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Self-assembly of charged corannulene with cesium ions: Always in the bowl

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ABSTRACT

Cesium salts of mono- and doubly-reduced bowl-shaped corannulene have been prepared in the presence of different O-donors and isolated as bulk crystalline solids. Crystallization of corannulene mono-anions with cesium ions from diglyme afforded green blocks of $[Cs(diglyme)^{+}(C_{20}H_{10}^{-})]$ (**1**). Its X-ray structural investigation revealed the formation of a 1D polymer built on simultaneous binding of large cesium ion to the convex and concave faces of the adjacent $C_{20}H_{10}^{\bullet-}$ anions, with each bowl functioning in the rare η^5-*endo*:η^6-*exo* bridging mode. The coordination environment of the Cs^{+} ion is completed by a side-bound diglyme molecule. The cesium salt of corannulene dianion, $C_{20}H_{10}^{2-}$, was crystallized in the presence of dicyclohexano-18-crown-6 ether as $[Cs_2(dc\text{-}18\text{-}crown\text{-}6)_{1.5}^{2+}(C_{20}H_{10}^{2-})]$ (**2**). This product has a discrete linear tetranuclear structure built by aggregation of two terminal *exo*-hub-bound $\{Cs(dc\text{-}18\text{-}crown\text{-}6)(C_{20}H_{10}^{2-})\}^{-}$ anionic moieties with the central $\{Cs_2(dc\text{-}18\text{-}crown\text{-}6)\}^{2+}$ cationic gluing block. The cesium ions of the latter, sharing one crown ether molecule, occupy the concave cavities of the doubly-charged corannulene bowls. As a result, each bowl functions in the symmetric η^5-*endo*:η^5-*exo* bridging mode which has not been previously seen. The bowl depths of the resulting carbanions in **1** and **2** are 0.915(15) Å and 0.852(13) Å, respectively, vs. that of 0.875(2) Å in neutral corannulene.

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Introduction

Reduction of non-planar polyaromatic compounds, structural deformations of the resulting carbanions and their supramolecular aggregation with alkali metal ions have been the focus of extensive investigations over the last 20 years [1]. Besides the broad fundamental interest, these studies are instigated by the discovered ferromagnetic and superconductive properties of metal-intercalated polyarenes [2] and fullerenes [3] as well as by emerging applications of carbonaceous materials for energy storage and conversion [4].

Geodesic polyarenes are known to readily uptake multiple electrons. For example, bowl-shaped corannulene, $C_{20}H_{10}$, which can be considered as one/third of the C_{60}-fullerene, can acquire four electrons owing to its doubly degenerate low-lying unoccupied molecular orbitals [5]. The first detection of negatively charged corannulene was reported back in 1967 [6]. Later, Scott and Rabinovitz with co-workers extensively investigated the *in situ* reduction reactions of various bowl-shaped polyarenes, including corannulene, using a combination of spectroscopic techniques [7]. A recent review by Eisenberg and Shenhar summarizes the results of these investigations [8]. In contrast to the above solution studies, we developed preparation procedures which allow one to isolate crystalline products of multiply-charged corannulene as salts with a variety of alkali metals [9]. We have also accomplished the first X-ray crystallographic characterization of a number of corannulene carbanions, $C_{20}H_{10}^{n-}$ ($n = 1$–4). These structural studies resulted in the correction of the previously proposed supramolecular aggregation model of the tetra-reduced corannulene with lithium ions [10], illustrating the need for a synergistic combination of X-ray diffraction and spectroscopic tools [11]. They also revealed the geometric perturbation of corannulene core upon stepwise electron addition and provided the experimental benchmarks for current theoretical methods [12]. Moreover, structural investigations demonstrated a remarkable face selectivity of corannulene in binding of alkali metal ions [13]. The large cesium ion was found to selectively coordinate to the concave cavity of the mono-reduced corannulene, while smaller alkali metal ions favored *exo*-binding or formation of solvent-separated ion pairs with $C_{20}H_{10}^{\bullet-}$ (Scheme 1) [13].

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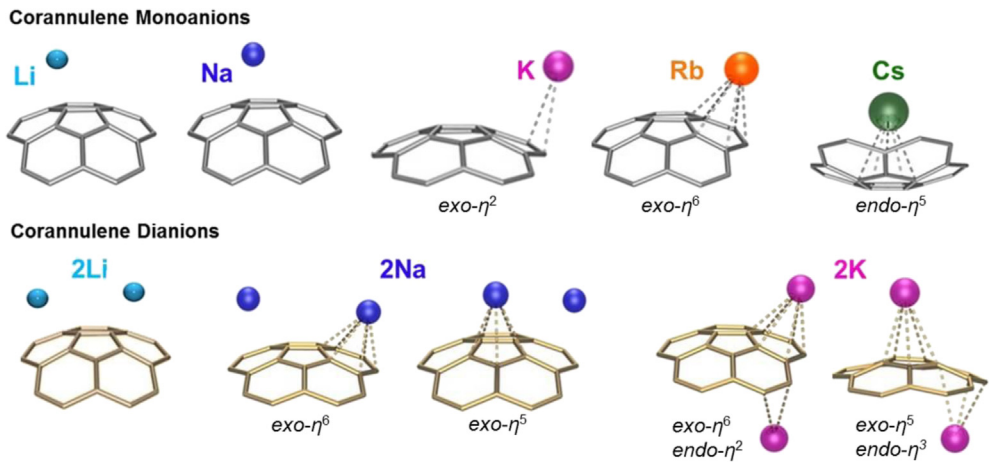


Scheme 1. Binding modes of corannulene mono- and dianions with Group 1 metal ions.

The isolated cesium product, [Cs(18-crown-6)$^+$($C_{20}H_{10}^-$)], was the first *endo*-bound complex of corannulene, as transition metals clearly showed preferential *exo*-coordination to corannulene [14]. Our X-ray data were supported by DFT calculations indicating that concave binding for corannulene bowl is favored for cesium ion only among the Group 1 metals [13a]. The examples of the concave metal placement inside π-bowls, other than sumanene [15], are limited [16].

In order to get further insights on binding of the large cesium ion, we set to investigate its behavior towards $C_{20}H_{10}^{\bullet-}$ and $C_{20}H_{10}^{2-}$ bowls under controlled experimental conditions. It is worth mentioning here that no crystalline products of doubly-charged corannulene with heavier alkali metal congeners have yet been isolated. At the same time, corannulene dianions, crystallized with light alkali metal ions (Li^+–K^+), showed a remarkable variation of metal binding modes in the solid state products (Scheme 1) [13,17]. Herein, we look into the first and second reduction stages of $C_{20}H_{10}$ using cesium metal as a reducing agent. We report two new crystalline cesium salts of $C_{20}H_{10}^{\bullet-}$ and $C_{20}H_{10}^{2-}$ anions and their full characterization by single-crystal X-ray diffraction and spectroscopic techniques.

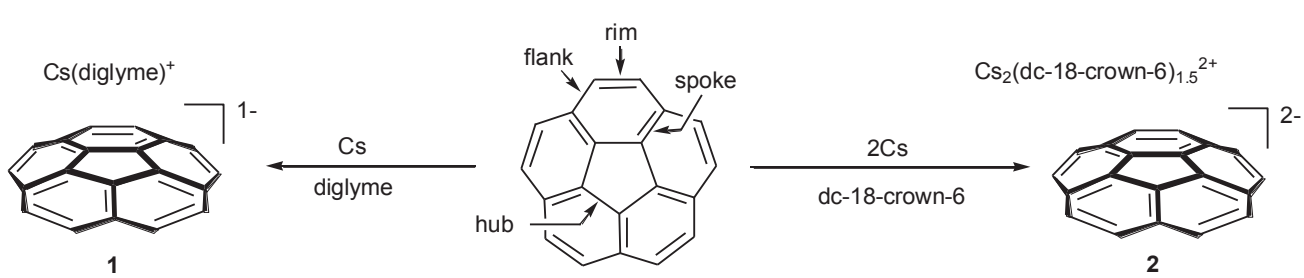
Results and discussion

Based on ^{1}H NMR investigations, it was previously reported that $C_{20}H_{10}$ can be reduced to the tetraanion stage with cesium metal over an extended period of time [18]. In our experience, even with very prolonged time, the highest reduction stage was never achieved with pure cesium based on low-temperature ^{1}H NMR measurements. We observed that addition of excess cesium metal to corannulene in diglyme allows the generation of an intense green color associated with the formation of $C_{20}H_{10}^{\bullet-}$ (Scheme 2), which subsequently undergoes further reduction to form a purple solution of $C_{20}H_{10}^{2-}$. Ultimately, the next reduction stage is observed by appearance of a deep purple-red color associated with the generation of $C_{20}H_{10}^{\cdot 3-}$. These stepwise reduction reactions can be limited to the first and second steps, when the amount of cesium metal is controlled.

Complex **1**, [Cs(diglyme)$^+$($C_{20}H_{10}^-$)], was prepared by the reduction of corannulene in diglyme with 1.5 equivalents of Cs metal and crystallized from the reaction mixture layered with hexanes at 10 °C. It was also found that reducing $C_{20}H_{10}$ to the dianion stage by adding 2.2 equivalents of cesium metal allows the selective formation of $C_{20}H_{10}^{2-}$. Its crystallization from diglyme in the presence of dc-18-crown-6 ether upon layering with THF/hexanes at 10 °C afforded **2**, [Cs_2(dc-18-crown-6)$_{1.5}^{2+}$($C_{20}H_{10}^{2-}$)].

The UV–vis spectra of **1** and **2** dissolved in diglyme show maxima at 658 nm for the monoanion and 508 nm for the dianion of corannulene. The maximum observed for the monoanion is bathochromically shifted in comparison to the wavelength of the *in situ* generated species, [Li(THF)$_n^+$][($C_{20}H_{10}^-$)] (648 nm), known to exist as a solvent-separated ion pair [7a]. The maximum wavelength observed for **2** is comparable to that of corannulene dianion generated with the use of light alkali metals previously (Table S1). The ESR spectrum of **1** dissolved in THF at room temperature (Fig. 1) is more complex than spectra observed for the corannulene monoanion with solvent-separated Li^+ or Na^+ ions but similar to that of the reported concave-bound cesium product [13a]. This again indicates that cesium ions remain bound to the $C_{20}H_{10}^{\bullet-}$ bowl in solution.

An X-ray diffraction study of **1** showed the symmetric insertion of the cesium ion capped by diglyme into the concave cavity of the mono-reduced corannulene in [Cs(diglyme)$^+$($C_{20}H_{10}^-$)] (Fig. 2a). The resulting Cs···C η^5-*endo* contacts (3.349(15)–3.425(17) Å) are



Scheme 2. Preparation of **1** and **2**.

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