvent separated ion pairs (SSIPs), due to their behavior observed when a common ion was added, which revealed that these ions could be easily exchanged.

Using semi empirical molecular orbital calculations, the authors supported their model in spite of its incompatibility with the observed equivalence in \(^1\text{H}\), \(^{13}\text{C}\) and \(^7\text{Li}\) NMR data. Despite the ambiguity of this report it served as the primary model for lithium ion intercalation into curved carbon systems and was widely accepted by the scientific community. The suggested intercalation model was applied to a variety of curved carbon derivatives containing the corannulene unit.\(^{119,120,121}\) Two specific examples are, bicorannuleny1 and 1,8-dicorannulenyloctane, both are biaryl derivatives which have two open concave \( \pi \)-carbon faces (corannulene subunits) that are sterically available for binding, making them exceptional ligands for lithium ion intercalation.\(^{120,121}\)

In 2010, Eisenberg et. al reported that bicorannuleny1 could be reduced to the octaanion using lithium metal in THF based on \(^1\text{H}\) and \(^7\text{Li}\) NMR investigations.\(^{120}\) The \(^1\text{H}\) NMR spectrum of the bicorannuleny1 octaanion at 210 K reveals over 30 peaks which are significantly broader when compared to 9 peaks observed in the \(^1\text{H}\) NMR spectrum of neutral bicorannuleny1.\(^{120}\)
Correspondingly, the $^7\text{Li}$ NMR spectrum of C$_{40}$H$_{18}$ at 190 K demonstrates 10 separate peaks in the high-field region (–10 to –14 ppm). This shift is characteristic of lithium ions sandwiched between the charged polyarenes. The $^7\text{Li}$ NMR spectrum of the bicorannulenyl octaanion is complex in comparison to the single peak observed in the $^7\text{Li}$ NMR spectrum of the corannulene tetraanion. Due to the complexity observed in both the $^1\text{H}$ and $^7\text{Li}$ NMR spectra of the bicorannulenyl octaanion the authors concluded that self-assembly of bicorannulenyl octaanions into highly charged supramolecular oligomers occurs in solution (Scheme 1.8, left). The model of four lithium ions sandwiched between the corannulene tetraanions was applied despite the observed complexity of the $^7\text{Li}$ NMR spectrum at 190 K.

Scheme 1.8: Proposed models for the intercalation of lithium ions into bicorannulenyl octaanion (left) and 1,8-dicorannulenyloctane octaanion (right).

In 2000, Shabtai et al. reported that 1,8-dicorannulenyloctane could be reduced to the octaanion using lithium metal in THF based on solution studies, namely $^1\text{H}$ and $^7\text{Li}$ NMR spectroscopy.$^{120}$ The $^1\text{H}$ NMR spectrum consisted for four broad peaks in the 2.2–3.2 ppm range.
(protons on the tether) and another set of peaks between 6.7−7.2 ppm (corannulene tetraanion region). The authors were very vague about the number of peaks observed in this region and did not assign intensities to any peaks. The $^7$Li NMR spectrum of 1,8-dicorannulenyloctane octaanion shows two singlets analogous to those observed for the corannulene tetraanion and no comment was made about the equivalence of these signals. Therefore, supramolecular dimers were proposed for the structure. Due to the octamethylene tether, 8 Å in length, the authors questioned whether intramolecular or intermolecular stacking was occurring in solution. To determine which were formed upon reduction with lithium, Shabtai et al. attempted to generate “mixed sandwiches” between the 1,8-linked corannulene and corannulene in a 1:10 ratio, respectively. Theoretically, one or both of the 1,8-dicorannulenyloctane octaanion moieties would be stacked with corannulene tetraanion. However, only signals of the tetraanion were observed in high concentration along with weak signals of the octaanion of the 1,8-dicorannulenyloctane. No new signals for mixed sandwich architectures were identified which argues in favor of intramolecular sandwich formation. Based solely on these solution studies the authors proposed the model of intramolecular sandwich formation analogous to the corannulene tetraanion dimer (four lithium ions sandwiched between corannulene tetraanions and four external lithium ions) (Scheme 1.8, right).

The intercalation patterns for these corannulene derivatives were based on the parent corannulene tetraanion model, even though they differ in intermolecular vs. intramolecular stacking and polymeric vs. discrete unit of the octaanion. No X-ray diffraction structural investigations have been reported; therefore, the intercalation pattern of lithium ions into these molecules has remained unproven.
1.5 Self-Assembly of Corannulene Tetraanions with Li⁺ Ions: Crystallographically Confirmed

In our laboratory the stepwise reduction of corannulene, C₂₀H₁₀, using lithium as a reducing agent has been investigated and followed by successful isolation of solid products of mono-, di-, and tetrareduced corannulene in the form of their crystalline lithium salts.¹²², ¹²³ The interaction of lithium ions with corannulene anions produced distinct supramolecular assembles ranging from discrete units (for mono- and dianions) to supercharged dimers (for tetraanions). The use of various donor solvents and crown ethers allowed for switching on and off metal binding interactions with the corannulene anions in the solid state. The analysis of single crystal X-ray diffraction data allowed for the first time the investigation into the geometrical perturbations upon charging the corannulene core and binding preferences of variably charged corannulene anions.¹²³

The controlled reduction of corannulene with lithium to the monoanion in the donor solvent, dimethoxyethane (DME), resulted in isolation of single-crystals suitable for X-ray diffraction studies. The two structurally characterized products containing monoreduced corannulene, [Li⁺(DME)₃][C₂₀H₁₀⁻] and [Li⁺(15-crown-5)]₂[C₂₀H₁₀⁻]₂ (Figure 1.11, top left and right), revealed the presence of “naked” bowl-shaped monoanions.¹²¹
Figure 1.11 Corannulene mono- (top, left and right) and dianions (bottom, left and right) with lithium countercations in different donor solvents and crown ethers.

The Li$^+$ cation is solvent-separated or captured by crown ether in the above structures with the monoanion, C$_{20}$H$_{10}$$^-$ (Figure 1.11 top, left and right). The isolation of these “naked” anions was important as it allowed for the structural investigation of the geometrical deformations of the monoreduced corannulene compared to the neutral ligand without the effects of metal binding. The acquisition of the negative charge results in shortening of the hub C–C bonds of C$_{20}$H$_{10}$$^-$ when compared to the parent bowl, whereas the spoke C–C and rim C–C bonds are slightly elongated in both monoanions. Notably, the negative charge does not considerably affect the bowl depth of corannulene (0.841(5) Å vs. 0.875(2) Å for neutral C$_{20}$H$_{10}$).$^{122,124}$

Controlled reduction of corannulene to the dianion with lithium in various donor solvents resulted in the isolation of the following salts, [Li$^+$ (diglyme)$_2$][C$_{20}$H$_{10}$$^{2-}$] and [{Li$^+$ (DME)}$_2${Li$^+$ (DME)$_{1.5}$}]$_2$[C$_{20}$H$_{10}$$^{2-}$]$_2$ (Figure 1.11 bottom, left and right).$^{121}$ The use of
different solvents demonstrated their role on the alkali metal coordination to the charged non-planar π-carbon surface. The dimethoxyethane (DME) adduct shows binding of the Li⁺ ions both to the five- and six-membered rings of the doubly-reduced corannulene convex face (Figure 1.11 bottom, right). In contrast, crystallization of the C_{20}H_{10}^{2−} from the strongly chelating donor solvent diglyme leads to the formation of the “naked” C_{20}H_{10}^{2−} anion, in which the geometrical parameters of corannulene core are not affected by direct coordination of alkali metal ions (Figure 1.11 bottom, left). The latter represents the first example of the “naked” corannulene dianion and allows for investigation of how charging the C_{20}H_{10} bowl with two electrons affects its core. Specifically, the acquisition of two electrons by corannulene results in a decreased bowl depth when compared to neutral corannulene (0.811(3) Å vs. 0.875(2) Å, respectively). Additiona l flattening of the curved carbon surface is observed upon metal coordination in [{Li⁺(DME)}_2{Li⁺(DME)_{1.5}}_2][C_{20}H_{10}^{2−}]_2, (0.796(4) Å).^{122}

Corannulene was reduced with an excess of lithium metal in tetrahydrofuran (THF) to the highest reduction stage under strictly anaerobic conditions.^{125} An X-ray diffraction study revealed a sandwich assembly, [{Li⁺5(C_{20}H_{10}^{4−})}_2{Li⁺(THF)_{2}}{Li⁺(THF)_{3}}][Li⁺(THF)_{4}] (Figure 1.12).^{125a}

**Figure 1.12** Molecular structure of the self-assembly formed by tetrareduced corannulene with lithium ions. Hydrogen atoms are for clarity.
In contrast to the previous model, which was based on solution studies and semi-empirical calculations,118 five lithium atoms are intercalated in the dimer.125a These five lithium ions are coordinated to the \textit{exo} faces of the two tetrarereduced corannulene decks. Additionally, two exterior Li$^+$ ions are bound to the \textit{endo} surface of this supercharged sandwich, while the remaining Li$^+$ cation is solvent-separated. The acquisition of four electrons by the corannulene core results in significant flattening of the bowl depth when compared to neutral corannulene (0.288(2) Å \textit{vs.} 0.875(2) Å, respectively).125a,124 Importantly, the supramolecular sandwich provides the new model for lithium intercalation between curved $\pi$-surfaces, with a ratio of LiC$_{5.7}$ as compared to the intercalation ratio of graphite, LiC$_{6.7}$.

Furthermore, the elucidation of the structure formed by the corannulene tetraanion with lithium ions disproves the previous model,118 which was widely used by the community in interpreting other spectroscopic results. This confirms that ion intercalation into polycyclic hydrocarbons cannot solely be determined by solution spectroscopies, validating the need for solid state X-ray diffraction structural studies of such complex supramolecular systems. As the understanding of complex intercalation patterns involving non-planar carbon-rich systems progresses, it becomes more apparent that although solution spectroscopic techniques can provide preliminary insight into these processes, they cannot determine with great accuracy the resulting structural motifs. The literature is plagued with proposed models supported by solution studies and calculations, some of which contradict our fundamental understanding of metal intercalation and atom coordination patterns.126,127,128

To further advance energy storage materials research, structural studies of carbonaceous compounds intercalated with alkali metal ions, namely lithium and sodium, are of great interest.
and importance. Structure-property relationships of electrode materials can be better understood with the gained fundamental knowledge stemming from a synergistic use of solid state and solution studies. We therefore set out to closely look into the models proposed by spectroscopic studies and systems for which alkali metal intercalation had been studied in solution only. We specifically targeted the isolation of solid crystalline products for structural investigation with the goal of adding X-ray diffraction supported information to the literature in the area of alkali metal intercalation in curved carbon systems.

1.6 References


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2.1 Introduction

Coronene (C_{24}H_{12}, 1) and corannulene (C_{20}H_{10}) are members of the circulene family, [6]circulene and [5]circulene, respectively. The siblings differ greatly, as the seven benzene rings of coronene form a planar system resembling a subunit of the graphite layer (Figure 2.1, left), while the conjugated benzene rings fused to a central 5-membered ring of corannulene result in a curved surface resembling C_{60}-fullerene (Figure 2.1, center and right).

Figure 2.1 Coronene (C_{24}H_{12}, 1) (left); corannulene (C_{20}H_{10}), face view (center) and side view (right) of corannulene bowl. Hydrogen atoms are omitted for clarity.

2.1.1 Structurally Characterized Complexes of Coronene

Coronene represents a primary model of the planar π-surface of graphene sheets and thus attracts significant attention from structural and materials chemists.\textsuperscript{1,2,3} The coordination chemistry of neutral coronene is limited to only a few examples of metal binding and one
cocrystallization product. Transition metal complexes of silver\textsuperscript{4} and rhodium\textsuperscript{5}, as well as two copper(I) complexes have been prepared and structurally characterized, the latter by our group (Figure 2.2).\textsuperscript{6}

![Figure 2.2 Crystallographically characterized complexes of neutral coronene reported in literature.\textsuperscript{6,7,8}](image)

Over the past few years coronene has been structurally characterized to form inclusion products with an assortment of molecular cages.\textsuperscript{7} The molecular cages are designed to have electron-poor cavities, making them great receptors for polycyclic aromatic hydrocarbons. Coronene serves as a good guest due to its planar structure and being rich in $\pi$-electrons. The resulting inclusion complexes are stabilized by $\pi-\pi$ interactions between the neutral coronene and the molecular cage (Figure 2.3). Due to the potential health risks associated with the release of
polyaromatic hydrocarbons (PAHs) into the environment the supramolecular chemistry of sequestering and detecting PAHs is of great importance.

Figure 2.3 Select crystallographically characterized inclusion products of neutral coronene reported in literature.\(^{7a,b}\) The counteranions and the solvent molecules in the superstructures are omitted for clarity.

Due to being rich in \(\pi\)-electrons coronene can also be used as the donor component in charge-transfer (CT) systems. The first charge transfer complex of coronene was structurally characterized in 2004 by Chi et al.\(^{8}\) This system exhibits semiconductor behavior and a larger degree of charge-transfer than similar hydrocarbon-based CT complexes. Yoshida et al. expanded on this work by investigating the motional properties of coronene-based CT solids.\(^{9}\) In the past few years, coronene has been broadly exploited as a donor in charge transfer complexes and structurally characterized in a handful of products.\(^{10}\) The recent interest in this field is due to applications in molecular electronics.
2.1.2 Redox Properties of Coronene

2.1.2.1 Coronene Cations

The redox behavior of coronene has been vastly studied by cyclic voltammetry in non-aqueous solvents. The first and second reduction and oxidation standard potentials have been measured for coronene in solution.\textsuperscript{11} Although there are numerous solution studies of the redox properties of coronene, the structural investigations of the resulting products are limited to only a few examples. The first coronene cation radical was isolated in the solid state in 2014 by Yoshida et al.; crystals of (coronene)\textsubscript{3}Mo\textsubscript{6}Cl\textsubscript{14} were grown from solution after electrochemical oxidation of coronene.\textsuperscript{12} Since isolating the coronene cation, Yoshida and co-workers have expanded the work by varying the nature of the counter anions. Interestingly, the authors found that the coronene cations in the solid state exhibit π-stacked columns (Figure 2.4). This is an important step towards developing an isotropic three-dimensional (3D) π-conducting system composed of planar π-conjugated molecules.\textsuperscript{13}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{coronene_cations.png}
\caption{Selected crystallographically characterized coronene cations reported in the literature with π-columnar structures.\textsuperscript{13} The counteranions are omitted for clarity.}
\end{figure}
2.1.2.2 Coronene Monoanions

Most relevant to our current work is the previous report of a one electron reduction of coronene using potassium metal to yield an $\eta^3$-bound complex, $[K^+(TMEDA)(THF)_2][1^-]$ (Scheme 2.1).$^{14}$ Janiak et al. structurally characterized the coronene monoanion using X-ray diffraction study as a model for potassium (adsorbate)-graphite surface interactions. The reported structure exhibits a solvated potassium cation asymmetrically $\pi$-coordinated to the external ring of the planar surface of 1 (Scheme 2.1).

**Scheme 2.1:** Reduction of 1 with potassium to form $[K^+(TMEDA)(THF)_2][1^-]^{14}$ (right). THF and TMEDA molecules are omitted for clarity.

Exploring the literature further and comparing coronene to the well-studied corannulene we found that the Hückel molecular orbital diagrams of corannulene and coronene are similar, as both possess doubly degenerate highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals (Figure 2.5).$^{15}$
As discussed in the introduction of this dissertation, corannulene has been proven by solution and X-ray diffraction studies to accept up to four electrons due to its low lying LUMOs. In contrast, coronene has been shown by solution spectroscopy to readily accept only two electrons (Scheme 2.2, top). Corannulene has lower lying unoccupied molecular orbitals when compared to coronene, and this may explain the difference in their reduction chemistry (Scheme 2.2, bottom).
Scheme 2.2: Coronene (top) and corannulene (bottom) reduction schemes with reduction potentials.\textsuperscript{11,17,18}

It should be noted here that another potassium coronene complex has been reported in the literature. Kubozono \textit{et al.} explored intercalating potassium metal into coronene by annealing. The authors reported the preparation of the K\textsubscript{3}coronene product and characterized the solid by powder X-ray diffraction (XRD).\textsuperscript{19} From the X-ray diffraction patterns, they concluded that potassium metal ions are inserted within the herringbone layers of coronene. However, they noted that the distance between layers was reduced. Most notably, the K\textsubscript{3}coronene solid product exhibits superconductivity similar to A\textsubscript{n}picene and AC\textsubscript{8} (A = alkali and alkali earth-metal atoms).\textsuperscript{20}

Although the monoanion of coronene had been structurally characterized, no reduction studies of coronene with other alkali metals have been conducted. Thus coronene has yet to be reduced with the remaining Group I metals in order to investigate if alkali metal size induces additional geometrical distortions or if a “naked” coronene monoanion could be isolated to evaluate the effect of the acquisition of one electron without metal binding. We set out to study the reduction of coronene with various alkali metals in solution and to isolate the products in single crystalline form. Our goal was to investigate the structures and aggregation behavior of the
resulting coronene anions by X-ray diffraction studies. We selected to use metallic sodium and rubidium as the reducing agents so we could compare the binding modes of coronene to corannulene, which has been well studied in the solid state by our lab.\textsuperscript{21}

\textbf{2.2 Controlled Reduction of Coronene}

Coronene reacts with one equivalent of sodium metal to afford an intense green solution characteristic of the radical anion, \(1^-\), in O-donor coordinating solvents. However, it is synthetically more convenient to use an excess of light alkali metal to reduce the polyarene to the dianion, \(C_{24}H_{12}^{2-}\), followed by the oxidation back to \(C_{24}H_{12}^{+}^-\) by addition of one equivalent of a neutral hydrocarbon (Scheme 2.3). In contrast with the heavier alkali metal rubidium, a slight excess (1.3 eq.) can be used in a straightforward synthetic procedure to achieve the reduction of coronene to the monoanion (Scheme 2.3).

\textbf{Scheme 2.3:} Synthesis of coronene monoanion-based products.
Due to the extreme sensitivity to moisture and air of all products formed by monoreduced coronene with various alkali metal counterions all manipulations were carried out using break-and-seal methods and glove-box techniques under an atmosphere of high-purity argon. The donor solvents, tetrahydrofuran (THF) and dimethoxyethane (DME), were dried over Na/benzophenone or sodium potassium alloy, respectively, and distilled prior to use. Crown ether, 18-crown-6, was used to provide additional coordination for the larger rubidium cation. The single crystals of the coronene monoanion salts suitable for X-ray diffraction studies were successfully obtained by the slow diffusion of freshly distilled hexanes into the THF or DME solutions of the corresponding products.

2.3 Monoreduced Coronene

2.3.1 Sodium Salt: \([\text{Na}^+(\text{DME})_3][\text{C}_{24}\text{H}_{12}^-]\)

The coronene monoanion with sodium cation was obtained as green plates, in moderate yield from the dimethoxyethane (DME) solution layered with hexanes. According to the X-ray diffraction study the resulting \([\text{Na}^+(\text{DME})_3][\text{I}^-]\) (2) product crystallizes in the orthorhombic space group \(Pna2_1\). The asymmetric unit contains one coronene monoanion and a DME solvated sodium countercation, forming a solvent-separated ion pair (SSIP). This structure contains the first structurally characterized “naked” monoanion of coronene (Figure 2.6).
The full encapsulation of the metal center by solvent molecules prevents metal binding to the \([C_{24}H_{12}^-]\) surface which has not been observed before. The acquisition of one electron by coronene causes geometrical deformation throughout the coronene surface and induces a slight out-of-plane twisting of \([C_{24}H_{12}^-]\). The maximum deviation of 0.14 Å between rim carbon atoms and the plane passing through the central 6-membered ring of coronene is observed. The hub C–C bond lengths of \([C_{24}H_{12}^-]\) (av. 1.424(3) Å) in the sodium salt are the same as in neutral \([C_{24}H_{12}]\) (1.425(3) Å, Table 2.1). However, the spoke and rim C–C bonds of the monoanion are elongated (av. 1.434(4) and 1.370(4) Å) vs. (1.416(3) and (1.358(3) Å). The flank C–C bond lengths are significantly shortened (av. 1.415(4) Å) compared to the parent coronene molecule (1.421(3) Å) (Table 2.1).
Table 2.1 Key bond length distances (in Å) for neutral 1 and 1− in 2.

![Diagram of C_{24}H_{12}]

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>hub</td>
<td>1.425(3)</td>
<td>1.418(3)−1.431(3)</td>
</tr>
<tr>
<td>spoke</td>
<td>1.416(3)</td>
<td>1.430(3)−1.441(3)</td>
</tr>
<tr>
<td>flank</td>
<td>1.421(3)</td>
<td>1.396(3)−1.430(4)</td>
</tr>
<tr>
<td>rim</td>
<td>1.358(3)</td>
<td>1.360(4)−1.384(4)</td>
</tr>
</tbody>
</table>

In 2, the sodium ion is coordinated to three DME molecules and the [Na^+(DME)_3] cation is solvent-separated from C_{24}H_{12}^−. The Na^+···O separations of the hexacoordinated Na^+ ion range from 2.346(18) to 2.411(2) Å; the interatomic distances are close to those observed in related compounds.\(^{23}\) Notably, in the solid state C−H···π interactions between DME moieties and the coronene monoanion as short as 2.61 Å can be identified. Importantly, the completion of this structural characterization allows us for the first time to evaluate the effect of distribution of a negative charge over the coronene surface without interfering metal binding effects.
2.3.1.2 Jahn–Teller Effect

Adding one electron to neutral C\textsubscript{24}H\textsubscript{12} leads to the geometric distortion of a negatively charged coronene, a distortion that is referred to as the Jahn–Teller (JT) effect (Scheme 2.4).\textsuperscript{24} The JT charge-induced geometric deformation of molecular structure plays a crucial role in the superconductivity mechanism of the alkali metal doped fullerides.\textsuperscript{25} For example, it proved to cause a metal-to-insulator transition in the K\textsubscript{4}C\textsubscript{60} system.\textsuperscript{25} Although, the occurrence of the JT effect has been predicted for the coronene monoanion,\textsuperscript{26} experimentally it was not observed for the coronene radical anion by ESR spectroscopy.\textsuperscript{26}

**Scheme 2.4:** Jahn–Teller distortions in coronene radical anion.

The high quality of our X-ray data and the lack of metal binding to the coronene surface in 2 allowed us to investigate the Jahn–Teller distortion, which occurs upon the addition of one electron to neutral C\textsubscript{24}H\textsubscript{12}. Early *ab initio* calculations suggested that the Jahn–Teller effect in coronene radical anion leads to the \( C_{2h} \) symmetrical structure, while the \( D_{2h} \) structure represents a saddle point.\textsuperscript{27} A group-theory analysis of JT distortions using the step-by-step symmetry descent
method suggested that the JT effect in the $D_{6h}$ parent symmetry group results in stable $D_{2h}$ geometries. Our density functional theory (DFT) calculations using the same functional and basis sets showed that both $C_{2h}$ and $D_{2h}$ structures correspond to true minima on the potential-energy surface. Our experimental diffraction data can also be fitted into the higher symmetry point group, $D_{2h}$, that has two perpendicular mirror planes (the third being the plane of the molecule) leaving only a quarter of the molecule symmetrically independent (Figure 2.7).

![Figure 2.7. A view of the coronene core. Dashed lines represent the mirror planes. The structure is drawn with thermal ellipsoids at the 40% probability level.](image)

Thus, there should be two symmetrically unique rim-, one spoke-, two hub-, and three flank C–C bonds for $C_{24}H_{12}^{\text{−}}$ in 2. The six sigma limit is 0.024 Å in 2. All bond-length deviations for the symmetrically related rim-, spoke-, and hub bonds are even less than half of that number and thus statistically equivalent at the 99.7% confidence level. For $C_{24}H_{12}^{\text{−}}$ in 2, the flank C–C bonds lie within the experimental error except for two pairs of outliers that have 0.023 and 0.025 Å bond length deviations. The average difference between the bond lengths is 0.011 Å. Taking into
account the presence of only two outliers, we may consider the structure of the coronene radical anion to possess the $D_{2h}$ symmetry. Nevertheless, if we reduce the symmetry down to the $C_{2h}$ point group, both outliers are eliminated and all bonds lie within the experimental error with the maximum deviation of 0.017 Å for the flank bonds. Despite some improvements in data fitting, it does not seem to warrant an assignment of the $C_{24}H_{12}^-\cdot\cdot\cdot\pi$ structure to the $C_{2h}$ group. Both outliers for the $D_{2h}$ point group lie on the border of the six sigma limit. Furthermore, the weak intermolecular $C$–$H$···$\pi$ interactions, may have some influence on the solid-state structure.

In 2, the coronene core is found to not be perfectly planar, an observation that merits special consideration. First, the observed twisting may slightly shift the bond length distribution relative to that of perfectly planar coronene core. However, this shift is not considered substantial, as the overall agreement between the calculated and experimental data is good. Second, $C_{24}H_{12}^-\cdot\cdot\cdot\pi$ of 2 cannot be ascribed to either the $D_{2h}$ or $C_{2h}$ point groups because the formal absence of a mirror plane perpendicular to a two-fold axis. The continuous symmetry measures (CSM) analysis provides an essentially perfect symmetry measure of 0.6% for the $C_2$ point group. The deviation from the ideal $D_{6h}$ symmetry (19.9%) is not due to a particularly strong JT effect but is rather related to the nonplanarity of the polyarene core; $S (C_s \text{ horizontal})$ is 19.2%. The deviation from planarity can be neglected for consideration of the JT effect on the basis of DFT calculations. Whereas, calculations of the naked $C_{24}H_{12}^-\cdot\cdot\cdot\pi$ radical anion predict no twisting, the introduction of a counter cation to the geometry optimization step (computed with four different theory models to avoid method-induced errors) results in a slight twisting of the coronene core. The only other reported structure of the coronene radical anion also exhibits an essentially planar polyarene skeleton (maximum deviation is 0.08 Å). Thus, the twisting effect may be attributed to intermolecular $C$–$H$···$\pi$ interactions and can be disregarded for a JT discussion. The CSM analysis
reveals two perpendicular mirror planes with values of 1.8 and 1.9%, with the other symmetry groups deviating by more than 4.7%. Assuming the core of the coronene radical anion is planar, the CSM data suggest the $D_{2h}$ point symmetry group. Notably, the overall extent of the JT distortion in C$_{24}$H$_{12}^-$ is less pronounced than in C$_{20}$H$_{10}^-$.\textsuperscript{21a}

\textbf{2.3.2 Rubidium Salt: [Rb\textsuperscript{+}(18-crown-6)][C$_{24}$H$_{12}$\textsuperscript{−}]}

The reduction of coronene to the monoanion stage was readily accomplished in THF by the addition of 1.3 equivalents of rubidium metal in the presence of 18-crown-6 ether. Single crystals of the product were grown from the THF solution by layering with hexanes. According to the X-ray diffraction study, the product crystallizes in the monoclinic space group $Cc$. The asymmetric unit consists of one coronene monoanion with two disordered rubidium cations and an 18-crown-6 molecule. The rubidium cation is disordered over two positions; this disorder was modeled with a 0.57:0.43 ratio. The Rb\textsuperscript{+} ion exhibits contacts to the coronene surface, constituting a CIP that reveals a new binding mode for the coronene monoanion. The molecular formula of this product is [Rb\textsuperscript{+}(18-crown-6)][C$_{24}$H$_{12}$\textsuperscript{−}] (3) (Figure 2.8).\textsuperscript{21b}
Notably, this is the first case of coronene monoanion with a metal bound to the central benzene ring. Previously, the external ring of C$_{24}$H$_{12}^-$ was engaged in an asymmetric $\eta^6$-binding of potassium ions in the structurally characterized [K$^+$(TMEDA)(THF)$_2$][C$_{24}$H$_{12}^-$. The hub C–C bond lengths of C$_{24}$H$_{12}^-$ (av. 1.424(13) Å) in the rubidium salt are the same as in neutral C$_{24}$H$_{12}$ (1.425(3) Å, Table 2.2). However, the spoke and rim C–C bonds of the monoanion are elongated (av. 1.430(13) and 1.371(14) Å) vs. (1.416(3) and (1.358(3) Å). The flank C–C bond lengths are significantly shortened (av. (1.411(15) Å) compared to the parent coronene molecule (1.421(3) Å). Notably, the C–C bond lengths of the polyarene core in [Rb$^+$(18-crown-6)][C$_{24}$H$_{12}^-$. experience the greatest fluctuation upon metal coordination to the hub site, when compared with sodium and potassium salts of monoreduced coronene (Table 2.2).
Table 2.2 Bond length (Å) comparisons of coronene in neutral C$_{24}$H$_{12}$ (1),$^1$ [Na$^+$(DME)$_3$][C$_{24}$H$_{12}$$^-$] (2),$^{21a}$ [Rb$^+$(18-crown-6)][C$_{24}$H$_{12}$$^-$] (3),$^{21b}$ and [K$^+(TMEDA)$(THF)$_2$][C$_{24}$H$_{12}$$^-$]$^{14}$ salts.

<table>
<thead>
<tr>
<th></th>
<th>“Naked” C$<em>{24}$H$</em>{12}$$^-$</th>
<th>Hub Coordinated C$<em>{24}$H$</em>{12}$$^-$</th>
<th>Rim Coordinated C$<em>{24}$H$</em>{12}$$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>hub</td>
<td>1.425(3) 1.418(3)$^-$1.431(3)</td>
<td>1.402(14)$^-$1.456(12)</td>
<td>1.415(5)$^-$1.434(5)</td>
</tr>
<tr>
<td>spoke</td>
<td>1.416(3) 1.430(3)$^-$1.441(3)</td>
<td>1.407(14)$^-$1.461(13)</td>
<td>1.414(4)$^-$1.438(4)</td>
</tr>
<tr>
<td>flank</td>
<td>1.421(3) 1.396(3)$^-$1.430(4)</td>
<td>1.391(15)$^-$1.440(15)</td>
<td>1.394(5)$^-$1.424(5)</td>
</tr>
<tr>
<td>rim</td>
<td>1.358(3) 1.360(4)$^-$1.384(4)</td>
<td>1.332(14)$^-$1.390(14)</td>
<td>1.366(5)$^-$1.382(5)</td>
</tr>
</tbody>
</table>

In 3, the Rb$^+$ ion is bound to the central benzene ring of C$_{24}$H$_{12}$$^-$ with the Rb···C distances ranging from 3.311(11) to 3.968(11) Å. Owing to the large size of rubidium, the ion is “sunrise coordinated” to 18-crown-6 ether,$^30$ with the Rb···O bond length distances ranging from 2.860(8) to 2.996(8) Å.

In the structure of [Rb$^+$(18-crown-6)][C$_{24}$H$_{12}$$^-$], the planar surface of C$_{24}$H$_{12}$$^-$ is engaged in intermolecular interactions with the crown moiety of [Rb$^+$(18-crown-6)]. Intermolecular
C−H···π contacts between the crown moieties and C$_{24}$H$_{12}^{-}$ are as short as 2.84 Å. Notably, the carbon-oxygen framework of 18-crown-6 ether almost mirrors the rim carbon atoms of C$_{24}$H$_{12}^{-}$ (Figure 2.9). In the solid state, each crown moiety is sandwiched between two planar surfaces of coronene radical anions, which results in multiple intermolecular C−H···π contacts (Figure 2.8, right). Such an alignment of the crown ether and coronene moieties most probably directs the Rb$^+$ binding to the central hub of C$_{24}$H$_{12}^{-}$ resulting in the coordination mode not seen previously.

**Figure 2.9** The ball and stick carbon-oxygen framework of 18-crown-6 ether overlay with the rim carbon atoms of the space-filling C$_{24}$H$_{12}^{-}$ in 3. The rubidium ion is omitted for clarity.

**2.3.2.1 Theoretical Modeling of [Rb$^+$(18-crown-6)][C$_{24}$H$_{12}^{-}$]**

We set out to study what effect, if any, the crown ether has on binding of the potassium ion to the coronene monoanion using a comprehensive theoretical investigation of the system. First, we considered the two possible coordination sites (hub and rim) on the surface of coronene with a “naked” Rb center, [Rb$^+][C_{24}H_{12}^-]$ (Figure 2.10).
Figure 2.10. Side and top views for the equilibrium geometry configurations of hub (left) and rim (right) isomers of \([\text{Rb}^+]\text{[C}_{24}\text{H}_{12}^-]\).

Both isomers correspond to true minima on the potential energy surface (PES), as indicated by all positive Hessian matrices. The energetic difference of 0.2 kcal/mol demonstrates that these isomers are indistinguishable in terms of relative stability. Such a degeneracy is also supported by the calculated weak bonding energy between the \text{Rb}^+ ion and the \text{C}_{24}\text{H}_{12}^- surface (-5.23 and -5.47 kcal/mol for the hub and rim isomers, respectively).

Lastly, we included 18-crown-6 ether into the investigation. Geometry optimization procedures for the rim and hub isomers of \([\text{Rb}^+(18\text{-crown-6})]\text{[C}_{24}\text{H}_{12}^-]\) smoothly converged to the structure where \text{Rb} is located at the center of the hub ring (Figure 2.11).
Careful examination of the geometry optimization results did not reveal the existence of the rim configuration. Therefore, the hub isomer is found as the only stable geometry configuration for the [Rb\(^+(18\text{-crown-6})\)][C\(_{24}\text{H}_{12}\text{•}^-\)] system corresponding to the minimum on the potential energy surface.\(^{21b}\)

### 2.3.2.2 Electronic Structure of [Rb\(^+(18\text{-crown-6})\)][C\(_{24}\text{H}_{12}\text{•}^-\)]

The coronene monoanion in the above CIP has an interesting feature of having one unpaired electron provided by the rubidium metal. The important question is where is this electron located in the resulting product? Is it fully delocalized over the polyaromatic surface of C\(_{24}\text{H}_{12}\text{•}^-\) or does it remain, at least in part, associated with the metal center? To address these questions, we performed a detailed analysis of the electronic structure of [Rb\(^+(18\text{-crown-6})\)][C\(_{24}\text{H}_{12}\text{•}^-\)] and compared it with that of the “naked” rubidium–coronene model. Notably, the calculated charge on the metal center in [Rb\(^+(18\text{-crown-6})\)] is slightly negative (−0.045e within the natural bond orbitals (NBO) formalism). This is consistent with the electron donating properties of 18-crown-6 ether.
In contrast, in the rubidium adducts with coronene the charge at the metal center becomes highly positive (+0.849e in $[\text{Rb}^+(18\text{-crown-6})][\text{C}_{24}\text{H}_{12}^+]$ and +0.986e in both isomers of $[\text{Rb}^+][\text{C}_{24}\text{H}_{12}^-]$). This formally indicates almost a full one electron transfer from the metal to a polyarene to form the contact-ion pair $[\text{Rb}^+(18\text{-crown-6})][\text{C}_{24}\text{H}_{12}^+]$ or $[\text{Rb}^+][\text{C}_{24}\text{H}_{12}^-]$.

Interestingly, an analysis of distribution of spin density function (Figure 2.12) shows that the unpaired electron in $[\text{Rb}^+(18\text{-crown-6})]$ is not localized on the rubidium center but is being pushed out to the side opposite to the bound crown ether ligand. This observation fully agrees with the atomic spin density on the Rb center, which is 0 for $[\text{Rb}^+(18\text{-crown 6})]$.

![Figure 2.12 Spin density distribution in $[\text{Rb}^+(18\text{-crown-6})]$, side view (left) and top view (right).](image)

At the same time, in the $[\text{Rb}^+(18\text{-crown-6})][\text{C}_{24}\text{H}_{12}^+]$ adduct the spin density is found to be delocalized over the $\pi$ surface of the coronene (Figure 2.13). Thus, the formation of a contact-ion pair can be described as a falling drop of spin density (here it corresponds to one unpaired electron) from $[\text{Rb}^+(18\text{-crown-6})]$ to the coronene surface.
The localization of spin density outside the metal center explains the relative ease of electron transfer to the polyaromatic system. The spin density distribution in [Rb⁺(18-crown-6)][C₂₄H₁₂⁻⁻] coincides precisely with the topology of the LUMO of neutral C₂₄H₁₂ (Figure 2.14). It fully supports the conclusion regarding the formation of C₂₄H₁₂⁻⁻ and the closed-shell Rb⁺ cation in this system.

Figure 2.14 LUMO of C₂₄H₁₂ (left) compared to spin density distribution in [Rb⁺(18-crown-6)][C₂₄H₁₂⁻⁻] (right).
From our X-ray diffraction studies of 3 and comprehensive theoretical investigation into this system we can conclude that 18-crown-6 ether directs the rubidium binding toward the hub site of the charged π surface of coronene. This type of binding most probably results from a good size match of the two complementary building blocks, allowing them to fully maximize C−H···π interaction upon their perfect overlap, as shown by X-ray crystallography and DFT calculation.

2.3.3 Solution Studies of Coronene Monoanion Radical

2.3.3.1 ¹H NMR Investigations

The “naked” coronene monoanion in [Na⁺(DME)₃][C₂₄H₁₂⁻] is NMR silent; there was no interaction between the [Na⁺(DME)₃] and [C₂₄H₁₂⁻] moieties observed in solution. In contrast, the ¹H NMR spectrum of crystals of [Rb⁺(18-crown-6)][C₂₄H₁₂⁻] dissolved in THF-d₈ reveals a low-field shift for the crown ether proton resonances, δ = 4.78 ppm (Figure 2.14). This low-field shift has also been observed by our group previously in CIP products with the general formula, [M⁺(18-crown-6)][C₂₀H₁₀⁻].³¹ These solution studies indicate that the interaction of the [Rb⁺(18-crown-6)] with the paramagnetic C₂₄H₁₂⁻ anion persists in solution.

Figure 2.15 Variable-temperature ¹H NMR spectra of 3 (THF-d₈). Free crown: 3.55 ppm.
2.3.3.2 UV-vis Spectroscopy Investigations

In the UV-vis spectra, the maxima of the two most intense absorption bands of the contact-ion pair in \([\text{Rb}^+(18\text{-crown-6})][\text{C}_{24}\text{H}_{12}^-]\) (475 and 625 nm, THF) are shifted compared to the solvent-separated ion pair in \([\text{Na}^+(\text{DME})_3][\text{C}_{24}\text{H}_{12}^-]\) (478 and 632 nm, DME) (Figure 2.16).\(^{21}\)

![UV-vis spectra comparison](image)

**Figure 2.16** UV-vis spectra of 3 (black) and 2 (purple).

2.3.3.3 ESR Studies

Crystals of 2 and 3 were dissolved in DME and THF, respectively, to allow for investigation of the coordination behavior of the coronene monoanion in solution. The ESR spectrum of 2 in solution (Figure 2.17, left) is identical to the spectrum previously reported;\(^{14}\) no additional hyperfine splitting of the ESR signal is prompted by the Na\(^+\) ions present in solution. On the other hand, the ESR spectrum of 3 exhibits hyperfine splitting of the ESR signal (Figure 2.17, right).
The ESR spectrum of 3 is more complex than that of 2. This most probably can be attributed to the coordination of [Rb⁺(18-crown-6)] to the $\text{C}_2\text{H}_{12}^-$ persisting in the solution of 3, as also supported by UV-vis and $^1\text{H}$ NMR spectroscopic studies.

2.4 Experiment Details

**Materials and Methods.** All manipulations were carried out using break-and-seal and glove-box techniques under an atmosphere of argon. Solvents (THF and hexanes) were dried over Na/benzophenone and distilled prior to use. DME and THF-$d_8$ was dried over sodium/potassium alloy and vacuum-transferred. Rubidium and sodium metals were purchased from Strem Chemicals. Coronene was purchased from TCI America and sublimed at 240 °C prior to use. NMR spectra were measured on a Bruker AC-400 spectrometer at 400 MHz for $^1\text{H}$. 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 UV-vis spectra were recorded on a PerkinElmer Lambda 35
spectrometer. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

**Crystal Structure Determinations and Refinement for 2 and 3**

Data collections were performed on a Bruker SMART\textsuperscript{32} APEX CCD-based X-ray diffractometer with graphite-monochromated Mo-K\textsubscript{\textalpha} radiation (\(\lambda=0.71073\) Å) at T = 100(2) K. Data were corrected for absorption effects using the empirical method SADABS.\textsuperscript{32} The structures were solved by direct methods and refined using the Bruker SHELXTL (Version 6.14) software package.\textsuperscript{33} All atoms were refined with anisotropic parameters. Hydrogen atoms were included at idealized positions using the riding model. In 3 the Rb center is disordered over two positions, and this disorder was modeled with a 0.57: 0.43 ratio of two parts.

**Synthesis and Crystal Growth of \([\text{Na}^+\text{(DME)}_3][\text{C}_{24}\text{H}_{12}\cdot^-]\) (2)**

DME (3 mL) was added to a flask containing excess of Na metal and coronene (10 mg, 0.033 mmol). The green solution was stirred at room temperature for 8 hours to give a deep brown mixture, which was filtered and combined with a solution of neutral coronene (10 mg, 0.033 mmol) in DME (3 mL). The resulting green solution was layered with hexanes (3 mL) and kept at 10 \(^\circ\)C. Dark green crystals deposited in a few days at 10 \(^\circ\)C in moderate yield (24 mg, 60%). UV-vis (DME, nm): \(\lambda_{\text{max}} = 478, 632\). \(^1\)H NMR silent. Elemental analysis calcd (%) for C\(_{36}\)H\(_{42}\)O\(_6\)Na (593.70): C 72.83, H 7.13; found: C 72.69, H 6.98.
Crystallographic Data for 2

Empirical formula: C\textsubscript{36}H\textsubscript{42}NaO\textsubscript{6}, \(M_r = 539.69\), orthorhombic, \(a = 22.621(3)\) Å, \(b = 9.5968(12)\) Å, \(c = 14.5060(18)\) Å, \(\alpha = 90^\circ\), \(\beta = 90^\circ\), \(\gamma = 90^\circ\), \(V = 3149.0(7)\) Å\(^3\), \(P\text{na}2_1\), \(Z = 4\), \(\rho_{\text{calcd}} = 1.252\) g/cm\(^3\), \(\mu = 0.095\) mm\(^{-1}\), \(T = 100(2)\) K, \(\lambda = 0.71073\) Å, 15553 measured intensities (7.20° \(\leq 2\theta \leq 111.52^\circ\)), 6922 unique intensities \(R_{\text{int}} = 0.0494\), \(R_1 = 0.0497\), with \(I \geq 2\sigma(I)\), \(wR_2 = 0.0973\) (6922), refinement of 394 parameters. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre, the CCDC identifier is 877544.

Synthesis and Crystal Growth of \([\text{Rb}^+\text{(18-crown-6)}][\text{C}_{24}\text{H}_{12}\text{•}^{-}]\) (3)

THF (3 mL) was added to a flask containing rubidium metal (3.7 mg, 0.043 mmol, 1.3 eq.), 18-crown-6 ether (15.8 mg, 0.06 mmol) and coronene (10 mg, 0.033 mmol). The initially green solution was stirred at room temperature for 8 hours to produce a deep green mixture. The mixture was filtered, layered with hexanes (3 mL), and kept at 10 °C. Dark green blocks were deposited in 48 hours in moderate yield (14 mg, 65%). UV-vis (THF, nm): \(\lambda_{\text{max}} = 475, 625\). \(^1\)H NMR (400 MHz, THF-\(d_8\), 25 °C, ppm): \(\delta = 4.78\) (OCH\(_2\), 18-crown-6). Elemental analysis calcd (%) for C\textsubscript{36}H\textsubscript{36}O\textsubscript{6}Rb: C 66.51, H 5.58; found: C 66.44, H 5.49.

Crystallographic Data for 3

Empirical formula: C\textsubscript{36}H\textsubscript{36}O\textsubscript{6}Rb, \(M_r = 650.12\), monoclinic, \(a = 19.740(8)\) Å, \(b = 8.213(3)\) Å, \(c = 20.445(11)\) Å, \(\alpha = 90^\circ\), \(\beta = 118.730(4)^\circ\), \(\gamma = 90^\circ\), \(V = 2907.0(2)\) Å\(^3\), \(Cc\), \(Z = 4\), \(\rho_{\text{calcd}} = 1.486\) g/cm\(^3\), \(\mu = 1.752\) mm\(^{-1}\), \(T = 100(2)\) K, \(\lambda = 0.71073\) Å, 11795 measured intensities (9.08° \(\leq 2\theta \leq 113.2^\circ\)), 6376 unique intensities \(R_{\text{int}} = 0.0577\), \(R_1 = 0.0953\), with \(I \geq 2\sigma(I)\), \(wR_2 = 0.2258\) (4689),
refinement of 398 parameters. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre, the CCDC identifier is 954420.

2.5 References


CHAPTER 3

Double Concave Binding of Bicorannulenyl Dianion: Cesium vs. Lithium Salts

3.1 Introduction

A new research direction in recent years is to design and synthesize dynamic π-systems using bowl-shaped polyarenes as building blocks. Novel electronic coupling and supramolecular oligomerization behavior can be tailored into molecules by changing the length and nature of the linkages between the curved carbon subunits. This gives rise to new properties and interesting applications in the resulting complex curved carbon-rich compounds. Due to the well-developed synthetic preparation of corannulene (C_{20}H_{10}), it is frequently incorporated into the design of such molecules. Corannulene has been incorporated into molecules structurally intended for host-guest and supramolecular chemistry. Examples of bowls bound through carbon-carbon single bond tethers include bicorannulenyl (C_{40}H_{18}, 4) and 1,8-dicorannulenyloctane (C_{48}H_{34}) (Figure 3.1). Sumanene (C_{21}H_{12}) has also been used in such work. Recently Hirao and co-workers linked sumanene bowls to produce bisumanenyl (C_{42}H_{22}), which exhibits isomerism similar to bicorannulenyl due to bowl-to-bowl inversions in the directly joined bowl-shaped fragments (Figure 3.1).

![Figure 3.1](image)

**Figure 3.1** Bicorannulenyl (C_{40}H_{18}, 4) (left), 1,8-dicorannulenyloctane (C_{48}H_{34}) (center), and bisumanenyl (C_{42}H_{22}) (right).
The buckycatcher (C\textsubscript{60}H\textsubscript{28}), which has corannulene pincers and a tetrabenzocyclooctatetraene tether, allows the molecule to become a remarkable molecular receptor. This molecule shows unique molecular recognition towards fullerene binding based on convex-concave $\pi$-$\pi$ stacking interactions\textsuperscript{5,7}.

![Buckycatcher (C\textsubscript{60}H\textsubscript{28}).](image)

**Figure 3.2** Buckycatcher (C\textsubscript{60}H\textsubscript{28}).

The above biaryl derivatives possess two open concave $\pi$-carbon faces that are sterically available for binding, making them exceptional ligands for further investigation (Figures 3.1 and 3.2). The chemistry of oligocorannulenes is predicted to range from multiplication of the properties of corannulene to novel phenomena which emerge from the interaction between the corannulene moieties\textsuperscript{1d,8}.

### 3.2 Bicorannulenyl: Prior Solution and Solid State Studies

#### 3.2.1 Synthesis of Bicorannulenyl

In 1996 Cheng \textit{et al.} synthesized bicorannulenyl from monobromocorannulene (C\textsubscript{20}H\textsubscript{9}Br) and characterized it by $^1$H NMR spectroscopy\textsuperscript{9,11}. Substituted corannulenes were first observed during the flash vacuum pyrolysis studies of Scott \textit{et al.} in low yields (30\%) with variable reproducibility\textsuperscript{9}. The solution synthesis of bromocorannulene was established by Cheng, by
brominating corannulene with elemental bromine and using iodide as a catalyst.\textsuperscript{9} Siegel \textit{et al.} modified this synthesis by using iron (III) trichloride (FeCl\textsubscript{3}) as the catalyst.\textsuperscript{10} Disadvantages to both procedures were mixture of products, including unreacted corannulene, mono-, di-, and tri-bromocorannulene, which is troublesome due to the fact that these products were inseparable by chromatography. Optimization of this process allowed for a high yield (95\%) synthesis of bromocorannulene by reacting 2.1 eq. of iodine monobromide (IBr) in dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}) at room temperature for 16 hours (Scheme 3.1).\textsuperscript{11}

\textbf{Scheme 3.1:} Synthesis of bromocorannulene.

\begin{center}
\includegraphics[width=0.5\textwidth]{Scheme3.png}
\end{center}

Twelve years after the initial synthesis of monobromocorannulene, Eisenberg \textit{et al.} reported the synthesis of bico-rannulenyl using monobromocorannulene as the precursor and utilizing a palladium catalyzed (Ullmann-type) homocoupling reaction.\textsuperscript{10,13,12} The homocoupling reaction required high temperature and long reaction time with the disadvantage that significant amounts of monobromocorannulene and corannulene were recovered along with the desired product. In 2011, Quimby \textit{et al.} improved upon the metal-catalyzed homocoupling by introducing the use of Ni(0), which reduced the reaction time to 6 hours and produced bico-rannulenyl in high yield (95\%).\textsuperscript{10} The bis-(1,5-cyclooctadiene)-nickel(0) (C\textsubscript{16}H\textsubscript{24}Ni) catalyst used has the disadvantage of being easily oxidized, leading to reduced yields and failed reactions. Moreover, the catalyst is light-, heat-, moisture-, and air-sensitive. The decomposition of the bis-(1,5-
cyclooctadiene)-nickel(0) catalyst can be avoided with the use of co-reagents like 1,5-cyclooctadiene (C₈H₁₂, COD) and 2,2-bipyridine (C₁₀H₈N₂).¹⁸

### 3.2.2. Bicorannulenyl Stereochemistry: Solution Studies

Bicorannulenyl is composed of two corannulene bowls tethered through a covalent bond (Figure 3.1, left).⁸,¹³,¹⁴,¹⁵ The rich stereochemistry of bicorannulenyl was elucidated in 2008 by Eisenberg et al., reporting that the compound possesses two degrees of freedom, bowl inversion, and bond rotation.¹⁴ The chirality of the molecule arises from the curvature of each bowl. Overall, four bowl combinations are possible (Figure 3.3) labeled PP, MM, PM and MP which are interconverted by bowl inversions.¹⁴

![Figure 3.3 Four bowl combinations interconverted by bowl inversion.](image)

Due to the rotation around the central bond, a 360° rotation of the molecule results in four stable conformations and four energy barriers. The four stable conformations are S.MM₄₅, R.PP-
The greatest energy barriers for bond rotation are reached when the torsion angles are close to 0° and 180°; these obstructions occur due to steric repulsion of hydrogen atoms. There is also a smaller energy barrier at ±90° due to the loss of π-conjugation when the bicorannulenyl bowls are at right angles to each other. This energy barrier is also observed in biphenyl (C_{12}H_{10}).

Eisenberg et al. combined the two degrees of freedom revealing the dynamic stereochemistry of C_{40}H_{18}, which contains twelve stable conformations proven by density functional theory (DFT) calculations. The energy barrier for breaking the π-conjugation between the units is low, resulting in only three pairs of enantiomers, which can be observed in the $^1$H NMR spectroscopic studies conducted by Eisenberg and coworkers.

### 3.2.3 Solid State Self-Assembly of Bicorannulenyl

Crystals of bicorannulenyl suitable for single crystal X-ray diffraction study were grown by sublimation over 2 weeks at 300 °C in our laboratory. The structural study revealed that bicorannulenyl crystallized in the centrosymmetric space group $\text{Pbc}a$ and contained two diastereomeric forms of the molecule (Figure 3.4). As a result, four of the twelve possible conformations of bicorannulenyl have been structurally characterized. The major isomer (70%) is the S.PP_{38}/R. MM-38 pair of enantiomers, whereas the minor isomer (30%) is the S.PM_{118}/R.MP_{118} enantiomer pair. It is worth mentioning that the solid state packing of bicorannulenyl reveals intermolecular interactions between corannulene subunits. One corannulene bowl is involved in hydrogen bonding forming a network, while the other corannulene subunit forms aligned stacks based on concave-to-convex π-π interactions (Figure 3.4, right). Remarkably, convex-to-convex interactions are also observed in the solid state packing. This interaction is a major motif in the
crystal packing of fullerenes, however it has not been observed in corannulene or other known buckybowls.\textsuperscript{14,18}

![Crystal structure of bicorannulenyl (left) and its intermolecular interactions (right).](image)

**Figure 3.4** Crystal structure of bicorannulenyl (left) and its intermolecular interactions (right).

### 3.2.4 Coordination of Bicorannulenyl

It should be mentioned here that only one coordination complex of bicorannulenyl has been structurally characterized. In 2010, our group reported the synthesis and X-ray diffraction study of $[(\text{Hg}_3)_2\text{C}_{40}\text{H}_{18}]$ (where $\text{Hg}_3$ is $[\text{C}_{18}\text{F}_{12}\text{Hg}_3]$) (at the time the synthesis of bicorannulenyl had not yet been adapted in our lab and the sample was supplied by the group of Prof. L. T. Scott).\textsuperscript{19} The study revealed alternating stacks of $\text{Hg}_3$ and $\text{C}_{40}\text{H}_{18}$, in which the trimercury units were coordinated to the convex surfaces of the bicorannulenyl bowls (Figure 3.5).\textsuperscript{19} As previously discussed, bicorannulenyl has twelve stable conformations; only four conformations have been crystallographically identified in the crystal structure of the neutral molecule.\textsuperscript{14} Remarkably, in $[(\text{C}_{18}\text{F}_{12}\text{Hg}_3)_2\text{C}_{40}\text{H}_{18}]$ only one enantiomer, namely S.MM144, is crystallized. The enantiomer is the first structurally characterized example of bicorannulenyl in which both convex surfaces of the corannulene subunits point in the same direction (Figure 3.5, right).\textsuperscript{19} The observed selectivity of
the achiral [C$_{18}$F$_{12}$H$_{3}$] complex towards a specific enantiomer of bicorannulenyl was quite surprising.

**Figure 3.5** Molecular packing of [(Hg$_3$)$_2$C$_{40}$H$_{18}$] (left) and change in conformation (right).$^{19}$

### 3.2.5 Bicorannulenyl Reduction with Alkali Metals

The reduction of bicorannulenyl with alkali metals was first investigated in solution in 2010 by Eisenberg *et al.*$^{15}$ It was postulated that upon acquisition of additional electrons the large biaryl is converted into a charged overcrowded ethylene (Scheme 3.2).$^{15}$ This transformation is realized by the single bond tethering the corannulene units gaining double-bond character upon formation of the dianion (Scheme 3.2).$^{15}$ The change in bond order in bicorannulenyl dianion is explained by Eisenberg *et al.* with frontier molecular orbital analysis. In the neutral molecule of bicorannulenyl the highest occupied molecular orbital (HOMO) contains an antibonding $\pi$ overlap along the tether. On the other hand, in the bicorannulenyl dianion, the HOMO features a bonding interaction, which contributes to the double-bond character.$^{15}$
Eisenberg and co-workers reduced bicorannulenyl with potassium metal in deuterated tetrahydrofuran (THF-\textit{d}_8) and performed variable temperature $^1$H NMR studies. The diamagnetic dianion was characterized by two sets of absorptions each with one singlet and eight doublets at 190 K.\textsuperscript{12} Along with $^1$H NMR, Eisenberg \textit{et al.} performed $^{13}$C NMR studies and DFT calculations to report the stereodynamics of bicorannulenyl dianion. Thirteen stable conformations, six pairs of enantiomers and a single achiral isomer are found for the bicorannulenyl dianion. Gas-phase calculations predicted three stable diastereomers (PM$_{180}$, S.MM$_{156}$/R.MM-156, and S.PP$_{20}$/R.MM-20).\textsuperscript{12} Due to the two sets of signals observed in the $^1$H NMR spectrum, Eisenberg proposed fast exchange between two stable diastereomeric conformations. The authors also comment that the calculated spectrum of PM$_{180}$ isomer resembles the experimental $^{13}$C NMR chemical shifts of the major isomer. This suggests that PM$_{180}$ is the major isomer in solution. The PM$_{180}$ conformation allows for minimized steric crowding and planarity of the central bond which is favorable for the double bond character of the tether.

Upon further reduction, the $^1$H NMR spectrum at 200 K exhibited a broad signal at $\delta = -$3.7 ppm, indicative of the paratropic corannulene dianion. Even further reduction of C$_{40}$H$_{18}$ to the octaanion has been achieved in solution by reduction with an excess of lithium in THF-\textit{d}_8. Eisenberg \textit{et al.} proposed aggregation of charged stacked bicorannulenyl based on $^1$H and $^7$Li
NMR studies. (Scheme 3.3). This proposed model of the lithium intercalation between the curved carbon decks of bicorannulenyl octaions should be reinvestigated, considering our recent results showing that the structural assignment for parent corannulene based on NMR studies was incorrect. Our work has illustrated that NMR spectroscopy alone does not provide sufficient and reliable information on alkali metal intercalation, especially when such complex systems are considered.

**Scheme 3.3:** Reduction of bicorannulenyl with lithium to the octaion and proposed self-assembly by Eisenberg et al.

The octaion exhibits complex $^1$H and $^7$Li NMR spectra supporting the proposed highly charged aggregation pattern. The $^1$H NMR spectrum of the bicorannulenyl octaion at 210 K reveals over 30 peaks which are significantly broadened when compared to the 9 peaks observed in the $^1$H NMR spectrum of neutral bicorannulenyl. Correspondingly, the $^7$Li NMR spectrum of C$_{40}$H$_{18}$$^-$ at 190 K demonstrates 10 separate peaks in the high-field region (–10 to –14 ppm). This shift is characteristic of lithium ions sandwiched between the charged polyarenes. The $^7$Li NMR
spectrum of the bicorannulenyl octaanion is complex in comparison to the single peak observed in the $^7$Li NMR spectrum of the corannulene tetraanion.\textsuperscript{8}

Although the anions of bicorannulenyl have been observed in solution, no investigations concerning their solid state structures and aggregation have been reported. Structural characterization of the reduced forms of bicorannulenyl will reveal if the tethered corannulene units have similar metal binding modes and coordination environments as the parent corannulene. X-ray diffraction studies of the products containing the C$_{40}$H$_{182}^{2-}$ dianion will allow for structural evaluation of the central tether to determine if the large biaryl is indeed converted to an overcrowded ethylene upon acquisition of two electrons, as proposed by solution studies. Moreover, the originally proposed 4 Li-model should also be revisited in this case to observe if the newly revealed encapsulation pattern discovered by our group for tetrareduced corannulene applies to the aggregation of bicorannulenyl octaanion with lithium ions.\textsuperscript{20} Although solution spectroscopy provides vital information for understanding of ion intercalation patterns, it does not always provide an accurate structural description. Thus, we set out to target the isolation of the anionic products of bicorannulenyl in single crystalline form with various alkali metals to allow for structural investigation of the resulting products using single crystal X-ray diffraction.

### 3.3 Controlled Reduction of Bicorannulenyl with Lithium and Cesium Metals

Although one coordination complex of bicorannulenyl has been structurally characterized,\textsuperscript{19} its reduction chemistry has only been studied \textit{in situ} in solution using NMR spectroscopy.\textsuperscript{8,14,15} However, no control over reduction reactions was achieved and multiple products often co-existed in solution. Thus, we had to develop stepwise preparation and crystallization approaches, focusing on the isolation of the target products in pure crystalline form.
The isolation of the solid state products containing bicoannulenyl anions has never been accomplished. Therefore, we set out to synthesize bicoannulenyl, purify and reduce it with alkali metals in order to isolate the first carbanions of bicoannulenyl in the solid state by using the break-and-seal method.21

We have adapted the synthesis of C_{40}H_{18} introduced by Quimby et al.\textsuperscript{10,12} in our laboratory. We found that bicoannulenyl could be produced in good yield; however, additional peaks were observed by \textsuperscript{1}H NMR in the 1-2 ppm region. These extra peaks coincided with an oily unidentified byproduct we were obtaining that hampered our reduction reactions. It should be mentioned, this byproduct was present even after sublimation/deposition procedures, used as a purification step. In order to obtain pure crystalline bicoannulenyl, we varied the co-reagents and found that using minimal amounts of 1,5-cyclooctadiene (COD) (0.4 equivalents with respect to monobromocorannulene, Scheme 3.4) resulted in bicoannulenyl suitable for gas-phase sublimation. We found that the purest form of bicoannulenyl is isolated by sublimation of the above product at 300 °C for 5 days in 55% yield.

\textbf{Scheme 3.4:} Metal-catalyzed homocoupling synthesis of bicoannulenyl.

Due to the extreme sensitivity to moisture and air of the bicoannulenyl anions all manipulations were carried out using break-and-seal methods and glove-box techniques under an atmosphere of high-purity argon.\textsuperscript{21} The O-donor solvent, tetrahydrofuran (THF), was dried over
Na/benzophenone and distilled prior to use. Crown ether (18-crown-6) was used in this work as received. We monitored the reduction reactions using literature data. Eisenberg et al. reported vivid color changes in the reduction of bicorannulenyl to dianion (purple), tetraanion (purple), and further reduction to the octaanion (brown) in the presence of excess lithium metal (Scheme 3.5).42,43,44

**Scheme 3.5**: Reduction of bicorannulenyl by lithium.

We selected lithium and cesium for this study, as these two alkali metals show distinctly different binding preferences toward corannulene anions.22,23 While lithium ions prefer to form solvent-separated ion pairs (SSIPs) (Scheme 3.6, left) with corannulene mono- and dianion,22 cesium exhibits a unique concave binding in the contact-ion pair (CIP) complex with the monoreduced bowl (Scheme 3.6, right).23

**Scheme 3.6**: Preferred metal binding of lithium (left) and cesium (right) to corannulene monoaion.22,23
If the trend persists for the biaryl comprised of two tethered corannulene units, the resulting products should provide us with an interesting pair for structural comparison: a “naked” dianion vs. one having both bowls occupied by large cesium ions.

### 3.3.1 Bicorannulenyl Dianion

#### 3.3.1.1 Lithium Salt: [Li⁺(THF)₄]₂[C₄₀H₁₈₂⁻]

In our work, crystals of bicorannulenyl were dissolved in THF in the presence of metallic lithium (2.5 eq.), the mixture was stirred at room temperature for several hours resulting in the intense purple solution characteristic of dianion, C₄₀H₁₈²⁻ (Scheme 3.7).

**Scheme 3.7:** Reduction of bicorannulenyl with lithium to the dianion state.

The first bicorannulenyl dianion with lithium counterions was obtained as dark blocks, in high yield from the above THF solution by slow diffusion of hexanes. According to an X-ray diffraction study of the resulting crystals, the product crystallizes in the monoclinic P2₁/n space group. The asymmetric unit contains one half of the bicorannulenyl dianion, as the central bond between the corannulene units resides on an inversion center. Also in the unit cell there is one lithium counterion which is solvated by four THF molecules. The overall molecular formula is [Li⁺(THF)₄]₂[C₄₀H₁₈²⁻] (5). The structural analysis reveals the presence of a solvent-separated ion
pair (SSIP) comprised of the $\text{C}_{40}\text{H}_{18}^{2-}$ anion and two THF-encapsulated $\text{[Li}^{+}\text{(THF)}_{4}]$ cations (Figure 3.6,left).\textsuperscript{24}

**Figure 3.6** Molecular structure (left) and space-filling depiction of solid state packing (right) of $\text{[Li}^{+}\text{(THF)}_{4}]_{2}\text{[C}_{40}\text{H}_{18}^{2-}]$ (5).

In the solid state structure, both convex and concave faces of the “naked” dianion, $\text{C}_{40}\text{H}_{18}^{2-}$, are involved in weak intermolecular interactions with hydrogen atoms of the $\text{[Li}^{+}\text{(THF)}_{4}]$ moieties with the shortest $\text{C}−\text{H}⋯\pi$ separations measured at 2.904 Å and 2.628 Å, respectively (Figure 3.8, right). In the cationic parts, the $\text{Li}^{+}$ ions are bound to four THF molecules with the $\text{Li}⋯\text{O}$ bond distances (1.916(4)−1.959(4) Å) being similar to those observed previously.\textsuperscript{20,22}

It should also be mentioned here that due to the flexibility around the central tether the corannulene cores of the bicorannulenyl dianion are disordered over two orientations in 5 (Figure 3.7). This disorder was modelled with a 0.65: 0.35 ratio. The geometrical parameters reported for the dianion are average values calculated based on the two orientations (see above).
3.3.2.1 Cesium Salt: [Cs⁺(18-crown-6)]₂[C₄₀H₁₈²⁻]

After isolation of the first solvent-separated product of bicorannulenyl dianion, we turned to studying the reduction of bicorannulenyl with the heaviest Group I metal, cesium. The latter was selected due to its large radius and observed preference in endo binding to the corannulene anions.23 After many attempts, the synthetic approach to the isolation of the cesium salt of bicorannulenyl dianion has been developed. Specifically, crystals of bicorannulenyl and 18-crown-6 (2.1 eq.) were dissolved in THF and stirred for 2 hours to afford a pale yellow solution. The solution was brought in contact with cesium metal (2.1 eq.) and the mixture was stirred for an additional 2 hours at room temperature resulting in an intense purple solution characteristic of the dianion, C₄₀H₁₈²⁻ (Scheme 3.8).

![Figure 3.7 Disorder of the corannulene cores in 5.](image)
Scheme 3.8: Reduction of bicorannulenyl with cesium to the dianion state.

The first bicorannulenyl dianion with cesium counterions was obtained as dark blocks from the above THF solution by slow diffusion of hexanes. According to an X-ray diffraction study of the resulting crystals, the product crystallized in the triclinic $P\bar{1}$ space group. The asymmetric unit contains two halves of two bicorannulenyl dianions, as the central bond between the corannulene units resides on an inversion center in both cases. Each half of the bicorannulenyl dianion is coordinated to a structurally independent cesium cation which is also bound to an 18-crown-6 ether molecule. The molecular formula for the isolated product is $[\text{Cs}^+ (18\text{-crown-6})]_2 [\text{C}_{40}\text{H}_{18}^{2-}]$ \((6)\). Our study revealed the formation of a contact-ion pair (CIP) composed of two $[\text{Cs}^+ (18\text{-crown-6})]$ cations bound to the $\text{C}_{40}\text{H}_{18}^{2-}$ dianion (Figure 3.8, left). Specifically, each corannulene bowl in $\text{C}_{40}\text{H}_{18}^{2-}$ has an endo bound Cs$^+$ ion capped with 18-crown-6 ether.

Figure 3.8 Molecular structure (left) and space-filling depiction (right) of $[\text{Cs}^+ (18\text{-crown-6})]_2 [\text{C}_{40}\text{H}_{18}^{2-}]$ \((6)\).
The cesium ions are bound to the concave faces of $\text{C}_{40}\text{H}_{18}^{2-}$ with the shortest $\text{Cs} \cdots \text{C}$ contacts observed with the two benzene rings adjacent to the central $\text{C} = \text{C}$ bond ($\text{Cs} \cdots \text{C}_{6(\text{centroid})} \ 3.198–3.493 \ \text{Å}$) and the central cyclopentadienyl ring ($\text{Cs} \cdots \text{C}_{5(\text{centroid})} \ 3.425–3.533 \ \text{Å}$). Concave metal binding to corannulene has been observed in several cesium salts formed by the monoanion, $[\text{Cs}^+ (18\text{-crown-6})][\text{C}_{20}\text{H}_{10}^-]^{23}$, dianion, $[\{\text{Cs}(\text{dicyclo-18-crown-6})(\text{C}_{20}\text{H}_{10}^2-\})^-\{\text{Cs}_2(\text{dicyclo-18-crown-6})\}^{2+}]^{25}$ and trianion, $[\text{Cs}^+/\text{(C}_{20}\text{H}_{10}^3-\})/4\text{Cs}^+/(\text{C}_{20}\text{H}_{10}^3-\})/\text{Cs}^+]^{26}$.

Owing to its large size, cesium does not fit inside the 18-crown-6 ring and is pulled out towards the bicorannulenyl dianion endo surface. The $\text{Cs} \cdots \text{O}$ bond distances (3.048(4)–3.284(4) Å) are close to those previously reported for $[\text{Cs}(18\text{-crown-6})]^+$ containing salts with corannulene monoanion.$^{23}$ In contrast to the symmetrical $\eta^5$-endo hub coordination ($\text{Cs} \cdots \text{C} \ 3.424–3.573$, $\text{Cs} \cdots \text{C}_{5(\text{centroid})} \ 3.285 \ \text{Å}$) found in the cesium salt with corannulene monoanion, the $\text{Cs}^+$ ions are shifted toward the central tether in 6 (Scheme 3.9, right).

**Scheme 3.9:** Cesium ion binding in $[\text{Cs}^+(18\text{-crown-6})][\text{C}_{20}\text{H}_{10}^-]^2$ (left) and 6 (right).

The shortest $\text{Cs} \cdots \text{C}$ contacts in 6 are observed with the two benzene rings adjacent to the double bond ($\text{Cs} \cdots \text{C}_{6(\text{centroid})} \ 3.304–3.425 \ \text{Å}$) and with the central five-membered ring ($\text{Cs} \cdots \text{C}_{5(\text{centroid})} \ 3.474 \ \text{Å}$). Additional $\text{Cs} \cdots \text{C}$ contacts with flank carbon atoms of the corannulene bowl are in the range of 3.616–3.899 Å.
It should be mentioned here that the corannulene cores of the bicorannulenyl dianion are disordered over two orientations in 6 (Figure 3.9). The geometrical parameters reported for the dianion are given as average values (see above). In addition, 6 contains solvent accessible voids within the crystal structure filled by disordered solvent molecules. The bulk solvent correction of the observed intensities was employed by using the SQUEEZE protocol.27 The volume of the void was 1022 Å with an electron count of 317 electrons per cell. These data are in agreement with four disordered THF molecules filling the void.24 The four THF molecules were removed by using the SQUEEZE protocol.

![Figure 3.9 Disorder of the corannulene cores in 6.](image)

### 3.4 Charged Overcrowded Ethylene

The X-ray diffraction study of the lithium (5) and cesium (6) salts of bicorannulenyl dianion confirms that upon acquisition of two electrons, the large biaryl is converted into a charged overcrowded ethylene, as predicted by Eisenberg et al.15 The central bond between the corannulene units has substantial double-bond character and the rim carbon bonds alternate between single and double bonds.
The X-ray diffraction study of 5 and 6 revealed that only one isomer is present in the solid state: the achiral PM180 isomer. The central bond between the corannulene units is substantially shortened in the Li⁺ and Cs⁺ salt of bicorannulenyldianion (1.42 (2) and 1.43 (4) Å, respectively) in comparison with a neutral bicorannulenyldianion (1.483(7) Å, Table 3.1), confirming a substantial double bond character in both products. The latter is supported by DFT calculations that show almost no difference between the Li and Cs products (the calculated bond orders are 1.40 and 1.39, respectively). For comparison, the bond order for the same bond in the “naked” C₄₀H₁₈²⁻ anion free of any interactions is equal to 1.39 calculated at the same level of theory.

The bond length distribution along the rim consists of alternating double and single C–C bonds and there is observed equalization of hub C–C bonds (Table 3.1). Despite different metal binding modes there is no substantial difference in geometric parameters of dianion in [Li⁺(THF)₄][C₄₀H₁₈²⁻] and [Cs⁺(18-crown-6)][C₄₀H₁₈²⁻].24
Table 3.1 Experimental values (averaged) of central bond length (Å), twist angle (°), along with rim and hub C–C bond lengths (Å) for 5 and 6, compared to neutral bicosannulenyl (4).14

<table>
<thead>
<tr>
<th></th>
<th>C_{40}H_{18}</th>
<th>[Li^+(THF)]<em>2[C</em>{40}H_{18}^{2-}]</th>
<th>[Cs^+(18-crown-6)]<em>2[C</em>{40}H_{18}^{2-}]</th>
</tr>
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<tr>
<td>Length</td>
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<td>1.43(4)</td>
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<td>Twist angle</td>
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<td>180</td>
<td>180</td>
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<tr>
<td>Rim</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>1.381(9)</td>
<td>1.479(15)</td>
<td>1.481(17)</td>
</tr>
<tr>
<td>b</td>
<td>1.344(10)</td>
<td>1.380(13)</td>
<td>1.377(13)</td>
</tr>
<tr>
<td>c</td>
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<td>1.401(15)</td>
<td>1.421(16)</td>
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<td>1.357(15)</td>
<td>1.362(15)</td>
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<td>e</td>
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<td>1.397(15)</td>
</tr>
<tr>
<td>Hub</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>1.456(9)</td>
<td>1.420(7)</td>
<td>1.424(10)</td>
</tr>
<tr>
<td>g</td>
<td>1.451(10)</td>
<td>1.411(7)</td>
<td>1.403(10)</td>
</tr>
<tr>
<td>h</td>
<td>1.475(10)</td>
<td>1.399(7)</td>
<td>1.406(10)</td>
</tr>
<tr>
<td>i</td>
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<td>1.416(7)</td>
<td>1.421(11)</td>
</tr>
<tr>
<td>j</td>
<td>1.448(9)</td>
<td>1.409(7)</td>
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</tr>
<tr>
<td>Bowl depth</td>
<td>0.85</td>
<td>0.88</td>
<td>0.89</td>
</tr>
</tbody>
</table>

It can be noted here that the PM\textsuperscript{180} conformation should be favorable for the double bond character of the tether, as it minimizes steric crowding around the central bond. The bond length distribution along the rim of the dianion consists of alternating double and single C–C bonds (Table 3.1). The hub bond length distribution is similar to that found in the monoanion of corannulene.\textsuperscript{23} Notably, despite different metal binding modes there is no substantial difference in geometric parameters of C\textsubscript{40}H\textsubscript{18}\textsuperscript{2–} in 5 and 6. Plus, the depth of each bowl in 5 and 6 (0.88 and
0.89, respectively) is not significantly different from neutral bicorannulenyl or the corannulene monoanion.21,23

3.5 Endo Coordination of Cesium to Corannulene Bowl

The concave binding of the Cs⁺ ion to the endo-surface of \( C_{40}H_{18}^{2-} \) is shifted, in contrast to the symmetric \( \eta^5 \)-endo hub coordination in the \([Cs^+(18\text{-crown-6})][C_{20}H_{10}^-]\) complex23 (Figure 3.10, right). In the above corannulene complex, the cesium cation is perfectly “dished-up”, whereas with bicorannulenyl dianion the asymmetrical double concave binding is observed (Figure 3.10, left).

**Figure 3.10** Space-filling depiction of 6 (left) and \([Cs^+(18\text{-crown-6})][C_{20}H_{10}^-]\)23(right), 18-crown-6 is omitted for clarity.

The asymmetrical endo binding of cesium cations to bicorannulenyl dianion in 6 prompted us to calculate the charge distribution in the \( C_{40}H_{18}^{2-} \) dianion. The molecular electrostatic potentials map (MEP) is often used for the visualization of the charge distribution over the \( \pi \)-surface. From the molecular electrostatic potentials map for bicorannulenyl dianion (Figure 3.11) it is observed that the electron density is not symmetrically distributed over the surface and is
mostly located along the double bond tether and the surrounding carbon atoms of the concave face. Since the interactions between the cesium ions and the bicoannulenylenyl dianion surface are predominately electrostatic, such a charge distribution leads to the observed asymmetrical coordination.

**Figure 3.11** Molecular electrostatic potential map of bicoannulenylenyl dianion, C$_{40}$H$_{182}^{2-}$.

Calculations of the model [Cs$^+$]$_2$[C$_{40}$H$_{182}^{2-}$] complex also showed a similar shift of the naked Cs$^+$ ions towards the tether. However, it is less pronounced than that observed experimentally in 6 (Cs···C$_5$(centroid) 2.979 Å vs. 3.474 Å) (Table 3.2), indicating possible involvement of the coordinated 18-crown-6 ether. The effect of crown ethers on geometry of products has been seen before in our work.$^{28}$ Reported earlier in this dissertation (see Chapter 2), intermolecular interactions between the crown moieties and coronene monoanions were found responsible for an aligned and compact solid state packing and new coordination mode of the radical-anion of coronene.$^{27}$

For the next step, calculations of a larger system, [Cs$^+$$(18$-crown-6)$]$_2$[C$_{40}$H$_{182}^{2-}$], have been carried out. The expanded model was found to be in a better agreement with the experimental structure, as both show a close shift in cesium binding towards the tether (distance from the hub is 3.574 Å (calc) vs. 3.474 Å (exp) (Table 3.2)). The calculated intermolecular C-H····π contacts
between the [Cs⁺(18-crown-6)] moieties and the charged bicorannulenyl range from 2.918 Å to 3.174 Å. Thus, the exact positioning of the Cs⁺ cation inside the bowl is determined by the interplay of the electrostatic forces with the dianionic bicorannulenyl core and the above intermolecular interactions.

**Table 3.2** Selected Cs···C distances (Å) in 6 compared to calculated [Cs⁺]₂[C₄₀H₁₈₂⁻] and [Cs⁺(18-crown-6)]₂[C₄₀H₁₈²⁻].

<table>
<thead>
<tr>
<th>Cs···C</th>
<th>[Cs⁺]₂[C₄₀H₁₈²⁻]</th>
<th>[Cs⁺(18-crown-6)]₂[C₄₀H₁₈²⁻]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hub</td>
<td>3.474</td>
<td>2.979</td>
</tr>
<tr>
<td>Ring A</td>
<td>3.304</td>
<td>3.065</td>
</tr>
<tr>
<td>Ring B</td>
<td>3.626</td>
<td>3.174</td>
</tr>
<tr>
<td>Ring E</td>
<td>3.425</td>
<td>3.112</td>
</tr>
<tr>
<td>C₆centroid</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For comparison, we have also modeled the lithium-based SSIP system 5. Geometrical parameters obtained for this model are in reasonable agreement with the experimental values. As in the structure of 6, the shift of [Li(THF)₄]⁺ ions towards the dianion tether was observed. Since the isolated model was considered in calculations, such shift cannot be attributed to the influence of crystal packing. It supports the previous conclusion about localization of the negative charge on the central carbon-carbon bond and its influence on the positioning of alkali metal counterions.
Interestingly, the impact of positively charged ions on the electronic structure of the dianionic biconannulene core was found most pronounced in the case of 6. Polarization of the hydrocarbon core in 6 can be illustrated by atomic charges located on the symmetrically unique tether C-atom and closely lying hub atoms of the g-bond (-0.11, -0.23 and -0.12 for 2 and -0.09, -0.01, and -0.11 for free [C_{40}H_{18}^2\]^2, respectively) and is graphically evidenced from the MEP distribution (Figure 3.12).

![Figure 3.12](image)

Figure 3.12 Molecular electrostatic potential map of [Cs^+(18-crown-6)]_2[C_{40}H_{18}^2]^2.

However, the nature of bonding between two bowls remains essentially the same in all computed systems. In addition to the standard single σ-bond, it contains a substantial π-contribution. In terms of natural bond orbital (NBO) analysis the first part is described as the result of coupling of two hybrid sp^{1.75}-orbitals with occupancy of the corresponding bonding NBO of ~1.97e, whereas the π-contribution comes from interaction of two pure p-orbitals of aimed carbon atoms with the NBO occupancy of ~1.75e. Importantly, the corresponding π*-orbital has notable occupancy equal to ~0.45e, while the occupancy of σ* NBO was found to be ~0.02e. These findings suggest the description of the tether bond as of σ-type with substantial π-component rather than a classical double bond. This description applies to all calculated systems, ranging from free [C_{40}H_{18}^2\]^2 to [Cs^+]_2[C_{40}H_{18}^2\]^2, [Cs^+(18-crown-6)]_2[C_{40}H_{18}^2\]^2, and [Li^+(THF)_4]_2[C_{40}H_{18}^2\]^2.
3.6 Solution Studies of Bicorannulenyldianions

In the UV-vis spectra, the maxima of the absorption band of the contact-ion pair in $[\text{Cs}^+ (18\text{-}\text{crown-6})]_2[\text{C}_{40}\text{H}_{18}^2^-]$ (935 nm, THF) is shifted compared to the solvent-separated ion pair in $[\text{Li}^+ (\text{THF})_4]_2[\text{C}_{40}\text{H}_{18}^2^-]$ (931 nm, THF) (Figure 3.13). It should be noted here that the maximum of the most intense band in the UV-vis spectrum of corannulene monoanion is 648 nm in $[\text{Li}(\text{THF})_n(\text{C}_{20}\text{H}_{10})]$ and 652 nm in $[\text{Cs}(18\text{-}\text{crown-6})(\text{C}_{20}\text{H}_{10})]$.\textsuperscript{29}

Figure 3.13 UV-vis spectra of $[\text{Cs}^+ (18\text{-}\text{crown-6})]_2[\text{C}_{40}\text{H}_{18}^2^-]$ (green) and $[\text{Li}^+ (\text{THF})_4]_2[\text{C}_{40}\text{H}_{18}^2^-]$ (purple).
3.7 Conclusions

In conclusion, the first X-ray structural characterization of bicorannulenyl dianion has been accomplished for two alkali metal salts revealing two different binding modes, namely the “naked” form in the solvent-separated ion pair with small lithium ions vs. the unique double concave metal coordination in the cesium product (Scheme 3.10).

Scheme 3.10: Prefered metal binding of cesium (left) and lithium (right) to dianion of

In both cases, the central carbon-carbon bond between the corannulene units is shortened in comparison with neutral bicorannulenyl, as confirmed by X-ray crystallographic investigation. Notably, only the achiral PM180 isomer is found in the solid state products. Theoretical analysis of these systems revealed that polarization of dianionic bicorannulenyl core is more pronounced in the case of $[\text{Cs}^+(18\text{-crown-6})_2\text{C}_{40}\text{H}_{18}^2]$, while the nature of bonding between two bowls remained essentially the same through the series.
3.8 Experimental Details

Materials and Methods. All manipulations were carried out using break-and-seal and glove-box techniques under an atmosphere of argon.\textsuperscript{21} Solvents (THF and hexanes) were dried over Na/benzophenone and distilled prior to use. THF-\textit{d}_8 was dried over sodium-potassium alloy and vacuum-transferred. Lithium and cesium metals were purchased from Strem Chemicals. Bicorannulenyl was synthesized in our lab following the procedure reported below and purified by sublimation at 300 °C before use. NMR spectra were measured on a Bruker AC-400 spectrometer at 400 MHz for \textit{^1}H, 100.6 MHz for \textit{^13}C and 155.5 MHz for \textit{^7}Li. The NMR spectra were referenced to the solvent signals for \textit{^1}H and 0.1M LiCl in THF-\textit{d}_8 for \textit{^7}Li. The UV-vis spectra were recorded on a Thermo Scientific Evolution 300BB spectrometer.

Crystal Structure Determinations and Refinement of 5 and 6

Data collections were performed on a Bruker SMART\textsuperscript{30} APEX CCD-based X-ray diffractometer with graphite-monochromated Mo-K\textalpha{} radiation (\(\lambda{} = 0.71073\ \text{Å}\)) at \(T = 100(2)\ \text{K}\). Data were corrected for absorption effects using the empirical method SADABS.\textsuperscript{29} The structures were solved by direct methods and refined using the Bruker SHELXTL (Version 6.14) software package.\textsuperscript{31} All atoms were refined with anisotropic parameters. Hydrogen atoms were included at idealized positions using the riding model. The corannulene cores were found to be disordered over two orientations in 5 and 6 (Figures 3.7 and 3.9, respectively). Crystal of 6 contains solvent accessible voids with the disordered solvent. The bulk solvent correction of the observed intensities was employed by using the SQUEEZE protocol. The program accounted for a void with a volume of 1022 \text{Å}^4 and an electron count of 317 electrons per cell. This is in agreement with what would be expected for four disordered THF molecules.
**Monobromocorannulene Synthesis**

In a 25 mL round bottom Schlenk flask under a nitrogen atmosphere was added 100 mg corannulene (0.40 mmol), which was dissolved in 5 mL dry CH₂Cl₂. Under agitation was added 0.88 mL (0.88 mmol) of IBr 1.0 M solution in CH₂Cl₂. The resulting purple solution was stirred at room temperature for 16 hours. GC-MS was used to monitor the reaction progress retention times, corannulene 12.80 minutes, monobromocorannulene 16.80 minutes. To push the reaction forward, 0.5 mL of IBr 1.0 M solution in CH₂Cl₂ was added to the reaction mixed. The reaction was continuously monitored by GC-MS every two hours until all corannulene was consumed. Upon completion of the reaction, the reaction mixture was diluted with 100 mL CH₂Cl₂. The reaction mixture was washed once with 10% NaHSO₃, twice with water and once with saturated sodium chloride solution. The resulting organic layer was dried over anhydrous calcium sulfate or sodium sulfate, filtered and concentrated to dryness under reduced pressure. The crude product was purified via silica gel column chromatography using cyclohexane as eluent to give 125 mg of monobromocorannulene as a pale yellow solid (95% yield). ¹H NMR (400 MHz, CDCl₃): 8.03 (s,1H), 7.93(d,1H), 7.87(d,1H), 7.78-7.82 (m,5H), 7.71(d,1H)

**Bicorannulenyl Synthesis (4)**

In a 10 mL Schlenk flask equipped with a stir bar was added 115 mg bis-(1,5-cyclooctadiene)nickel(0) (0.42 mmol), 59 mg bipyridine (0.38 mmol), 0.5 mL N,N-dimethylformamide, and 15 µL 1,5-cyclooctadiene (0.12 mmol). The purple solution was stirred for 5 minutes. Then 100 mg monobromocorannulene (0.31 mmol) was added, causing the solution to quickly change to red. The reaction flask was heated in a 60 °C oil bath causing the solution to darken; the reaction was heated for 6 hours. Upon cooling the reaction mixture was filtered through a silica plug and washed with dichloromethane. The organic layer was washed with 40 mL of 0.6
M FeCl₃ in three portions followed by washing with deionized water and brine. The organic layer was dried over calcium sulfate or sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was absorbed onto silica gel and purified by column chromatography with hexanes as the eluent, then 1:1 hexanes: dichloromethane to give 70 mg (95%) of bicosorannulenyln as a pale yellow solid. ¹H NMR (400 MHz, CDC1₃): 8.17 (s,2H), 7.89(d,2H), 7.87(d,2H), 7.86 (d,2H), 7.87 (d,2H), 7.82 (d,2H), 7.79 (d,2H), 7.73 (d,2H), 7.65 (d,2H).

**Synthesis and Crystal Growth of [Li⁺(THF)₄][C₄₀H₁₈²⁻] (5)**

THF (2 mL) was added to a flask containing lithium metal (0.14 mg, 0.02 mmol, 2.5 eq.) and crystals of bicosorannulenyln (4 mg, 0.008 mmol). The mixture was stirred for 6 hours at room temperature and then filtered to afford a purple solution which was layered with hexanes (2 mL) and kept at 10 °C. Dark purple blocks of 5 were collected in 48 h. The crystals were washed several times with hexanes and dried. Yield: 5.2 mg, 60%. UV-vis (THF, nm): λ_max = 931; ⁷Li NMR (155.5 MHz, THF-d₈, −60 °C, ppm): δ = 2.02; ¹H NMR (400 MHz, THF-d₈, −80 °C, ppm): δ = 4.33(2H), 5.41(2H), 5.53 (2H), 5.82 (2H), 5.93 (2H), 6.39 (2H), 6.64 (2H), 6.76 (2H), 7.46 (2H).

**Crystallographic Data for 5**

Empirical formula:C₇₂H₈₂Li₂O₈, Mr = 1089.26, monoclinic, a = 12.3460(17) Å, b = 9.6936(14) Å, c =24.074(3) Å, α = 90°, β = 94.461(2)°, γ = 90°, V = 2872.3(7) Å³, P2₁/n, Z = 2, ρ_calcd = 1.259 g/cm³, μ = 0.080 mm⁻¹, T = 100(2) K, λ = 0.71073 Å, 24148 measured intensities (6.80° ≤ 2θ ≤ 113.08°), 6707 unique intensities R_int = 0.0286, R₁ = 0.0661, with I ≥ 2σ(I), wR₂ = 0.1236 (6707), refinement of 580 parameters. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre, the CCDC identifier is 991234.
Variable-temperature $^7\text{Li}$ NMR spectra of 5

Synthesis and Crystal Growth of $[\text{Cs}^+(18\text{-crown}-6)]_2[\text{C}_{40}\text{H}_{182}^-]$ (6)

THF (5 mL) was added to a flask containing crystals of bicroannulenyli (4 mg, 0.008 mmol) and 18-crown-6 (4.32 mg, 0.017 mmol, 2.1 eq.). The mixture was sonicated and stirred for ca. 2 hours to produce a pale yellow solution. Cesium metal (2.4 mg, 0.017 mmol, 2.1 eq.) was added to the solution and stirring was continued for another 2 hours. The resulting purple mixture was filtered; the filtrate was layered with hexanes (5 ml) and kept at 10 °C. Dark purple plates of 6 were collected in 70 h. They were washed several times with hexanes and dried in vacuo. Yield: 6.7 mg, 65%. UV-vis (THF, nm): $\lambda_{\text{max}} = 935$; $^1\text{H}$ NMR (400 MHz, THF-$d_8$, −80 °C, ppm): δ = 2.55(2), 4.37 (2H), 4.74(2H), 5.01(18-crown-6), 5.48(2H), 5.64 (2H), 5.82 (2H), 5.96 (2H), 6.09 (2H), 6.42 (2H), 6.66 (2H), 6.80 (2H), 7.01 (2H), 7.17 (2H), 7.29 (2H), 7.46 (2H), 7.631 (2H), 8.49 (2H).
Crystallographic Data for 6

Empirical formula: C₆₄H₆₄Cs₂O₁₂, \( M_r = 1290.97 \), triclinic, \( a = 9.7188(9) \, \text{Å}, \ b = 18.3660(16) \, \text{Å}, \ c = 21.6364(19) \, \text{Å}, \ \alpha = 69.9880(10)^\circ, \ \beta = 86.2130(10)^\circ, \ \gamma = 87.6200(10)^\circ, \ \nu = 3620.2(6) \, \text{Å}^3, \ P-1, \ Z = 2, \ \rho_{\text{calcld}} = 1.184 \, \text{g/cm}^3, \ \mu = 1.057 \, \text{mm}^{-1}, \ T = 100(2) \, \text{K}, \ \lambda = 0.71073 \, \text{Å}, \ 32377 \, \text{measured intensities (}5.04^\circ \leq 2\theta \leq 111.76^\circ\)), 16423 unique intensities \( R_{\text{int}} = 0.0273, \ R_1 = 0.0346, \) with \( I \geq 2\sigma(I)\), \( wR_2 = 0.0823 \) (16423), refinement of 1060 parameters. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre, the CCDC identifier is 991235.

3.9 References


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CHAPTER 4

Successive Single-Electron Charging of Rubrene:

Structural Investigation of Rubrene Anions

4.1 Introduction

Organizing non-planar carbon-rich molecules into supramolecular assemblies is of growing interest due to their extensive applications in materials science in addition to their fundamental importance. The physical properties of these molecules such as magnetism, electronic structure, conductivity, etc. can be transformed by addition of multiple electrons to their \( \pi \)-systems. Subsequently, the properties of supramolecular assemblies formed from charged carbanions with various metal ions are predicted to be different than those of assemblies of neutral carbonaceous materials. However, there are limited reports on structural studies of self-assembling of charged polycyclic hydrocarbons in the literature to date.

Therefore we have selected, rubrene (C\(_{42}\)H\(_{28}\), 7), a commercially available non-planar polyarene for this investigation. Rubrene was synthesized early in the last century and is well known for its excellent electrochemiluminescent properties. Furthermore, rubrene is an organic molecular semiconductor and therefore functions as an effective material for the fabrication of organic field-effect transistors and organic light emitting diodes.

Rubrene has a planar tetracene core and four phenyl rings at the 5-, 6-, 11-, and 12-positions, providing potential multiple sites for metal binding (Figure 4.1, left). Additionally, the tetracene core of the molecule is also known to have sufficient flexibility due to the presence of the flank phenyl rings.

A literature search revealed that in 1996, Bock et al. conducted the first structural determination of the rubrene tetraanion by reducing 7 with excess sodium metal mirror. Isolation
and X-ray diffraction study of the single crystalline product revealed the unprecedented distortion of the rubrene geometry upon acquisition of four electrons (Figure 4.1, right). In $7^{4-}$ there are four sodium ions bound to the tetraanion core, each is also doubly solvated by tetrahydrofuran (THF) molecules. Two of the sodium cations are located above and below the tetracene core while the other two sodium cations are located between the exterior phenyl pincers. The acquisition of four electrons drastically distorts the planar core of 7 resulting in a “chair” conformation of the tetracene framework.

![Image of chemical structure and molecule](image)

**Figure 4.1** Neutral rubrene ($C_{42}H_{28}$, 7) (left) and the reduction product with sodium$^{13}$, $[Na^+(THF)_2]_4[C_{42}H_{28}^{4-}]$ (right). Hydrogen atoms are omitted for clarity.

Although the tetraanion of rubrene had been structurally characterized in its sodium salt, the effects of successive addition of electrons to $C_{42}H_{28}$ had not been yet investigated, nor has the chemical reduction of rubrene with other alkali metals been studied to reveal if larger Group I metals induce additional geometrical distortions and different binding modes. We therefore set out to study the stepwise reduction of rubrene with various alkali metals in solution and to isolate the
products in single crystalline form to investigate the structures and aggregation behavior of the resulting carbanions by X-ray crystallography.

4.2 Controlled Reduction of Rubrene

The reduced rubrene species were generated in a controlled manner by the addition of an appropriate amount of alkali metal to 7 in O-donor coordinating solvents (Scheme 4.1). Due to the extreme sensitivity to moisture and air of all products formed by rubrene anions with various alkali metal counterions all manipulations were carried out using break-and-seal methods and glove-box techniques under an atmosphere of high-purity argon. The donor solvents, tetrahydrofuran (THF) and dimethoxyethane (DME), were dried over Na/benzophenone or sodium potassium alloy, respectively, and distilled prior to use. The single crystals of the rubrene mono-, di- and tetraanions suitable for X-ray diffraction studies were successfully obtained by the slow diffusion of freshly distilled hexanes into the THF or DME solutions of the appropriate product.

Scheme 4.1: Preparation of the rubrene$^n$/nM$^+$ adducts.
4.3 Monoanion

4.3.1 Cesium Salt: $[\text{Cs}^+(\text{THF})][\text{C}_{42}\text{H}_{28}^-] \cdot 0.6 \text{ THF} \cdot 0.2 \text{ C}_6\text{H}_{12}$

The first rubrene monoanion with cesium cation was obtained as dark blocks, in high yield, from the THF solution layered with hexanes.$^{15}$ According to an X-ray diffraction study, the resulting $[\text{Cs}^+(\text{THF})][\text{C}_{42}\text{H}_{28}^-] \cdot 0.6 \text{ THF} \cdot 0.2 \text{ C}_6\text{H}_{12}$ (8·0.6 THF·0.2 C6H12) product crystallizes in the monoclinic $P2_1/n$ space group. The asymmetric unit contains one rubrene monoanion with a bound cesium ion which also coordinates a THF molecule, forming a contact-ion pair (CIP) (Figure 4.2).

Figure 4.2 Side (left) and top (right) views of the asymmetric unit of $[\text{Cs}^+(\text{THF})][\text{C}_{42}\text{H}_{28}^-]$ (8). Hydrogen atoms, non-coordinated THF and hexane molecules are omitted for clarity.

The acquisition of one electron by rubrene results in a twisted tetracene core; the value of the angle $\phi$ at the principal $\text{C}^2\text{C}^1\text{C}^2''\text{C}^1'\text{C}^2'''$ bond is 29.4 (3)$^\circ$ (Figure 4.2, left, Table 4.1) in contrast to 0$^\circ$ in neutral rubrene (Figure 4.1, left). The central $\text{C}^1\text{C}^{1'}$ bond of the tetracene core is marginally shorter (1.453 (4) Å) in comparison to the neutral ligand (1.462 (3) Å). The deflection of the phenyl rings of the $\text{C}_{48}\text{H}_{12}$ core is measured by the angle $\theta$ between the $\text{C}^1\text{C}^2\text{C}^3$ and $\text{C}^7\text{C}^6\text{C}^7'$ planes ranging over 56.9(3)–67.6(4)$^\circ$. These angles are in good agreement with the value of 65$^\circ$
previously calculated from the ESR spectrum.\cite{16} The \(\pi-\pi\) interactions between the neighboring phenyl groups of the rubrene core are preserved in the reduced species as the shortest intramolecular C–C distance between the two slanting phenyl groups is 2.862 (5) Å (Figure 4.2, right), which is close to the separation in neutral rubrene of 2.827 (2) Å (Figure 4.1, left).\cite{17a} The delocalization of the single negative charge results in only slight changes in C–C distances throughout the tetracene moiety (Table 4.1). In 8, significant distortion of the core was revealed when compared to neutral \(\text{C}_{48}\text{H}_{18}\) due to the inherent flexibility of this polyaromatic hydrocarbon.\cite{17}
Table 4.1 Key bond length distances (in Å) and angles (°) for neutral 7 and 7⁻ in 8.

<table>
<thead>
<tr>
<th>Bond</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₁–C')</td>
<td>1.462(3)</td>
<td>1.453(4)</td>
</tr>
<tr>
<td>(C₁–C₂)</td>
<td>1.432(2)</td>
<td>1.414(5)–1.435(5)</td>
</tr>
<tr>
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<td>1.416(4)–1.432(4)</td>
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<td>1.413(5)–1.430(5)</td>
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<td>1.443(5), 1.445(5)</td>
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<tr>
<td>(C₄–C₅)</td>
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<td>1.374(5)–1.381(5)</td>
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<td>1.401(5)</td>
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<tr>
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<td>1.377(5)–1.393(5)</td>
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<tr>
<td>θ</td>
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<td>56.9(3)–67.6(4)</td>
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<tr>
<td>ω</td>
<td>7.2(1)</td>
<td>5.1(3), 6.5(3)</td>
</tr>
</tbody>
</table>

There is strong $\eta^6$-binding of the Cs⁺ ion to the exterior benzene ring of the tetracene core, with Cs⋯C contacts ranging from 3.277(3) to 3.628(3) Å, with the distance to the C₆ centroid, Cs⋯C₆(centroid) measured as 3.237(3) Å (Figure 4.2, left).\(^{18}\)

In the solid state structure, a 1D network arises from the additional $\eta^6$-contact of Cs⁺ with the phenyl ring of the adjacent C₄₈H₁₂⁻ anion with the cesium carbon distances ranging from Cs⋯C 3.504(3) to 3.611(3) Å, (Cs⋯C₆(centroid) 3.282(3) Å) (Figure 4.3).
Figure 4.3 Fragment of a 1D polymeric arrangement of 8. Hydrogen atoms and non-coordinated THF and hexane molecules are omitted for clarity.

The large Cs$^+$ ions in the one dimensional (1D) column additionally interact with the phenyl groups of the neighboring polymeric chain. The corresponding Cs$^+\cdots \eta^3$–C intermolecular contacts (3.436(3)–3.852(3) Å) hold together the two chains into a 1D helix (Figure 4.3). To fill its coordination sphere the cesium ion additionally coordinates one THF molecule; the Cs$^+\cdots$O interatomic distance is close to those observed in related compounds.$^{19}$ The packing of the bulky rubrene anion and cesium counterion in the single crystal of 8 results in the formation of voids that are filled with non-coordinating THF and ½ of a hexane molecule. These non-coordinating solvents are crystallized at the same spatial position; this disorder was modelled with a 6:4 ratio (THF:hexanes).

It should be mentioned here that recently a density functional theory (DFT) study was conducted by Li et al. which investigated the intramolecular intercalation of alkali metals, namely Li, Na and K into rubrene monoanions.$^{20}$ The authors report that, due to the small ionic size of Li
and Na, intercalation between the phenyl groups is favorable and does not significantly deform the rubrene frame. On the other hand, with the larger alkali metal, potassium binding to the rubrene core is favorable and is analogous to our rubrene monoanion with cesium cation.

4.3.2 Solution Studies of Rubrene Monoanion Radical

4.3.2.1 ESR Studies

Crystals of 8 were dissolved in THF to allow for investigation into the structure and coordination behavior of the rubrene monoanion in solution. The ESR spectrum of 8 in solution (Figure 4.4) is identical to the spectrum previously reported;16 no additional hyperfine splitting of the ESR signal is prompted by the Cs⁺ ions present in solution.

![ESR spectrum](image)

**Figure 4.4** ESR spectrum of 8 (THF, 20 °C).

Therefore, it can be assumed that in the THF solution of 8 at 20 °C only solvent-separated ion pairs (SSIPs) are present, due to the agreement of the ESR spectrum of rubrene monoanion prepared by electrochemical or chemical reduction.
4.4 Dianions

4.4.1 Cesium salt: \([\text{Cs}^+]_4[\text{C}_{42}\text{H}_{28}^2^−]_2[\text{Cs}^+(\text{DME})]_2[\text{C}_{42}\text{H}_{28}^2^−]·\text{C}_6\text{H}_{14}\)

The first rubrene dianion with cesium counterions was obtained as dark blocks, in moderate yield, from the DME solution layered with hexanes.\(^{15}\) According to an X-ray diffraction study of the resulting crystals the product crystallizes in the triclinic \(P-1\) space group. The asymmetric unit contains two rubrene dianions: one of those is situated on the face of the unit cell on an inversion center resulting in only half of the dianion being structurally independent, whereas the other one has a full occupancy in the unit cell. There are four crystallographically independent cesium ions in the asymmetric unit, two of which exhibit 50% occupancy in the unit cell. The Cs3 ion is positioned on the corner of the primitive triclinic unit cell, while the Cs4 is positioned on the edge of the unit cell. Therefore, the overall formula of this product containing two types of rubrene dianions, \(9a\) and \(9b\) in a ratio of 2:1, is \([\text{Cs}^+]_4[7^2^−]_2[\text{Cs}^+(\text{DME})]_2[7^2^−]·\text{C}_6\text{H}_{14}\) \((9·\text{C}_6\text{H}_{14})\). The product also has an interstitial hexane molecule; \(½\) of the hexane molecule is present in the asymmetric unit. The hexane molecule is positioned on the face of the unit cell on an inversion center, resulting in only one half of the molecule being in the unit cell.

In \(9a\), the rubrene dianion exhibits a twisting around the principal \(C^1−C^{1'}\) bond of the tetracene core; the deviation from the plane is observed by the angle between the \(C^2C^{1}C^{2''}\) and \(C^2C^{1'}C^{2'}\) planes. The angle is measured in \(9a\) as \(φ = 21.4 (3)^\circ\) (Figure 4.5, left). This twisting out of the plane is comparable to the deformation observed in \(7^-\) where the corresponding angle is \(φ = 29.4 (3)^\circ\) (Figure 4.2,left).

In the case of \(9a\) there are cesium ions bound to each benzene ring of the twisted core in an \(η^6\)-fashion. The shortest Cs⋯C contacts are between Cs3 and Cs4 to the central C\(_6\) ring; these distances range from 3.164(3) to 3.544(3) Å with the distance to the C\(_6\) centroid measured at 3.023
(3) Å. In comparison, the Cs2 and Cs1 connections to the peripheral benzene rings in 9a measured to the C6 centroid (3.166 (3) Å and 3.232 (3) Å respectively) are longer than those observed in Cs3 and Cs4. (Figure 3.5, left). Also in 9a, there are $\eta^2$-contacts to the nearby Cs2' ion (Cs2'···C 3.535(3) Å and 3.717(3) Å).

Figure 4.5 Side views and coordination environments of 9a (Cs3 and Cs4 have occupancies of 0.5 in the asymmetric unit (left)) and 9b (right). Hydrogen atoms, hexane and DME molecules are omitted for clarity.

In 9b, the rubrene dianion exhibits a planar configuration of the tetracene core as in neutral rubrene (Figure 4.5, right). In 9b only the peripheral benzene rings are coordinated to cesium ions, Cs1 and Cs1' in an $\eta^6$-binding mode with the cesium distance to the C6 centroid of 3.226 (3) Å. In addition the Cs2 and Cs2' ions are positioned above C–C bonds between the two benzene rings with the Cs···C distances ranging from 3.203(3) Å to 3.664(3) Å (Figure 4.5, right).

The geometrical deformations of 9 (twisted (9a) and planar (9b)) are compared to the monoanion and neutral ligand in Table 4.2.
Table 4.2 Key bond length distances (in Å) and angles (°) for 7, 8 and 9 (twisted (9a) and planar (9b)).

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</tr>
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</table>

Despite the numerous Cs···C contacts in 9, the cesium ion additionally coordinates a DME molecule to fill its coordination sphere. The Cs···O interatomic distances are close to those observed in related compounds.\textsuperscript{19} The sandwiching of cesium ions between 9a and 9b results in a 2D polymeric network in the crystal lattice of 9, which is held together by cesium η\textsuperscript{6} and η\textsuperscript{2}-binding to the rubrene dianions (Figure 4.6). It should be noted here that the phenyl groups of 9 are not involved in any metal binding in contrast to the cesium ion binding observed in 8.
Figure 4.6 Fragment of the 2D polymeric network in [Cs⁺]₄[C₄₂H₂₈²⁻]₂[Cs⁺(DME)]₂[C₄₂H₂₈²⁻] (9). Hexane molecules and hydrogen atoms are omitted for clarity.

The two-dimensional (2D) polymeric packing of the rubrene dianion and cesium counterions in 9 results in the formation of a cavity that is filled with a non-coordinating hexane molecule.

The non-rigidity of the rubrene-dianion is exhibited by a twisted (9a, Figure 4.5, left) and planar (9b, Figure 4.5, right) conformation of the tetracene core existing in the same cesium product.
4.4.2 Solution Studies of Rubrene Dianions

4.4.2.1 $^1$H and $^{13}$C NMR Investigations

We attempted to isolate the lithium dianion salt of rubrene; however, due to the low solubility of the product, we could not obtain high quality single crystals for X-ray diffraction studies. Therefore, we set out to compare 9 and the lithium dianion salt in solution using $^1$H NMR spectroscopy at variable temperatures. The $^1$H NMR spectrum of $7^{2-}$ in the THF-$d_8$ solution of the lithium salt exhibits five signals in the range of $\delta = 6.78$–$5.20$ ppm (Figure 4.7). The corresponding signals are significantly high-field shifted in the dianion compared to neutral rubrene ($\delta = 7.34$–$6.83$ ppm). The presence of five signals with the relative ratio of 2:2:1:1:1 in the $^1$H NMR spectrum and nine resonances in the $^{13}$C NMR spectrum indicates that the rubrene moiety adopts the $C_{2v}$, $C_{2h}$, or $D_{2h}$ symmetry in solution. At temperatures below $-60 \, ^\circ$C, two resonances of phenyl groups ($\delta = 6.78$ and 6.58 ppm) appear as very broad signals (Figure 4.7).

![Variable-temperature $^1$H NMR spectra of lithium salt of $7^{2-}$ in THF-$d_8$.](image)

**Figure 4.7** Variable-temperature $^1$H NMR spectra of lithium salt of $7^{2-}$ in THF-$d_8$. 
This observation demonstrates the symmetry reduction of the phenyl rings in the rubrene dianion at low temperature as the result of blocked rotation about the C−Ph bond or/and metal binding. In contrast to the temperature dependent $^1$H NMR spectra of the lithium salt, the analogous cesium salt (9) does not show any significant change for all five resonances in the $^1$H NMR spectra upon cooling to $-80 \, ^\circ\mathrm{C}$ (Figure 4.8).

![Variable-temperature $^1$H NMR spectra of cesium salt of $7^2$− in THF-$d_8$.](image)

**Figure 4.8** Variable-temperature $^1$H NMR spectra of cesium salt of $7^2$− in THF-$d_8$.

### 4.4.2.2 $^7$Li and $^{133}$Cs NMR Investigations

We set out to study the coordination of the alkali metals in solution in both lithium and cesium dianion salts using $^7$Li and $^{133}$Cs NMR spectroscopy. In the lithium salt of $7^2$−, only one resonance was detected in the $^7$Li NMR spectra in THF-$d_8$ in the temperature range of 20 °C to $-80 \, ^\circ\mathrm{C}$ (Figure 4.9, left). Its chemical shift ($\delta_{\text{Li}} = -2.3 \, \text{ppm}$) indicates the presence of a contact-ion pair; however, it lies below the typical range of sandwiched lithium ions observed in the past by our group.\textsuperscript{21} This observation shows only one type of Li$^+$ ions coordinated to the $7^2$− surface in solution.
The $^{133}\text{Cs}$ NMR spectrum for 9 has one broad resonance at $\delta_\text{Cs} = -70$ ppm at 20 °C, which is slightly low-field shifted ($\Delta\delta = 10$ ppm) upon cooling to −80 °C (Figure 4.9, right). The broadness and significant up-field shift, compared to the chemical shifts of reported solvated cesium ions, are indicative of the presence of several types of $\pi$-complexed Cs$^+$ ions, which is in good agreement with our X-ray diffraction study in the solid state (Figures 4.5 and 4.6).

![Figure 4.9](image)

**Figure 4.9** $^7\text{Li}$ NMR spectra of lithium salt of $7^{2-}$ (left) and $^{133}\text{Cs}$ NMR spectra of 9 (right) in THF-$d_8$ at 20 °C and −80 °C.

### 4.5 Tetraanions

#### 4.5.1 Lithium Salt: $[\text{Li}^+(\text{THF})_2]_4[C_{42}\text{H}_{28}^4]$  

The tetraanion of rubrene was produced by lithium reduction of C$_{42}$H$_{28}$ in THF and single crystals were grown upon layering of the reaction solution with hexanes. According to an X-ray diffraction study of the resulting crystals, the product crystallizes in the triclinic space group, P$-1$. In the asymmetric unit, the rubrene tetraanion central C$^1$–C$^{1'}$ bond resides on an inversion center resulting in only half the rubrene tetraanion being structurally independent. There are two structurally independent lithium ions with contacts to the rubrene tetraanion, constituting a CIP (Figure 4.10). These lithium ions both additionally coordinate two THF molecules each. The
molecular formula of this product is \([\text{Li}^+{(\text{THF})_2}_4\text{[C}_{42}\text{H}_{28}^{4-}] (10}\). It should be noted that this lithium salt of the tetraanion is analogous to the sodium salt isolated by Bock et al. (Figure 4.1).^{13}

![Molecular structure of \([\text{Li}^+{(\text{THF})_2}_4\text{[C}_{42}\text{H}_{28}^{4-}] (10}\). Hydrogen atoms are omitted for clarity.](image)

**Figure 4.10** Molecular structure of \([\text{Li}^+{(\text{THF})_2}_4\text{[C}_{42}\text{H}_{28}^{4-}] (10}\). Hydrogen atoms are omitted for clarity.

Gaining four electrons causes substantial changes in the bond lengths, angles and conformation of the rubrene framework (Figure 4.10). The two central aromatic rings of the rubrene core are considerably distorted upon lithium metal coordination and the addition of four electrons, leading to the “chair” conformation of the tetracene core. The deviation from the plane is measured by the angle between \(C^2\text{C}^4\text{C}^1\text{C}^2\) and \(C^2\text{C}^3\text{C}^3\text{C}^2\) in 10 (\(\omega = 42.1(2)^\circ\)), which is greatly distorted when compared to neutral rubrene where the angle \(\omega = 7.2 (1)^\circ\). This clearly shows that the tetraanion of rubrene exhibits the unrestricted flexibility of its tetracene core.

The central Li2 ions coordinate to the rubrene core with Li···C contacts ranging from 2.332(4) to 2.414(4) Å. The lithium ions are also weakly bound to the ipso carbon atom of the
phenyl group (Li⋯C 2.830(4) and 2.860(4) Å) (Figure 4.10). The phenyl groups of 7^{4−} bind Li ions through intermolecular Li⋯C η^6-interaction. The Li⋯C distances range from 2.382(4) to 2.854(4) Å, with the distance to the centroid measured as Li⋯C_{6(centroid)} 2.243(4) Å (Figure 4.11, left). There are also much weaker η^2-contacts (2.834(4) Å and 3.117(4) Å) (Figure 4.11, left). Each lithium ion in 10 has two coordinated THF molecules; the Li⋯O distances range from 1.934(4) to 1.991(4) Å, which are similar to the distances observed in other adducts with π-complexed lithium ions.\textsuperscript{22}

![Figure 4.11 Top (left) and side (right) views of the rubrene tetraanion with coordinated Li^+ ions in 10. Coordinated THF molecules and hydrogen atoms are omitted for clarity.](image)

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4.5.2 Rubidium Salt: \([\text{Rb}^+4(\text{THF})_5]\text{[C}_{42}\text{H}_{28}^{4-}]\)

Next, we investigated the reduction of rubrene with a heavy alkali metal to evaluate if any additional geometrical perturbations would be induced in the flexible rubrene tetraanion upon metal coordination. The tetraanion of rubrene was produced by the rubidium metal reduction of \(\text{C}_{42}\text{H}_{28}\) in THF and single crystals were grown upon layering of the resulting solution with hexanes. According to the X-ray diffraction study the product crystallizes in the triclinic \(P\bar{1}\) space group. In the asymmetric unit, there are two rubrene tetraanions in which the central \(\text{C}_1^1-\text{C}_1^{11}\) bond resides on an inversion center resulting in only half the rubrene tetraanion being structurally independent. There are four structurally independent rubidium ions with contacts to the two rubrene tetraanions, constituting a CIP. The rubidium ions additionally coordinate THF molecules in the asymmetric unit. In the asymmetric unit, there are two THF molecules coordinated to Rb1. Additionally, there is a THF molecule which bridges Rb1 and Rb2 in a symmetric manner. There is one THF molecule coordinated to Rb3. In addition there is another THF molecule which bridges Rb3 and Rb4 in an asymmetric mode. In total there are 5 THF molecules in the asymmetric unit. The molecular formula is \([\text{Rb}^+4(\text{THF})_5][7^{4-}]\) (11). The X-ray diffraction study revealed that the product contains two isomers 11a (Figure 4.12 left) and 11b (Figure 4.12 right) in a ratio of 1:1 the similar metal coordination and geometrical parameters.
As observed in 10, gaining four electrons causes substantial changes in the bond lengths, angles and conformation of the rubrene tetracene core (Figure 4.12). The two central aromatic rings of the rubrene core are considerably distorted upon rubidium metal coordination and the addition of four electrons, leading to the “chair” conformation of the tetracene core shown by the angle $\omega = 40.6(3)^\circ$ and 42.3(3)$^\circ$ for 11a and 11b, respectively (Figure 4.12).

In 11a, the shortest Rb···C separations are observed for the central Rb3 ions bound to the C1–C1' bond on the tetracene core, measured as 3.066(3) Å and 3.078(3) Å.\textsuperscript{23} The Rb3 ions gain additional electron density from two coordinated THF molecules. The Rb2 ions coordinate to the phenyl rings of the rubrene tetraanion in the $\eta^6$-fashion with the Rb···C contacts ranging from 3.223(3) Å to 3.372(3) Å. The distance to the C6 centroid measured as 2.986(3) Å. These Rb2 ions are also $\eta^2$-bound to the phenyl rings (Rb2···C 3.238(3) Å and 3.315(3) Å) (Figure 4.12, left).

In 11b, two rubidium ions, Rb4, are captured by two adjacent phenyl rings in an $\eta^6$-fashion. The Rb4···C distances range from 3.101(3) to 3.602(3) Å, with the distance to the C6 centroid
measured as 2.937(3) and 3.043(3) Å (Figure 4.12, right). The Rb1···C separations to the C\(^1\)--C\(^{1'}\) bond of 3.333(3) Å and 3.350(3) Å are much longer than those in 11a. Both rubidium ions additionally coordinate one THF molecule each.

In contrast to the monomeric arrangement of molecules in the solid structures of 10 and [Na\(^{+}\) (THF)\(_2\)]\(_4\)[7\(^{4-}\)]\(_{13}\) the rubidium ions are further linked to the neighbouring rubrene tetraanions forming a 2D polymeric network. The 2D network arises from additional \(\eta^4\)-contacts between Rb4 in 11b with the neighbouring phenyl ring of 11a (Rb4···C 3.158(3)–3.586(3) Å). There is also \(\eta^6\)-binding of Rb2 in 11a with the adjacent peripheral benzene ring of the tetracene core in 11b (Rb2···C 3.214(3)–3.579(3) Å), with the distance to the C\(_6\) centroid measured as 3.090(3) Å, (Figure 4.13).

![Fragment of the 2D polymeric network formed in 11. THF molecules and hydrogen atoms are omitted for clarity.](image)

**Figure 4.13** Fragment of the 2D polymeric network formed in 11. THF molecules and hydrogen atoms are omitted for clarity.
Through our in-depth X-ray diffraction study of the tetraanions of rubrene (the geometrical parameters of tetraanions are compared in Table 3.3) we proved that although its tetracene core indeed exhibits great flexibility, the effect of alkali metal ion size is neither straightforward nor significant. As shown above, there are no additional deformations induced by heavy alkali metal binding in comparison with light congeners of Group I. These observations are in contrast to our previous work with alkali metal adducts of bowl-shaped corannulene.\textsuperscript{24}

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4.5.3 Solution Studies of Rubrene Tetraanions

4.5.3.1 $^1$H and $^{13}$C NMR Investigations

We conducted the $^1$H NMR study of the tetrareduced rubrene at variable temperatures in order to investigate the behavior of the phenyl groups in the reduced products. A sample of 10 was prepared by dissolving crystals in THF-$d_8$ and then $^1$H NMR spectra were measured starting from 40 °C. The spectrum at 40 °C shows three sharp and three broad resonances (Figure 4.14). The sample was then cooled to low temperatures (below 0 °C) to exhibit seven sharp resonances observed at low temperatures.

![Figure 4.14 Variable-temperature $^1$H NMR spectra in THF-$d_8$ for 10.](image)

The temperature-dependent $^1$H NMR spectra of 10 are attributed to the symmetry reduction of the phenyl rings with the appearance of their five magnetically non-equivalent protons upon cooling (Figure 4.15). As in the case of the lithium dianion salt of rubrene, such behavior can be
explained by freezing the rotation about C–Ph bonds or/and by lowering the symmetry of the phenyl groups upon coordination of alkali metal ions to rubrene tetraanion.

**Figure 4.15** Classification of the symmetry related protons of phenyl groups in neutral, dianion (9) and tetraanion of rubrene (10, 11).

In contrast, the $^1$H NMR spectra of rubrene tetraanion in 11 and in its cesium salt ($7^4-/4\text{Cs}^+$) exhibit seven signals at 20 °C (Figure 4.16, bottom). This is consistent with the equivalence of all four phenyl rings with five magnetically non-equivalent hydrogen atoms (Figure 4.15, right). The two spectra are comparable to each other, representative of essentially analogous conformations of the rubrene tetraanion and their metal binding in solutions of both salts. This statement is also supported by the similarity observed in their $^{13}$C NMR spectra.
4.5.3.2 $^7$Li and $^{133}$Cs NMR Investigations

The variable-temperature $^7$Li NMR study of 10 revealed the presence of two kinds of coordinated lithium ions in solution at low temperatures. At 20 °C, one singlet is observed at $\delta = -2.9$ ppm for crystals of 10 dissolved in THF-$d_8$ (Figure 4.17, top). This signal undergoes decoalescence around −20 °C into two signals at −2.9 ppm and −3.7 ppm with relative intensities of 1:1 (Figure 4.17, bottom). This observation is in good agreement with the solid state structure of 10 in which two different binding sites were confirmed for lithium ions, namely coordination to the tetracene core and in between the phenyl pincers of the rubrene tetraanion (Figure 4.10).
The $^{133}$Cs NMR spectroscopic investigation of $^{74}$/4Cs$^+$ in solution reveals one broad resonance signal at $\delta = -90$ ppm at 20 °C (Figure 4.18, top). This signal is high-field shifted compared to that discovered for $9$ ($\delta = -78$ ppm, Figure 4.9, right). Upon cooling of the probe to −20 °C, this signal splits into two resonances. At much lower temperature (−80 °C), the signals appear as two sharp singlets at $\delta = -43$ and −117 ppm (Figure 4.18, bottom). Their integration shows the intensity ratio of 1:1.
The occurrence of two types of alkali metal ions in solution of $^{74-}/^{4Cs^+}$ indicates two favoured sites of the rubrene tetraanion for metal coordination. Almost certainly, those consist of the binding of alkali metal ions to the tetracene core and/or the sandwiching between the phenyl rings, consistent with the X-ray crystallographic studies.\textsuperscript{15}

### 4.6 Conclusions

The controlled preparation and isolation of rubrene mono-, di-, and tetraanions has been achieved in our laboratory with a series of alkali metal ions ranging from Li to Cs. The tendencies in geometrical deformation of the rubrene skeleton upon the stepwise acquisition of electrons and binding of multiple metal ions have been revealed by X-ray diffraction studies.\textsuperscript{15} The observed conformations of the resulting rubrene anions compared to the neutral ligand as well as the revealed alkali metal binding modes of mono-, di-, and tetraanions are summarized in Scheme 4.2.
Scheme 4.2: Stepwise deformation of the rubrene core upon electron acquisition and metal binding.

In addition to the solid state structures, the detailed multinuclear NMR investigation was also undertaken in order to elucidate the rigidity/flexibility of anionic rubrene species and their coordination environment in solution.15

4.7 Experimental Details

Materials and Methods. All manipulations were carried out using break-and-seal and glove-box techniques under an atmosphere of argon.14 Solvents (THF and hexanes) were dried over Na/benzophenone and distilled prior to use. DME and THF-$d_8$ was dried over sodium/potassium alloy and vacuum-transferred. Lithium, rubidium and cesium metals were purchased from Strem Chemicals. Rubrene (99%) was purchased from Acros Organics and sublimed at 275 °C prior to use. NMR spectra were measured on a Bruker AC-400 spectrometer at 400 MHz for $^1$H, 100.6 MHz for $^{13}$C, 155.5 MHz for $^7$Li, and 52.5 MHz for $^{133}$Cs. The NMR spectra were referenced to
the solvent signals for $^1$H and $^{13}$C, 0.1 M LiCl in THF-$d_8$ for $^7$Li, and 0.1 M CsNO$_3$ in D$_2$O for $^{133}$Cs.

The probe for the ESR study was prepared by dissolving crystals of 8 in THF and transferring the resulting solution ($\approx 10^{-6}$ M) into the quartz capillary (2.0 mm), which was then sealed. 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 UV-vis spectra were recorded on a Thermo Scientific Evolution 300BB spectrometer. Elemental analyses were performed by Complete Analysis Laboratories, Ins., Parsippany, NJ.

Crystal Structure Determinations and Refinement of 8–11

Data collections were performed on a Bruker SMART$^{25}$ APEX CCD-based X-ray diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at $T = 100(2)$ K. Data were corrected for absorption effects using the empirical method SADABS.$^{25}$ The structures were solved by direct methods and refined using the Bruker SHELXTL (Version 6.14) software package.$^{26}$ Hydrogen atoms were included at idealized positions using the riding model. In 8, the interstitial THF and $\frac{1}{2}$ of the hexane molecules crystallized at the same spatial position. This disorder was modelled with a 6:4 ratio of the respective units.

Monoanion Preparation

Synthesis and Crystal Growth of [Cs$(\text{THF})$][C$_{42}$H$_{18}$]$^-$·0.6 THF·0.2 C$_6$H$_{12}$ (8·0.6 THF·0.2 C$_6$H$_{12}$)

THF (2 mL) was added to a flask containing cesium metal (2.6 mg, 0.020 mmol) and rubrene (10 mg, 0.019 mmol). The resulting green mixture was stirred for 3 h and then filtered. The dark green
solution was layered with 2 ml of hexanes. Dark blocks were deposited at 25 °C in a few days in high yield (~80%). The product is $^1$H NMR silent. UV-vis (THF, nm): $\lambda_{\text{max}} = 314, 384, 436, 736, 776, 830$.

Crystallographic Data for $8 \cdot 0.6 \text{ THF} \cdot 0.2 \text{ C}_6\text{H}_12$

Empirical formula: $\text{C}_{49.60}\text{H}_{43.60}\text{CsO}_{1.60}$, $M_r = 798.15$, monoclinic, $a = 13.9700(13)\ \text{Å}$, $b = 10.2594(10)\ \text{Å}$, $c = 26.115(3)\ \text{Å}$, $\alpha = 90^\circ$, $\beta = 95.4210(10)^\circ$, $\gamma = 90^\circ$, $V = 3726.1(6)\ \text{Å}^3$, $P2_1/n$, $Z = 4$, $\rho_{\text{calcld}} = 1.423 \ \text{g/cm}^3$, $\mu = 1.034 \ \text{mm}^{-1}$, $T = 100(2) \ \text{K}$, $\lambda = 0.71073 \ \text{Å}$, 30708 measured intensities ($6.28^\circ \leq 2\theta \leq 113.12^\circ$), 8700 unique intensities $R_{\text{int}} = 0.0701$, $R_1 = 0.0486$, with $I \geq 2\sigma(I)$, $wR_2 = 0.1068$, refinement of 466 parameters. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre, the CCDC identifier is 864112.

UV-vis spectrum of 8
Dianion Preparation

Synthesis and Crystal Growth of [Cs⁺]₄[C₄₂H₂₈²⁻]₂[Cs⁺(DME)]₂[C₄₂H₂₈²⁻]·Cs(DME)·C₆H₁₄ (9·C₆H₁₄)

DME (3 mL) was added to a flask containing cesium metal (0.1 mmol, excess) and rubrene (10 mg, 0.019 mmol). The mixture was stirred for 15 h resulting in a deep green solution indicative of the rubrene tetraanion. The solution was then filtered from the metal into a flask, containing neutral rubrene (10 mg, 0.019 mmol). The resulting blue mixture was stirred for an additional hour and then layered with 3 ml of hexanes. Dark blue-green opalescent crystals were grown at 25 °C in a few days in moderate yield (~75%). ¹H NMR (400 MHz, THF-d₈, 20 °C, ppm): δ = 6.73–6.67 (m, 16H), 6.49 (m, 4H), 5.08 (m, 4H), 5.20 (m, 4H), 5.02 (m, 4H). ¹³³Cs NMR (52.5 MHz, THF-d₈, 20 °C, ppm): δ = −78. ¹³³Cs NMR (52.5 MHz, THF-d₈, −80 °C, ppm): δ = −68. UV-vis (THF, nm): λ max = 490.

Crystallographic Data for 9·C₆H₁₄

Empirical formula:C₇₀H₅₉Cs₃O₂, M r = 1330.90, triclinic, a = 13.338(3) Å, b = 14.189(4) Å, c = 16.036(4) Å, α = 72.485(3)°, β = 77.808(3)°, γ = 82.367(3)°, V = 2821.0(12) Å³, P-1, Z = 2, ρ calc = 1.567 g/cm³, μ = 1.974 mm⁻¹, T = 100(2) K, λ = 0.71073 Å, 24768 measured intensities (6.04° ≤ 2θ ≤ 113.72°), 12671 unique intensities R int = 0.0269, R₁ = 0.0387, with I ≥ 2σ(I), wR₂ = 0.1038, refinement of 682 parameters. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre, the CCDC identifier is 864113.
Kinetic UV-vis study of rubrene reduction with Cs metal

Synthesis of $7^{2-}/2\text{Li}^+$

THF (3 mL) was added to a flask containing lithium metal (0.1 mmol, excess) and rubrene (10 mg, 0.019 mmol). The mixture was stirred for 15 h resulting in a deep green solution indicative of the rubrene tetraanion. The solution was then filtered from the metal into a flask, containing neutral rubrene (10 mg, 0.019 mmol). The resulting blue mixture was stirred for an additional hour and then layered with 3 ml of hexanes. The crystalline solid which precipitated was dried in vacuo for 3 h. Yield: 80%. $^1\text{H}$ NMR (400 MHz, THF-$d_8$, 20 °C, ppm): $\delta = 6.78$ (d, $J_{HH} = 7.5$ Hz, 8H), 6.58 (t, $J_{HH} = 7.5$ Hz, 8H), 6.32 (t, $J_{HH} = 7.3$ Hz, 4H), 5.20 (m, 4H), 4.90 (m, 4H). $^1\text{H}$ NMR (400 MHz, THF-$d_8$, $-80$ °C, ppm): $\delta = 6.50$ (br s, 16H), 6.24 (m, 4H), 5.19 (m, 4H), 4.76 (m, 4H). $^{13}\text{C}$ NMR (100.6 MHz, THF-$d_8$, 20 °C, ppm): $\delta = 151.5$, 142.7, 136.0, 127.9, 120.3, 114.6, 111.9, 107.7, 102.4. $^7\text{Li}$ NMR (155.5 MHz, THF-$d_8$, 20 °C, ppm): $\delta = -2.3$. $^7\text{Li}$ NMR (155.5 MHz, THF-$d_8$, $-80$ °C, ppm): $\delta = -2.2$. UV-vis (THF, nm): $\lambda_{\text{max}} = 394$. 
**Tetraanion Preparation**

**Synthesis and Crystal Growth of [Li(THF)$_2$]$^+$$[C_{42}H_{28}^-]$ (10)**

THF (3 mL) was added to a flask containing freshly cut Li metal (excess) and rubrene (10 mg, 0.019 mmol). The mixture was sonicated for a few minutes for metal activation. After stirring for 15 h, the intense green solution was filtered and layered with 3 ml of hexanes. Dark green opalescent crystals were deposited in a few days at 10 °C in moderate yield (~65%).$^1$H NMR (400 MHz, THF-$d_8$, 20 °C, ppm): $\delta$ = 7.42 (m, 4H), 7.18 (br s, 4H), 6.45 (br s, 4H), 6.39 (m, 4H), 6.28 (br s, 4H), 6.12 (br s, 4H), 5.03 (t, $J_{HH} = 6.4$ Hz, 4H). $^1$H NMR (400 MHz, THF-$d_8$, −60 °C, ppm): $\delta$ = 7.40 (m, 4H), 7.21 (d, $J_{HH} = 8.6$ Hz, 4H), 6.53 (d, $J_{HH} = 6.3$ Hz, 4H), 6.30 (m, 4H), 6.21 (t, $J_{HH} = 7.2$ Hz, 4H), 6.02 (t, $J_{HH} = 8.4$ Hz, 4H), 4.98 (t, $J_{HH} = 6.3$ Hz, 4H).$^7$Li NMR (155.5 MHz, THF-$d_8$, 20 °C, ppm): $\delta$ = −3.6. $^7$Li NMR (155.5 MHz, THF-$d_8$, −60 °C, ppm): $\delta$ = −2.9 (2Li), −3.7 (2Li). UV-vis (THF, nm): $\lambda_{max}$ = 600.

**Crystallographic Data for 10**

Empirical formula:C$_{74}H_{92}$Li$_4$O$_8$, $M_r = 1137.24$, triclinic, $a = 10.866(2)$ Å, $b = 12.000(2)$ Å, $c = 12.880(2)$ Å, $\alpha = 76.419(3)^\circ$, $\beta = 89.732(2)^\circ$, $\gamma = 69.348(2)^\circ$, $V = 1522.0(5)$ Å$^3$, $P-1$, $Z = 1$, $\rho_{calcd} = 1.241$ g/cm$^3$, $\mu = 0.077$ mm$^{-1}$, $T = 100(2)$ K, $\lambda = 0.71073$ Å, 13376 measured intensities ($6.52^\circ \leq 2\theta \leq 113.36^\circ$), 6847 unique intensities $R_{int} = 0.0354$, $R_1 = 0.0543$, with $I \geq 2\sigma(I)$, $wR_2 = 0.1351$, refinement of 388 parameters. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre, the CCDC identifier is 864114.
Kinetic UV-vis study of rubrene reduction with Li metal

Synthesis and Crystal Growth of [Rb⁺₄(THF)₅][C₄₂H₁₈₄⁻] (11)

THF (3 mL) was added to a flask containing Rb metal (excess) and rubrene (10 mg, 0.019 mmol). After stirring for 15 h, the intense green solution was filtered and layered with 3 ml of hexanes. Dark green opalescent crystals were deposited in a few days at 10 °C in moderate yield (~70%).

¹H NMR (400 MHz, THF-d₈, 20 °C, ppm): δ = 7.28 (m, 4H), 6.97 (d, J_HH = 8.4 Hz, 4H), 6.47 (m, 4H), 6.23 (t, J_HH = 6.9 Hz, 4H), 6.15 (t, J_HH = 6.9 Hz, 4H), 5.95 (d, J_HH = 8.4 Hz, 4H), 4.84 (t, J_HH = 6.5 Hz, 4H). UV-vis (THF, nm): λ_max = 610.

Crystallographic Data for 11

Empirical formula:C₆₂H₆₈Rb₄O₅, M_r = 1235.04, triclinic, a = 13.482(2) Å, b = 14.092(2) Å, c = 17.194(2) Å, α = 86.137(1)°, β = 73.258(1)°, γ = 61.725(1)°, V = 2745.6(5) Å³, P-1, Z = 2, ρ_calcd = 1.494 g/cm³, μ = 3.593 mm⁻¹, T = 100(2) K, λ = 0.71073 Å, 23968 measured intensities (6.60° ≤ 2θ ≤ 112.96°), 12290 unique intensities R_int = 0.0269, R_1 = 0.0421, with I ≥ 2σ(I), wR² = 0.1351,
refinement of 640 parameters. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre, the CCDC identifier is 864115.

**Synthesis of 7^4/4Cs^+**

THF (3 mL) was added to a flask containing Cs metal (excess) and rubrene (10 mg, 0.019 mmol). After stirring for 15 h, the intense green solution was filtered and layered with 3 ml of hexanes. The black solid which precipitated was dried in vacuo for 3 h. Yield: 70%. $^1$H NMR (400 MHz, THF-$d_8$, 20 °C, ppm): $\delta = 7.27$ (m, 4H), $6.89$ (d, JHH = 8.8 Hz, 4H), $6.47$ (m, 4H), $6.20$ (t, JHH = 7.5 Hz, 4H), $6.13$ (t, JHH = 7.5 Hz, 4H), $5.93$ (d, JHH = 8.6 Hz, 4H), $4.85$ (t, JHH = 6.5 Hz, 4H).

$^{13}$C NMR (100.6 MHz, THF-$d_8$, 20 °C, ppm): $\delta = 143.0, 135.3, 131.6, 128.8, 123.7, 117.1, 117.0, 109.5, 109.5, 97.8, 97.7$. $^{133}$Cs NMR (52.5 MHz, THF-$d_8$, 20 °C, ppm): $\delta = -90$ (br). $^{133}$Cs NMR (52.5 MHz, THF-$d_8$, −80 °C, ppm): $\delta = -43$ (2Cs), −117 (2Cs). UV-vis (THF, nm): $\lambda_{\text{max}} = 604$.

**4.8 References**


CHAPTER 5

Exploration into Group II Reduction of Polycyclic Aromatic Hydrocarbons

5.1 Introduction

Magnesium and lithium have similar properties due to the diagonal rule of the periodic table.\textsuperscript{1} Owing to their similar ionic radii, they may have similar intercalating properties with respective electrode component of a battery (Table 5.1). As noted in Chapter 1 of this dissertation, the production of lithium-ion batteries (LIBs) is on the rise; however, the natural abundance of lithium is low (Table 5.1) and the LIB is nearing its energy limit. For these reasons alternatives to LIBs are being broadly explored and researchers are considering other metals with higher abundance and similar electrochemical properties to lithium.\textsuperscript{2} The fact that magnesium has similar properties and a much higher natural abundance (Table 5.1) makes it a clear choice for investigation.

<table>
<thead>
<tr>
<th>Ionic Radii</th>
<th>Lithium</th>
<th>Magnesium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic Radii</td>
<td>0.60 Å  (Li\textsuperscript{+})</td>
<td>0.65 Å  (Mg\textsuperscript{2+})</td>
</tr>
<tr>
<td>Reduction Potential</td>
<td>-3.0 V vs. SHE</td>
<td>-2.4 V vs. SHE</td>
</tr>
<tr>
<td>Volumetric Capacity</td>
<td>2062 mAh/mL</td>
<td>3833 mAh/mL</td>
</tr>
<tr>
<td>Abundance in Earth's Crust</td>
<td>20 mg per kg</td>
<td>23,300 mg per kg</td>
</tr>
</tbody>
</table>

Table 5.1 Comparison of the properties of lithium and magnesium.\textsuperscript{1,3}

Graphite intercalation compounds used as anode materials are the main reason behind the success of lithium-ion battery technology. Lithium-ion batteries with carbon anodes (lithiated
graphite) constitute the most advanced energy storage technology currently commercially available. However, in order to support longer use of electronics, extended ranges on electric vehicles and efficient storage of electricity further development and advancement of battery technologies is required.\textsuperscript{4} Theoretically, pure lithium metal anodes could be substituted for the lithiated graphite anode. Lithium metal has a high volumetric capacity of 2062 mAh/mL and has a reduction potential of $-3.0 \text{ V}$ vs. the standard hydrogen electrode (SHE),\textsuperscript{3b} making it a good candidate.\textsuperscript{5} However, lithium-ion batteries with lithium metal anodes have not been commercialized because dendritic growth is observed during the charging cycles. This is due to the intrinsic instability of lithium metal. Dendritic growth has been linked to short circuiting, which leads to thermal runaway due to the exothermic chemical reactions in the battery.\textsuperscript{6}

For these reasons, researchers are investigating the advantages of using magnesium and calcium instead of lithium for future battery technologies. This is due to the fact that magnesium and calcium have higher volumetric capacities, 3833 and 2073 mAh/mL, and reduction potentials of $-2.4 \text{ V}$ and $-2.9 \text{ V}$ vs. the SHE, respectively (Figure 5.1).\textsuperscript{3b,7}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.1.png}
\caption{Comparison of capacities and reduction potentials of lithium, magnesium and calcium.\textsuperscript{5}}
\end{figure}
An advantage of magnesium-based batteries is that theoretically higher storage capacities are possible over the current LIBs. As lighter batteries are needed for our portable electronic devices, magnesium ion batteries could be used to store more charge per gram. Unlike lithium, magnesium has not shown dendritic growth during electrodeposition studies.\textsuperscript{8} Magnesium is inherently safer than lithium as it does not violently react with moisture or air. Additionally, magnesium is the eighth most abundant element in the earth’s crust, making it a sustainable and lower cost choice for battery technology. For these reasons the use of magnesium metal as the anode is a viable option.

Little research has been conducted into the intercalation of magnesium into graphite. Some literature even reports that intercalation of magnesium into graphite is difficult or impossible.\textsuperscript{9} However, in 2017 God \textit{et al.} investigated the intercalation behavior of magnesium into natural graphite using common organic electrolytes for the study. The intercalation was observed by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). The investigation revealed that magnesium can be intercalated into graphite.\textsuperscript{10} However, the experimentally detected capacity was only one tenth of the theoretical capacity assuming that the composition of the anode was Mg\textsubscript{0.5}C\textsubscript{6}.\textsuperscript{8} The intercalation of magnesium is known to be more sluggish than lithium due to the higher charge density on the divalent ion with an equivalent ionic radius.\textsuperscript{11} More intercalation studies are needed to fully understand the mechanism of magnesium insertion into the graphite layers.

A battery based off of a calcium anode has potential advantages over that of magnesium and lithium. Calcium has an increased negative reduction potential (−2.9 vs. the standard hydrogen electrode), 0.5 V less than magnesium and a volumetric capacity which is 11 mAh/mL higher than lithium (Figure 5.1).\textsuperscript{3b} Additionally, the ionic radius of calcium is 0.99 Å (6 coordinate ionic radii
value), which is larger than Mg$^{2+}$ by approximately 0.34 Å.$^{3a}$ The larger radius of Ca$^{2+}$ results in lower charge density compared to Mg$^{2+}$. In addition, faster diffusion is observed for Ca$^{2+}$. Calcium is the fifth most abundant element in the earth’s crust making it an ecological choice for battery technology.$^{12}$ However, the research into calcium cathodes and electrolytes is minimal in comparison to other alternatives of lithium-ion batteries (magnesium or sodium).$^{13}$

Some interesting results from the literature involving calcium in battery research include mixed metal systems. For example, the use of a calcium-organic framework as an anode material for sodium ion batteries has been explored by Zhang et al. in 2016.$^{14}$ Calcium is also the only alkaline earth metal shown by XRD studies to be co-intercalated into graphite with lithium.$^{9a}$ It should be noted here that pure calcium graphite intercalation compounds have been proven to be superconductive with the transition to a superconducting state at approximately 11 K (Chapter 1, Figure 1.2).$^{15}$ Thus, the hypothetical and cost-effective initiative for converting from lithium-ion batteries to a technology based on calcium or magnesium could be significant. However, the chemistry involved in making a calcium ion battery work capably has yet to be developed.$^{16}$

The development of multivalent ion batteries is considerably more multifaceted than the monovalent alkali metals and more research is needed to understand the fundamentals behind the complexity.$^{1}$ Due to the polymeric structures and insolubility in common solvent of intercalated carbonaceous materials, studies of structures and structure-property correlations must be conducted on smaller subunits. As discussed in Chapters 1 and 2 of this dissertation, planar polycyclic aromatic hydrocarbons (PAHs) (i.e., coronene) can serve as models for the infinite planar π-carbon surface of graphite. In contrast, non-planar PAHs (i.e., corannulene) have been utilized to study the reactivity of carbon allotropes with curved π-surfaces. However, upon searching the literature we were surprised to find that the coordination and reduction chemistry of
alkaline earth metals towards polycyclic aromatic hydrocarbons has been very scarce. This is apparent by the very limited number of structural data reported for alkaline earth metal compounds in general (especially those of the heavier Ca, Sr, and Ba metals). Only a few notable references could be found in the literature; this is in stark contrast to the numerous reports for alkali metal compounds with PAHs.\textsuperscript{17}

5.2 Structurally Characterized Anions of PAHs with Magnesium and Calcium Countercations

One prominently known reaction is the reduction of a planar PAH with fused six-membered rings, anthracene (C\textsubscript{14}H\textsubscript{10}). Anthracene can be reduced with excess magnesium metal (previously activated with 1,2-dibromoethane, C\textsubscript{2}H\textsubscript{4}Br\textsubscript{2}) in tetrahydrofuran (THF). The resulting product was crystallized by Engelhardt \textit{et al.}, and the X-ray diffraction study revealed the formation of a contact-ion pair (CIP) consisting of an anthracene dianion with a magnesium cation coordinated to the central six-membered ring in an $\eta^2$-fashion. The magnesium cation additionally binds three THF molecules, therefore the formula of this product is [Mg\textsuperscript{2+}(THF)\textsubscript{3}][C\textsubscript{14}H\textsubscript{10}\textsuperscript{2–}] (12) (Figure 5.2).\textsuperscript{18}

![Molecular structure of [Mg\textsuperscript{2+}(THF)\textsubscript{3}][C\textsubscript{14}H\textsubscript{10}\textsuperscript{2–}] (12), reported by Engelhardt \textit{et al.}]

\textbf{Figure 5.2} Molecular structure of [Mg\textsuperscript{2+}(THF)\textsubscript{3}][C\textsubscript{14}H\textsubscript{10}\textsuperscript{2–}] (12), reported by Engelhardt \textit{et al.}\textsuperscript{18}
The above alkaline earth metal salt is also well known for its use as an exceptional reducing agent for transition metal salts and can be used in the preparation of Grignard compounds under mild conditions.\textsuperscript{19} Two anthracene derivatives have also been reduced to the dianion stage with magnesium using three different synthetic approaches. The reduction of 1,4-dimethylnaphthalene (C\textsubscript{16}H\textsubscript{14}) was carried out with magnesium metal (previously activated with bromoethane, C\textsubscript{2}H\textsubscript{5}Br) in THF. The resulting product was crystallized and an X-ray diffraction study revealed the formation of a CIP containing a 1,4-dimethylnaphthalene dianion with a magnesium cation coordinated to the central six-membered ring in a $\eta^2$-fashion. The magnesium cation additionally binds three THF molecules, therefore the formula of this product is [Mg\textsuperscript{2+}(THF)\textsubscript{3}][C\textsubscript{16}H\textsubscript{14}\textsuperscript{2−}] (Figure 5.3, left).\textsuperscript{20} It should be noted here that this structure is analogous to 12.

![Figure 5.3](image)

**Figure 5.3** Molecular structures of [Mg\textsuperscript{2+}(THF)\textsubscript{3}][C\textsubscript{16}H\textsubscript{14}\textsuperscript{2−}] (left) [Mg\textsuperscript{2+}(THF)\textsubscript{2}][(Me\textsubscript{3}Si)\textsubscript{2}C\textsubscript{14}H\textsubscript{8}\textsuperscript{2−}][Mg\textsuperscript{2+}(TMEDA)][(Me\textsubscript{3}Si)\textsubscript{2}C\textsubscript{14}H\textsubscript{8}\textsuperscript{2−}] (center) and [Mg\textsuperscript{2+}(THF)\textsubscript{2}][(Me\textsubscript{3}Si)\textsubscript{2}C\textsubscript{14}H\textsubscript{8}\textsuperscript{2−}] (right). Hydrogen atoms are omitted for clarity.
The reduction of the silylated anthracene, 9,10-bis(trimethylsilyl)anthracene ((Me₃Si)₂C₁₄H₈), was performed by a metathetical exchange reaction involving 12 and the neutral silylated anthracene in THF. The product was crystallized from a 1:25 ratio of tetramethylethylenediamine (TMEDA) and THF. The resulting product was isolated in the solid state. An X-ray diffraction study conducted by the authors revealed two CIPs: one consisting of [Mg²⁺(THF)₂][(Me₃Si)₂C₁₄H₈²⁻] and the other containing [Mg²⁺(TMEDA)][(Me₃Si)₂C₁₄H₈²⁻] in the same unit cell (Figure 5.3, center).²¹ The CIP of [Mg²⁺(THF)₂][(Me₃Si)₂C₁₄H₈²⁻] can also be synthesized from magnesium powder (previously activated by bromoethane, C₂H₅Br) in THF (Figure 5.3, right).²²

Structures of solvent-separated ion pairs (SSIPs) are even more limited in the literature due to the lack of X-ray diffraction data for alkaline earth metals in general, but also due to the stronger electrostatic bonding between the doubly charged cations and carbanions. The reaction of 12 and neutral anthracene in a concentrated solution of magnesium chloride (MgCl₂) results in the formation of a SSIP in the solid state, as determined by an X-ray diffraction study conducted by Bogdanović and co-workers.²⁰ The SSIP consists of an anthracene monoanion and μ-trichlorodimagnesium cation coordinated with six THF molecules; therefore, the formula of this product is [(Mg²⁺)₂Cl₃(THF)₆][C₁₄H₁₀⁻] (Figure 5.4, left).²⁰
Figure 5.4 Molecular structure of \([(\text{Mg}^{2+})_2\text{Cl}_3(\text{THF})_6][\text{C}_{14}\text{H}_{10}^-]\) (left), fragment of polymeric structure of \([\text{Mg}^{2+}(\text{C}_9\text{H}_7^-)_2]\) (center) and molecular structures of \([\text{Mg}^{2+}(\text{THF})_6][(\text{C}_9\text{H}_7^-)_2]\) (top right), \([\text{Mg}^{2+}(\text{DMSO})_6][(\text{C}_9\text{H}_7^-)_2]\) (bottom right). Hydrogen atoms and interstitial solvent molecules are omitted for clarity.

The reduction of a planar PAH with fused five- and six-membered rings, indene (C\(_9\)H\(_8\)), with dibutlymagnesium ([CH\(_3\)(CH\(_2\))\(_3\)]\(_2\)Mg) produces \([\text{Mg}^{2+}(\text{C}_9\text{H}_7^-)_2]\) as a contact-ion pair (CIP) in the solid state (Figure 5.4, center).\(^{23}\) However, when \([\text{Mg}^{2+}(\text{C}_9\text{H}_7^-)_2]\) is dissolved in strong donor solvents, such as tetrahydrofuran (THF) or dimethyl sulfoxide (DMSO), the polymeric structure is broken resulting in two uncoordinated indene anions (C\(_9\)H\(_7^-\)) and \([\text{Mg}^{2+}(\text{THF})_6]\) or \([\text{Mg}^{2+}(\text{DMSO})_6]\) cation, respectively (Figure 5.4, right).\(^{23}\)

The reduction of another planar PAH with fused five- and six-membered rings, fluorene (C\(_{13}\)H\(_{10}\)), with amine adducts of Me\(_2\)Mg(L) with chelating amines (L = TMEDA or pentamethylethlenetriamine, PMDTA) results in the formation of SSIP and CIP organomagnesium complexes depending on the chelating solvent molecules.\(^{24}\) In 1994, Viebrock
and co-workers revealed the structures of \([\text{Mg(TMEDA)Me}]^+\text{[C}_{13}\text{H}_9^-]\) (Figure 5.5, left) constituting a CIP and \([\text{Mg}_2\text{Me}_2(\text{PMDTA})_2]^{2+}\text{[C}_{13}\text{H}_9^-]^2\) (Figure 5.5, right) as a solvent-separated ion pair.\(^{24}\)

**Figure 5.5** Molecular structure of \([\text{Mg(TMEDA)Me}]^+\text{[C}_{13}\text{H}_9^-]\) (left) and \([\text{Mg}_2\text{Me}_2(\text{PMDTA})_2]^{2+}\text{[C}_{13}\text{H}_9^-]^2\) (right). Hydrogen atoms are omitted for clarity.

It should be mentioned here that \(\text{C}_{60}\)-fullerene has been intercalated with magnesium, either by thermal decomposition of 12 or by a solid state reaction between \(\text{C}_{60}\) and magnesium metal. The resulting \(\text{Mg}_2\text{C}_{60}\) polymeric product has only been studied by high resolution powder synchrotron and neutron diffraction data. Pontiroli *et al.* report that the product is isostructural to \(\text{Li}_4\text{C}_{60}\) having a body centered monoclinic cell.\(^{25}\) To the best of our knowledge, the above structural studies are the only organomagnesium complexes with PAHs, both planar and curved, structurally characterized and reported to date.
The reports on the reduction chemistry of polycyclic aromatic hydrocarbons with calcium are even more limited. Interestingly, all calcium complexes reported with PAHs are based on metathetical reactions with alkali metal salts and are not produced by direct metalation from activated calcium. This may explain why many monoanions of polyaromatic hydrocarbons have been isolated with calcium cations, unlike the direct metalation with magnesium metal which produces PAH dianions.

The reduction of indene (C₉H₈) with calcium is achieved by a metathetical reaction starting from potassium indenide, ([K+(THF)]ₙ(C₉H₇⁻)) and calcium iodide (CaI₂). The resulting product, [Ca²⁺(THF)₂][(C₉H₇⁻)₂] crystallizes in the solid state as a CIP comprised of two indenide monoanions coordinated to a calcium cation, which additionally coordinates two THF molecules (Figure 5.6, left). The reaction of potassium 1,3-dissoproplindenide, ([K+(THF)](C₁₅H₁₉⁻)) with calcium iodide produces an analogous complex in the solid state, [Ca²⁺(THF)][(C₁₅H₁₉⁻)₂], differing only by a number of THF molecules coordinated to the calcium cation (Figure 5.6, right).

![Figure 5.6](image)

**Figure 5.6** Molecular structure of [Ca²⁺(THF)₂][(C₉H₇⁻)₂] (left) and [Ca²⁺(THF)][(C₁₅H₁₉⁻)₂] (right). Hydrogen atoms are omitted for clarity.
To the best of our knowledge, the first PAH dianion encapsulating a calcium cation was isolated in 1997 by Harder et al.\textsuperscript{27} Harder reported the structure of an Si-bridged fluorenyl metallocene with calcium, \([\text{Ca}^{2+}(\text{THF})_3][\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)_2]^{2-}\) (Figure 5.7).

Figure 5.7 Molecular structure of \([\text{Ca}^{2+}(\text{THF})_3][\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)_2]^{2-}\). Hydrogen atoms are omitted for clarity.

The first organocalcium compound that crystallized as a completely solvent-separated ion pair was isolated in 2002 by Harder and co-workers.\textsuperscript{28} Bis(9-trimethylsilylfluorenyl)-calcium was synthesized from a metathesis reaction between the corresponding potassium compound and \(\text{CaI}_2\) in THF. The resulting product was revealed in the solid state to be a SSIP consisting of two 9-trimethylsilylfluorenyl anions and a calcium cation solvated by six THF molecules, \([\text{Ca}^{2+}(\text{THF})_6][\text{Me}_3\text{Si}(\text{C}_{13}\text{H}_8^{•-})]_2\) (Figure 5.8, left). It should be mentioned here that the magnesium analogue, \([\text{Mg}^{2+}(\text{THF})_6][\text{Me}_3\text{Si}(\text{C}_{13}\text{H}_8^{•-})]_2\), is isostructural.\textsuperscript{28}
In the same report, Harder structurally characterized bis(7,9-diphenylcyclopenta[a]acenaphthadienyl)calcium, $[\text{Ca}^{2+}\text{(THF)}_6][\text{(Me}_3\text{Si(C}_{13}\text{H}_{8^-})_2]]$ (Figure 5.8, right). Both structures in Figure 5.8 are described by the “metal-in-a-box” model by Harder, in which the Group II cation is encapsulated in a box made of PAH anionic ligands. The authors report this to be a general structural feature of solvent-separated ion pairs with large planar carbanions. It should be noted here that numerous short $C^–H\cdots\pi$ interactions between THF hydrogen atoms and the walls of the box hold the solvated cation in place and greatly stabilize this form of crystal packing.

In 2004, Fedushkin et al. reported the reaction involving fluoranthene ($\text{C}_{16}\text{H}_{10}$, Figure 5.9 right), which interestingly is a planar fragment of corannulene (Figure 5.9, left). It has been proven that fluoranthene can be reduced to monoanion and dianion using alkali metals in both solution and the solid state.
Fedushkin reports that the one-pot reaction of CaI$_2$(THF)$_2$ with potassium metal and fluoranthene (molar ratio 0.5:1:1) in THF affords [Ca$^{2+}$(THF)$_6$][(C$_{16}$H$_{10}^+$)$_2$]$\cdot$2 C$_{16}$H$_{10}$. An X-ray diffraction study conducted by the authors revealed the asymmetric unit to contain a solvent-separated ion pair (SSIP) consisting of three radical anions of C$_{16}$H$_{10}$, one and a half of a THF encapsulated [Ca$^{2+}$(THF)$_6$] cation and three neutral fluoranthene molecules (Figure 5.10).

**Figure 5.9** Corannulene (C$_{20}$H$_{10}$, 13) (left) and fluoranthene (C$_{16}$H$_{10}$) (right).

**Figure 5.10** Molecular structure of [Ca$^{2+}$(THF)$_6$][(C$_{16}$H$_{10}^+$)$_2$]$\cdot$2 C$_{16}$H$_{10}$, reported by Fedushkin et al. Hydrogen atoms and carbon atoms of THF are omitted for clarity.
To the best of our knowledge, the several aforementioned X-ray studies represent the full extent of organocalcium complexes with PAHs structurally characterized and reported to date. Therefore, we have set out to investigate the intercalation of magnesium and calcium ions into negatively charged curved carbon systems, as part of fundamental structural studies needed for the post lithium-ion movement. We selected corannulene (C$_{20}$H$_{10}$, 13) as a curved carbon $\pi$-system for this exploration, since it has a 1.6 times greater lithium capacity than graphite, the currently used anode in commercially available LIBs (See Chapter 1 for more details). We intended to investigate if a similar intercalation pattern would be revealed for magnesium.

Although our group has extensively investigated the single crystalline anionic products of corannulene reduced with alkali metals using X-ray crystallography, we have yet to expand these studies past Group I metals.$^{32,33,34}$ Prior to us, the reduction chemistry of corannulene with alkali metals had been studied in solution mainly by Scott and Rabinowitz with co-workers and some structural models were proposed based on spectroscopic investigations.$^{35}$ However, no control over reduction reactions was achieved and multiple products often co-existed in solution. Thus, we had to develop the stepwise preparation and crystallization approaches, focusing on the isolation of the target products in pure crystalline form.$^{36}$ In contrast to Group I reduction reactions, when we set out to study the intercalation of the alkaline earth (Group II) metals into corannulene (C$_{20}$H$_{10}$) we found practically no information on solution studies or synthetic approaches reported in the literature. Only one density functional theory (DFT) study was conducted on comparing the metal-ion binding preferences towards corannulene, concluding that Ba$^{2+}$ shows a strong preference for inside (endo) coordination.$^{37}$ We therefore had to focus on the development of the synthetic toolbox for Group II reduction reactions with corannulene.
5.3 Synthetic Methods

It has been well established by now that, in the presence of excess lithium metal, corannulene can be reduced to the tetraanion state in a stepwise manner.\textsuperscript{34a} We set out to investigate the reduction of corannulene with a commercially available high purity magnesium metal powder under the same conditions, conducting all manipulations using break-and-seal and glove-box techniques under an atmosphere of argon (Scheme 5.1).\textsuperscript{38}

Scheme 5.1: Reaction conditions for corannulene reduction with Mg metal analogous to Li.

However, upon reacting corannulene with excess magnesium even after extended periods of time (weeks), sonication, varied reaction temperatures (low and high), and different methods of physical activation of magnesium metal, no reduction of corannulene was observed. We quickly learned that Group II reactivity towards corannulene is very different from that of Group I metals, despite their similar atomic and ionic radii size. This has required the introduction of new synthetic techniques into the reduction chemistry. Thus, while alkali metals (Li, Na, K, Rb and Cs) only require physical removal of the oxidized layer to expose the fresh metal surface prior to the reduction reactions, all alkaline earth metals require chemical activation.
Using the literature examples, we synthesized \([\text{Mg}^{2+}(\text{THF})_3][\text{C}_{14}\text{H}_{10}^2^-](12)\), confirmed its purity by checking the unit cell parameters by X-ray diffraction, and used it as an active soluble form of magnesium (Scheme 5.2, right). Others have attempted to use the magnesium reagent 12 in reactions with several planar polyaromatic hydrocarbons. Namely, the silylated anthracene derivatives, cyclooctatetraene and fluoranthene were reacted with \([\text{Mg}^{2+}(\text{THF})_3][\text{C}_{14}\text{H}_{10}^2^-]\) in THF solutions resulting in ligand exchange reactions.\(^{39}\) We also tried to decompose the anthracene dianion magnesium salt in order to obtain finely divided active magnesium metal (\(\text{Mg}^*\)) (Scheme 5.2, left).\(^{19}\) A similar synthetic approach was successfully used to isolate the \(\text{Mg}_2\text{C}_{60}\) polymer as a crystalline powder for XRD studies.\(^{25}\)

**Scheme 5.2:** Synthetic approach using \([\text{Mg}^{2+}(\text{THF})_3][\text{C}_{14}\text{H}_{10}^2^-](12)\) as a starting material.

Both of the abovementioned approaches reduced corannulene to a dark green reaction mixture which is characteristic of the corannulene monoanion.\(^{32}\) However, we were never able to isolate the resulting product in the form of single crystals in order to confirm its identity. Therefore, we set out to find another method to achieve the activation of magnesium which would allow for crystallization of the product.

Several methods have been found in the literature to activate magnesium metal; one report was based on using an entrainment reagent (Scheme 5.3, bottom).\(^{40}\) Another alternative is a
metathesis reaction starting from alkali metal and alkaline earth metal salts. A commonly known metathesis reaction is the Rieke metal synthesis, where naphthalene or biphenyl is used as an electron transporter (Scheme 5.3, top). Rieke magnesium yields a very fine active form of magnesium which does not react with naphthalene or biphenyl due to their high reduction potentials, $-2.6 \text{ V}$ and $-2.7 \text{ V}$ vs. SHE, respectively.

**Scheme 5.3:** Synthetic approaches to activate magnesium metal (Mg*).

Methods for activation of calcium are similar to those for magnesium. The preparation of highly reactive calcium was reported by Rieke *et al.* in 1990 by reduction of calcium salts with lithium biphenylide. However, from the literature examples of PAHs reduced with calcium no direct metal reduction reactions were reported.

Our preferred method of magnesium activation is entrainment with alkyl halides, 1,2-dibromoethane (C$_2$H$_4$Br$_2$) or 1,2-diiodoethane (C$_2$H$_4$I$_2$), because the side products are innocuous, ethylene gas (C$_2$H$_4$) and magnesium bromide (MgBr) or magnesium iodide (MgI$_2$) (Scheme 5.3. bottom activation of magnesium with 1,2-dibromoethane). It should be noted here that this approach can also be used to activate calcium metal. We found that anhydrous liquid 1,2-dibromoethane or solid crystalline 1,2-diiodoethane could be added directly to the reaction mixture
and did not inhibit the formation of the target corannulene anion. This one pot synthetic approach is preferable over the two step Rieke metal synthesis or a metathesis reaction where alkali metal salts are used in stoichiometric amounts.

Once we figured out a way to activate the magnesium surface, the reaction with corannulene was performed in THF at room temperature. The formation of the green color, characteristic of the monoreduced corannulene (Figure 5.11),\textsuperscript{32} has been observed in solution within 2 hours and remained unchanged over the course of a month.

![Figure 5.11](image)

**Figure 5.11** Comparison of corannulene reduced with Li metal and activated Mg metal in THF (left) and UV-vis spectra (right).

We have broadly varied experimental conditions but observed that even with extended reaction times, additional heating/cooling and controlling/altering the amounts of Mg and activator only a vibrant green reaction mixture was obtained, indicating that the reaction did not surpass the first reduction step. We monitored the reaction over the course of 1 month using UV-vis spectroscopy and observed no change in the spectra (Figure 5.12).
Figure 5.12 UV-vis kinetic study of corannulene reduction with Mg metal in THF.

The difference in reduction potentials between lithium and magnesium could explain why corannulene reduction does not proceed past the monoanion stage, when magnesium is used as the reducing agent (Scheme 5.4).

Scheme 5.4: Comparison of reduction potentials and reduction scheme of corannulene with lithium, sodium and magnesium.35f
The reduction potential for magnesium is lower than sodium by 0.3 V,\(^3\) which has been shown by solution\(^3\) and solid state studies\(^3\) to only reduce corannulene to the dianion. No further reduction of corannulene to the trianion or tetraanion stage has ever been observed for sodium metal. Corannulene has been reduced with cesium (−3.0 vs. the standard hydrogen electrode) to the trianion.\(^3\) It should be noted here that mixed metals systems of Li/K, Li/Rb, Li/Cs reduce corannulene to the tetraanion, resulting in “metal-rich” heterobimetallic sandwiches.\(^3\) Although, reduction potentials determined by electrochemical cyclic voltammetry (CV) measurements do not always accurately determine the reduction chemistry of a compound, in our experience with corannulene they do give a good guideline, as our prior work with alkali metals illustrates.

Based on our experience with magnesium, we moved to calcium next. The reaction of activated Ca metal with corannulene was performed in THF at room temperature. The green colored solution characteristic of the corannulene monoanion (Figure 5.13, left)\(^3\) has been observed in solution within 2 hours and remained unchanged over the course of a month.

![Figure 5.13](image)

**Figure 5.13** Comparison of corannulene reduced with Na metal and activated Ca metal in THF (left) and UV-vis spectra (right).
We observed that even with extended reaction times (months), heating and controlling/altering the amounts of Ca and activator only a vibrant green reaction mixture was obtained, again indicating that this reaction stops at the first reduction step. We monitored the reaction over the course of 1 month using UV-vis spectroscopy and observed no significant changes in the spectra (Figure 5.14).

![Figure 5.14](image)

**Figure 5.14** UV-vis kinetic study of corannulene reduction with Ca metal in THF.

Theoretically, calcium should be able to reduce corannulene to the dianion stage as it has a reduction potential greater than sodium, $-2.6 \text{ V} \text{ vs. } -2.7 \text{ V} \text{ vs. SHE}$, respectively (Scheme 5.5).\(^3\) However, using the above experimental conditions we have never observed corannulene reduction past the monoanion stage. Based on the color change and UV-vis spectroscopy monitoring, no further reduction has been seen even after months of carrying out the reaction (Figure 5.14).
As we established that corannulene would only be reduced to the monoanion stage with magnesium and calcium metals, at least under the conditions used, we decided to target the isolation of the resulting products.

5.4 Monoanions of Corannulene with the Light Group II Metals

5.4.1 Magnesium Salts

5.4.1.1 \([\text{Mg}^{2+}(\text{THF})_6][\text{(C}_{20}\text{H}_{10}^-)_{2}]\]

The first corannulene monoanion with magnesium countercation has been isolated in the solid state as dark green blocks, in moderate yield from the THF solution layered with hexanes. According to an X-ray diffraction study, the resulting \([\text{Mg}^{2+}(\text{THF})_6][\text{(C}_{20}\text{H}_{10}^-)_{2}]\) product crystallizes in the tetragonal \(P4/nnc\) space group. The X-ray diffraction study revealed the formation of a solvent-separated ion pair (SSIP) comprised of two corannulene monoanions and one THF encapsulated \([\text{Mg}^{2+}(\text{THF})_6]\) cation (Figure 5.15).
Our first attempt at X-ray diffraction data collection did not result in high quality results. The data collection was conducted with theta (max) set at 20 degrees (Mo source), which is much lower than the minimum value of 25 degrees (Mo source) required for publication. The final R1 value of this data set is \(~11\%\) and the structural model is clear and adequate. However, the data is insufficient for a detailed discussion of geometrical parameters, but overall this structure provides a good initial model and confirms the success of our synthetic approach.

**5.4.1.2 [Mg\(^2+\)(diglyme)\(_2\)][(C\(_{20}\)H\(_{10}\)\(^{−}\))\(_2\)]**

In an attempt to collect better X-ray data, the magnesium-induced reduction of corannulene has been conducted again. With the goal of isolating suitable crystals, crystallization conditions were changed to improve the quality of the crystals. The green block-shaped crystals of 14 were re-dissolved in fresh diglyme and the resulting solution was layered with hexanes for slow crystal growth (Scheme 5.6).
Scheme 5.6: Synthetic approach to corannulene monoanion with magnesium.

From the above reaction, the corannulene monoanion with magnesium counterion has been isolated as dark green blocks in moderate yield. According to an X-ray diffraction study, the resulting \([\text{Mg}^{2+}(\text{diglyme})_2][(\text{C}_{20}\text{H}_{10}^-)_2] (15)\) product crystallizes in the monoclinic \(P2_1/c\) space group. The asymmetric unit contains two corannulene monoanions, one magnesium cation and two diglyme molecules. The structural analysis reveals the formation of a SSIP comprised of two corannulene monoanions and one diglyme-encapsulated \([\text{Mg}^{2+}(\text{diglyme})_2]\) cation (Figure 5.16).

Figure 5.16 Asymmetric unit of \([\text{Mg}^{2+}(\text{diglyme})_2][(\text{C}_{20}\text{H}_{10}^-)_2] (15)\).

The full encapsulation of the metal center by solvent molecules in 15 prevents metal binding to the \(\text{C}_{20}\text{H}_{10}^-\) surface, as has been observed before with the lighter Group I metals.
32b-d The acquisition of one electron by corannulene causes slight geometrical deformation of its carbon framework. It should be noted that the hub C–C bond lengths of the “naked” C$_{20}$H$_{10}$\(^-\) anion (av. 1.407(7) Å) are slightly shortened compared to the neutral corannulene bowl (av. 1.415(2) Å) (Table 5.2).\(^{44}\) The C–C spoke (av. 1.400(7) Å) and rim bonds (av. 1.401(7) Å) are noticeably elongated in comparison to those (av. 1.379(2) and 1.381(2) Å, respectively) in neutral corannulene.\(^{44}\)

Table 5.2 Key distances (in Å) for neutral C$_{20}$H$_{10}$ and C$_{20}$H$_{10}$\(^-\) in 15 and in previously reported [Li\(^+\)(DME)$_3$][C$_{20}$H$_{10}$\(^-\)].\(^{32d,36}\)

<table>
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<th>C$<em>{20}$H$</em>{10}$</th>
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<td>1.388(5)–1.462(5)</td>
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<td>0.824(7)</td>
<td>0.841(5)</td>
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</tbody>
</table>

Most notably, the bowl depth of the “naked” C$_{20}$H$_{10}$\(^-\) in 15 is significantly decreased (0.824(7) (av.) vs. 0.875(2) Å for C$_{20}$H$_{10}$).\(^{44}\) This is the greatest flattening of the bowl so far.
observed in the corannulene monoanion without any metal coordination. In comparison, all
“naked” monoanions isolated with alkali metal countercations had only a slight decrease in the
bowl depth (0.850 (av.) vs. 0.875(2) Å for C_{20}H_{10}).{32b-d} See Table 5.2 for bond length comparison
between [Mg^{2+}(diglyme)_{2}][(C_{20}H_{10}^{−})_{2}] and [Li^{+}(DME)_{3}][C_{20}H_{10}^{−}], as well as neutral C_{20}H_{10}.

In the solid state structure of 15, a two-dimensional (2D) network arises from short contacts
between the [Mg^{2+}(diglyme)_{2}] moieties and the corannulene monoanion. Both the concave and
convex faces of the “naked” carbanions are involved in weak intermolecular interactions with
hydrogen atoms of the [Mg^{2+}(diglyme)_{2}] cations along the \( a \) axis, forming a 1D polymeric chain.
The shortest C–H⋅⋅⋅π separations are measured to be 2.683 Å for the concave and 2.674 Å for the
convex carbon surfaces along the \( a \) axis (Figure 5.17).

**Figure 5.17** Space-filling depiction of the solid state packing of 15.

Furthermore, the [Mg^{2+}(diglyme)_{2}] cations in 1D polymeric chain have short contacts
along the \( c \) axis to both the concave and convex faces of the corannulene anions, thus forming a
2D polymeric layer. The shortest C−H···π separations are measured to be 2.588 Å for the concave and 2.550 Å for the convex carbon surfaces along the c axis (Figure 5.17).

In the [Mg^{2+}(diglyme)_{2}] moiety, the Mg^{2+} ions are bound to six oxygen atoms with the Mg···O bond length distances ranging from 2.026(4) to 2.085(4) Å. Those are slightly shorter than the Mg···O bond length distances observed in [Mg^{2+}(diglyme)][(CsH_{5})_{2}], in which only two of the three O-atoms of diglyme are coordinated to the Mg cation, as the cation additionally coordinates two cyclopentadienyl rings.45

5.4.2 Calcium Salt

5.4.2.1 [Ca^{2+}(THF)_{6}][(C_{20}H_{10}^-)_{2}]·2 THF

We then moved to the next Group II metal, calcium, in order to investigate its binding with the curved π-carbon surface of corannulene. From the aforementioned reaction upon layering the THF reaction solution with hexanes, we were able to isolate black block-shaped crystals that were suitable for the crystallographic study. According to an X-ray diffraction analysis of the resulting crystals, the product crystallized in the triclinic P-1 space group. The asymmetric unit contains two corannulene monoanions and two crystallographically independent calcium ions exhibiting 50% occupancy. The Ca1 ion is located on the corner, while the Ca2 is positioned on the face of the primitive triclinic unit cell. Each calcium ion has three crystallographically independent THF molecules. The product also has two interstitial THF molecules; therefore, its overall formula can be written as [Ca^{2+}(THF)_{6}][(C_{20}H_{10}^-)_{2}]·2 THF (16·2 THF). The X-ray diffraction study revealed the formation of a solvent-separated ion pair comprised of two C_{20}H_{10}^- anions and one THF encapsulated [Ca^{2+}(THF)_{6}] cation (Figure 5.18).
The acquisition of one electron by corannulene causes slight geometrical deformation of the bowl framework. Specifically, the hub C–C bond lengths of the “naked” C$_{20}$H$_{10}^{\cdot}$ anion in 12 (av. 1.400(5) Å) are slightly shortened compared to the neutral corannulene bowl (av. 1.415(2) Å) (Table 5.3)$^{44}$. In contrast, the spoke bonds (av. 1.399(5) Å) are noticeably elongated in comparison to C$_{20}$H$_{10}$ (av. 1.379(2) Å). Similarly, the rim C–C bond lengths (av. 1.413(5) Å) in the anion become longer compared to those in neutral corannulene (av. 1.381(2) Å).$^{44}$
Table 5.3 Key distances (in Å) for neutral C_{20}H_{10} and C_{20}H_{10}^{-} in 15 and 16.

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<th>[Mg^{2+}(diglyme)<em>{2}][(C</em>{20}H_{10}^{-})_{2}]</th>
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<td>1.389(5)−1.416(5)</td>
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<td>spoke</td>
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<td>1.388(5)−1.420(5)</td>
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<tr>
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<td>1.404(7)−1.464(8)</td>
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</tr>
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The bowl depth of C_{20}H_{10}^{-} in 16 is notably different for the two crystallographically independent anions (0.738(5) and 0.779(5) Å) with their average of 0.759(5) Å decreased vs. 0.824(7) Å in 15. This is the largest flattening of the bowl observed in the structurally characterized examples of corannulene monoanion isolated without any metal coordination. Remarkably, the bowl depth of 16 is even shallower than the values observed in the corannulene dianion salts with alkali metal coordinated to the surface which range from 0.799 to 0.785 Å.\textsuperscript{36} See Table 5.3 for bond length comparison between [Mg^{2+}(diglyme)_{2}][(C_{20}H_{10}^{-})_{2}] and [Ca^{2+}(THF)_{6}][(C_{20}H_{10}^{-})_{2}], as well as for neutral C_{20}H_{10}.

In the solid state structure, a 2D network arises from short contacts between the [Ca^{2+}(THF)_{6}] (Ca2 and Ca1) cationic moieties and the corannulene monoanion. Along the $a$ axis,
the THF encapsulated Ca2 cation exhibits interactions to the convex face of the corannulene monoanion with the shortest H⋯C distance of 2.679 Å. Also along the \( a \) axis, the THF encapsulated Ca1 ion has interactions to the concave face of the same corannulene monoanion with the shortest H⋯C contact of 2.719 Å (Figure 5.19).

![Space-filling depiction of the solid state packing of 16](image)

**Figure 5.19** Space-filling depiction of the solid state packing of 16. Interstitial THF molecules are omitted for clarity.

Along the \( b \) axis, the THF encapsulated Ca2 cation exhibits interactions to the concave face of the corannulene monoanion with the shortest H⋯C distance of 2.689 Å. Also along the \( b \) axis, the THF encapsulated Ca1 moiety exhibits contacts to the concave face of the same corannulene monoanion with the shortest H⋯C distance of 2.719 Å. (Figure 5.17).

In the [Ca\(^{2+}\)(THF)\(_6\)] part, the Ca\(^{2+}\) ions are bound to six oxygen atoms with the Ca⋯O bond distances ranging from 2.304(3) to 2.350(4) Å. Those are similar to the distances observed in other adducts with polyaromatic anions having calcium counterions solvated by THF molecules.\(^{28}\)
5.5 Conclusions

The synthetic approach based on the use of alkaline earth metals as reducing agents towards curved carbon $\pi$-systems has been developed in our laboratory. The first corannulene monoanions with light alkaline earth metals, magnesium and calcium, have been isolated from THF and diglyme solutions. The resulting products have been studied in solution and solid state, revealing the initial tendencies of these two metals to produce solvent-separated ion pairs. Additionally, these are the first example of “naked” corannulene monoanions showing a great variation of the bowl depth compared with the previously reported alkali metal ions salts. This might be the effect of dicationic moieties that were found to be engaged in multiple intermolecular $\text{C} \cdots \text{H}$ interactions with corannulene anions. However, this effect merits further investigation confirming if this trend persists with the remaining alkaline earth metals.

5.6 Experimental Details

Materials and Methods. All manipulations were carried out using break-and-seal and glove-box techniques under an atmosphere of argon.$^{38}$ Solvents (THF and hexanes) were dried over Na/benzophenone and distilled prior to use. Diglyme and THF-$d_8$ were dried over sodium/potassium alloy and vacuum-transferred. Magnesium and calcium metals were purchased from Strem Chemicals. Corannulene was prepared as described previously$^{46}$ and doubly sublimed at 175 °C prior to use. 1, 2-Dibromoethane was purchased from Sigma Aldrich, prior to use it was dried over sieves and degassed. NMR spectra were measured on a Bruker AC-400 spectrometer at 400 MHz for $^1$H, 100.6 MHz. The UV-vis spectra were recorded on a Thermo Scientific Evolution 300BB spectrometer.
**Monoanion Preparation**

**Synthesis and Crystal Growth of \([\text{Mg}^{2+}(\text{diglyme})_2][\text{C}_{20}\text{H}_{10}^{1-}]_2\) (15)**

To a closed system, corannulene (10 mg, 0.04 mmol, doubly sublimed) and excess of Mg metal (~5 mg, 2.1 mmol) were added. Under argon, 10 mL of freshly distilled THF and 5 μL of 1,2-bromoethane (0.05 mmol) were added to the system. The reaction mixture was initially clear, after 2 hours of stirring, it turned green and became deep green within 4 hours. The reaction mixture was then filtered and concentrated (approx. 5 mL) under reduced pressure. The deep green solution was then layered with hexanes (1 mL) and kept at 10 °C for crystallization. After 4 days small green crystals were observed, the crystals were dried and dissolved in freshly distilled diglyme (1.5 mL). The resulting green solution was then filtered and layered with hexanes (1.0 mL). After two weeks at 10 °C small dark green block crystals were present in 70% yield. ^1H NMR (400 MHz, THF-\(d_8\), 25 °C, ppm): \(\delta = 3.57, 3.48, 3.31\); ^1H NMR (400 MHz, THF-\(d_8\), −60 °C, ppm): \(\delta = 3.54, 3.46, 3.29\). UV-vis (THF, nm): \(\lambda_{\text{max}} = 437, 656, 805, 904\).

**Crystal Structure Determination and Refinement for 15**

Data collection was performed on a Bruker D8 VENTURE X-ray diffractometer with PHOTON 100 CMOS shutterless mode detector equipped with a Cu-target X-ray tube (\(\lambda = 1.54178\ \text{Å}\)) at T = 100(2) K. Data reduction and integration were performed with the Bruker software package SAINT. (version 8.37A)\(^{47}\). Data were corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2).\(^{48}\) The structure was solved by SHELXT\(^{49}\) and refined by full-matrix least-squares procedures using the Bruker SHELXTL (version 2016/6)\(^{50}\) software package. All non-hydrogen atoms (including those in disordered parts) were refined anisotropically. The H-atoms were also included at calculated positions and refined as riders, with
\( U_{\text{iso}}(H) = 1.2 \ U_{\text{eq}}(C) \) and \( U_{\text{iso}}(H) = 1.5 \ U_{\text{eq}}(C) \) for methyl groups. The anisotropic displacement parameters in the direction of the bonds of the whole structure model, except Mg atom, were restrained to be equal with a standard uncertainty of 0.005 Å². They were also restrained to have the same \( U_{ij} \) components, with a standard uncertainty of 0.01 Å².

Crystallographic Data for 15

Empirical formula: \( 2(\text{C}_{20}\text{H}_{10}) \cdot \text{C}_{12}\text{H}_{28}\text{MgO}_{6}, \ M = 793.21, \) monoclinic, \( a = 10.9009(4) \ \text{Å}, \ b = 15.0302(6) \ \text{Å}, \ c = 24.2425(8) \ \text{Å}, \alpha = 90^\circ, \beta = 90.6020(19)^\circ, \gamma = 90^\circ, \ V = 3971.7(3) \ \text{Å}^3, \ P2_1/c, \ Z = 4, \ \rho_{\text{calcld}} = 1.327 \ \text{g/cm}^3, \ \mu = 0.82 \ \text{mm}^{-1}, \ T = 100(2) \ \text{K}, \ \lambda = 1.54178 \ \text{Å}, \ 51402 \) measured intensities \( (6.920^\circ \leq 2\theta \leq 106.274^\circ) \), 4504 unique intensities \( R_{\text{int}} = 0.1081, \ R_1 = 0.0791, \ wR_2 = 0.1362 \) for 2153 intensities with \( I \geq 2\sigma(I) \), \( wR_2 = 0.1672 \) (4504), refinement of 520 parameters against \( |F^2| \) of all unique reflections with hydrogen atoms on calculated position.

Synthesis and Crystal Growth of \( [\text{Ca}^{2+}(\text{THF})_6][(\text{C}_{20}\text{H}_{10}^-)_2] \) (16)

THF (5 mL) was added to a flask containing excess calcium (16 mg, 0.4 mmol) and doubly sublimed corannulene (10 mg, 0.04 mmol) with a catalytic amount (5%) of 1,2-diiodoethane (5.6 mg, 0.02 mmol) for metal activation. Upon activation of the metal, the solution slowly changed to green, after 48 hours of stirring the solution became deep green in color. The reaction mixture was filtered and layered with hexanes (2.0 mL) containing drops of tetrahydropyran (THP). The sealed ampoule was kept at −10 °C. After 72 hours dark green block crystals were present in 70% yield. UV-vis (THF, nm): \( \lambda_{\text{max}} = 440, 655, 802, 904 \).
Crystal Structure Determination and Refinement for 16

Data collection was performed on a Bruker D8 VENTURE X-ray diffractometer with PHOTON 100 CMOS shutterless mode detector equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) at $T = 100(2)$ K. Data reduction and integration were performed with the Bruker software package SAINT. (version 8.37A). Data were corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2). The structure was solved by SHELXT and refined by full-matrix least-squares procedures using the Bruker SHELXTL (version 2016/6) software package. All non-hydrogen atoms (including those in disordered parts) were refined anisotropically. The H-atoms were also included at calculated positions and refined as riders, with $U_{\text{iso}}(H) = 1.2 U_{eq}(C)$. The structural model was a non-merohedral twin with twin law [-1 0 0 0 -1 0 0 0 1] with BASF refined to 0.31509.

Crystallographic Data for 16

Empirical formula: $C_{24}H_{48}CaO_{6} \cdot 2(C_{20}H_{10}) \cdot 2(C_{4}H_{8}O)$, $M = 1117.47$, triclinic, $a = 12.6272(14)$ Å, $b = 13.5286(15)$ Å, $c = 17.5299(19)$ Å, $\alpha = 89.645(3)^{\circ}$, $\beta = 89.937(3)^{\circ}$, $\gamma = 84.026(3)^{\circ}$, $V = 2978.3(6)$ Å$^3$, $P-1$, $Z = 2$, $\rho_{\text{calc}} = 1.246$ g/cm$^3$, $\mu = 0.163$ mm$^{-1}$, $T = 100(2)$ K, $\lambda = 0.71073$ Å, 178620 measured intensities ($6.056^{\circ} \leq 2\theta \leq 55.926^{\circ}$), 14254 unique intensities $R_{\text{int}} = 0.0587$, $R_1 = 0.0658$, $wR_1 = 0.1336$ for 12045 intensities with $I \geq 2\sigma(I)$, $wR_2 = 0.1447$ (14254), refinement of 734 parameters against $|F^2|$ of all unique reflections with hydrogen atoms on calculated position.
5.7 References


SAINT; part of Bruker APEX3 software package (version 2016.9–0): Bruker AXS, 2016.

SADABS; part of Bruker APEX3 software package (version 2016.9–0): Bruker AXS, 2016.
