

# Convex and Concave Encapsulation of Multiple Potassium Ions by Sumanenyl Anions

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## Supporting Information

**ABSTRACT:** Herein we report the novel complex consisting of di- and tripotassiumsumanenide,  $K_7(C_{21}H_{10}^{2-})_2(C_{21}H_9^{3-}) \cdot 8THF$  (**2**), which was prepared by the treatment of sumanene ( $C_{21}H_{12}$ , **1**) with excess K metal in THF. The X-ray structural determination revealed unique self-assembly of six potassium ions sandwiched by convex faces of two sumanenyl trianions in addition to novel interaction involving all 15 carbon atoms of three Cp-like moieties on the concave surface of the sumanenyl bowls outside the sandwich. The unique structural features of **2** are rationalized with the help of DFT calculations.

Cyclopentadienyl (Cp) ligand is one of the most important ligands, and the Cp metal complexes have given a tremendous impact in the field of organometallic chemistry. A milestone in this field is the synthesis of ferrocene<sup>1</sup> followed by the preparation of numerous Cp transition metal complexes. In contrast, the studies of Cp alkali metal complexes are still relatively limited compared to transition metal complexes although their history is much older.<sup>2</sup> Concerning the binding in alkali metal complexes, Cp coordinates mainly in an  $\eta^5$ -fashion.<sup>3</sup> Coulombic force predominates bonding over the covalent character, inducing the longer M–Cp bond distances. The structures of Cp alkali metal complexes can be broadly classified by six major types (A–F, Figure 1a), which are well summarized in several reviews.<sup>3,4</sup> In addition to discrete mononuclear (A–C) and dinuclear products (D), multinuclear sandwich polymers (E and F) are often observed in Cp alkali metal complexes. Notably, the self-assembly can be controlled by functionalization of the Cp-based ligands<sup>3–6</sup> and it is expected that sophisticated ligand design could lead to the discovery of new classes of organometallic supramolecules.

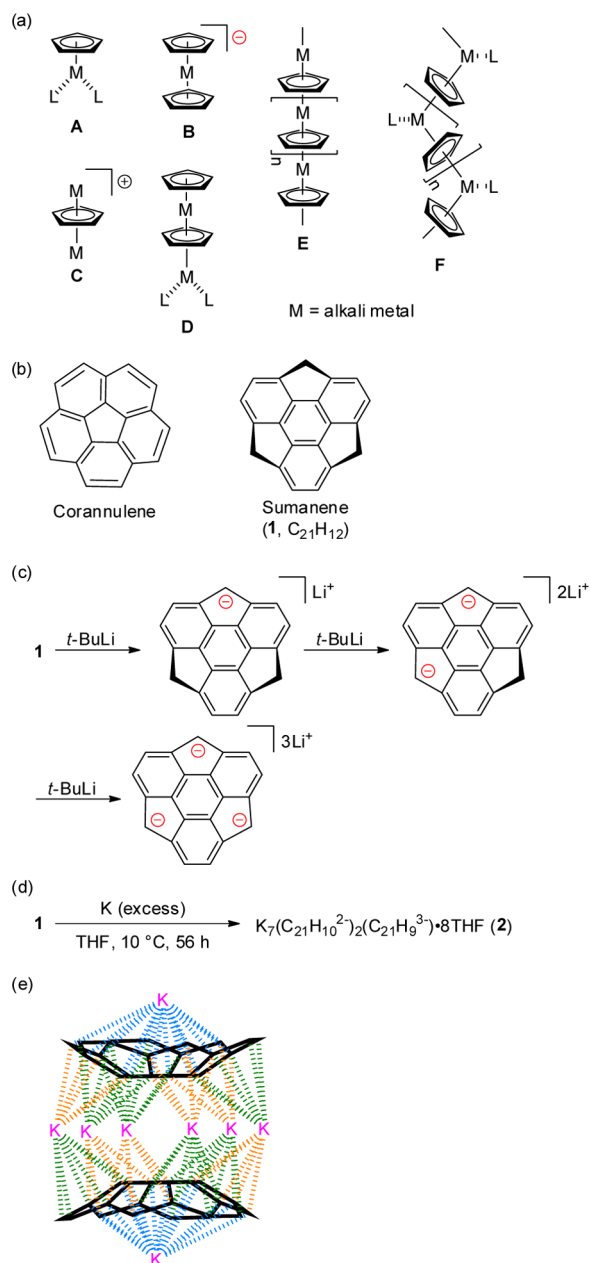
On the other hand, metalation of curved carbon  $\pi$  surfaces is of fundamental interest in organometallic and coordination chemistry. Such complexes have been studied since the discovery of fullerenes. Among these studies, bowl-shaped  $\pi$ -conjugated molecules (open geodesic polyarenes,<sup>7</sup> buckybowl,<sup>8</sup> or  $\pi$  bowls; here we use  $\pi$  bowls) are especially interesting since their *exo*- and *endo*- $\pi$  surfaces are both available for coordination. So far,  $\pi$  bowl complexes of various transition and alkali metals in a variety of coordination modes have been prepared and characterized.<sup>6,9</sup>

Study on alkali metal complexes started from the lithiation of the  $C_5$ -symmetric fullerene fragment, corannulene (Figure 1b) by Rabinovitz, Scott, and co-workers in 1992.<sup>10</sup> The doubly degenerate LUMO levels of corannulene allow it to accept up to four electrons to form an aromatic Cp anion suspended by an aromatic annulenyl trianion. The resulting corannulene tetraanion assembles into sandwich-type supramolecular aggregates with encapsulated lithium ions based on NMR investigations.<sup>11</sup> In 2011, we have revealed the triple-decker structure consisting of five lithium cations jammed between two corannulene tetraanions using X-ray crystallographic analysis.<sup>12</sup> Furthermore, the first mixed alkali metal supramolecular aggregates including up to six alkali metals sandwiched between two corannulene tetraanions have recently been reported.<sup>13</sup> The observed multi-electron reduction properties and unique binding abilities<sup>13,14</sup> of curved carbon-rich polyarenes are of great potential for applications in superconductive materials and lithium-ion batteries.<sup>15</sup> We have also investigated the coordination chemistry of the  $C_3$ -symmetric fullerene fragment, sumanene (**1**) and reported its first concave-bound complex,  $[CpFe(\text{sumanene})]PF_6$ .<sup>16,17</sup> The characteristic structural feature of **1** is three  $sp^3$  hybridized carbon atoms at the benzylic positions, which is in contrast to the structure of corannulene. We have revealed that sumanenyl mono-, di-, and trianions can be generated selectively by treatment with a strong base like *t*-BuLi (Figure 1c)<sup>18</sup> and have recently synthesized the convex-bound mono- and trinuclear zirconocene complexes using such Cp-like anions.<sup>16d</sup>

Herein we undertake the first investigation of the reaction of **1** with alkali metals. We are strongly intrigued by the unique structure of bowl-shaped sumanenyl trianion,  $C_{21}H_9^{3-}$  ( $1^{3-}$ ), consisting of triply fused Cp-like anions as a novel ligand for alkali metal binding. In the present communication, we report the complex consisting of di- and tripotassiumsumanenide,  $K_7(C_{21}H_{10}^{2-})_2(C_{21}H_9^{3-}) \cdot 8THF$  (**2**), which was prepared by the treatment of **1** with excess K metal in THF (Figure 1d). In the X-ray crystal structure, not only remarkable self-assembly of six potassium ions sandwiched by convex faces of two sumanenyl trianions is found but also novel interaction by all 15 carbon

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**Figure 1.** (a) Structural classification of Cp alkali metal complexes. (b) Corannulene and sumanene (**1**). (c) Selective generation of sumanenyl mono-, di-, and trianions. (d) Synthesis of di- and tripotassiumsumanenide K<sub>7</sub>(C<sub>21</sub>H<sub>10</sub><sup>2-</sup>)(C<sub>21</sub>H<sub>9</sub><sup>3-</sup>)·8THF (**2**). (e) The convex and concave encapsulation of multiple potassium ions by sumanenyl trianion extracted from the X-ray crystallographic structure of **2**. Blue dotted line, concave binding; orange dotted line, η<sup>5</sup> coordination; green dotted line, η<sup>6</sup> coordination.

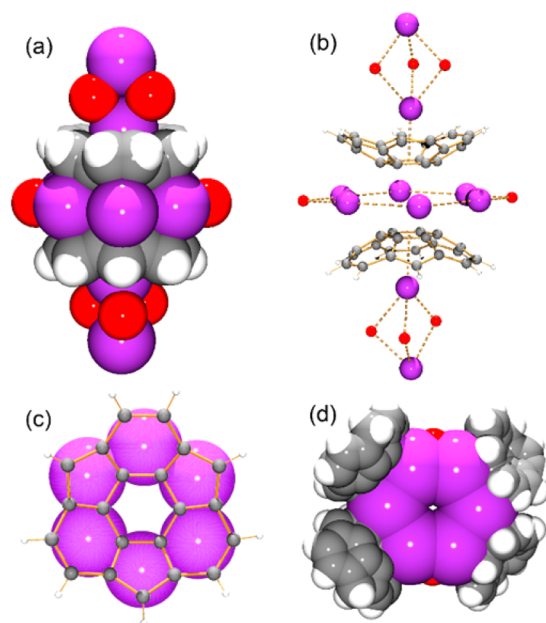
atoms of three Cp-like moieties on the concave surface of **1**<sup>3-</sup> is revealed (Figure 1e).

When sumanene (**1**) was reacted with excess K metal in THF at room temperature, a red suspension was formed within 12 h. This reaction was stopped after 56 h (see Supporting Information for more details). The resulting mixture was filtered, and the red filtrate was layered with hexanes to afford dark-red blocks of K<sub>7</sub>(C<sub>21</sub>H<sub>10</sub><sup>2-</sup>)(C<sub>21</sub>H<sub>9</sub><sup>3-</sup>)·8THF (**2**) in moderate yield in ca. 3 days at 10 °C (Figure 1d). In attempt to push the reduction further, we prolonged the reaction time up to 5 days or used gentle heat (~50 °C) combined with extended time

periods. Despite these efforts, all these reactions stop at the same stage, affording the same red suspension. The formation of **2** has been confirmed by single-crystal X-ray diffraction analysis on multiple occasions as the only crystalline product of these reactions.

An X-ray diffraction characterization<sup>19</sup> of **2** revealed that its crystal structure consists of sumanenyl di- and trianions crystallized with K<sup>+</sup> counterions (Figure S1). There are two crystallographically unique dianions (one disordered) and one trianion of the corresponding sumanenyl ligands, along with seven potassium ions and eight THF molecules in the asymmetric unit to give the overall formula as K<sub>7</sub>(C<sub>21</sub>H<sub>10</sub><sup>2-</sup>)<sub>2</sub>(C<sub>21</sub>H<sub>9</sub><sup>3-</sup>)·8THF.

Interestingly, the highly charged sumanenyl trianions self-assemble into a novel organometallic sandwich (Figure 2a,b)



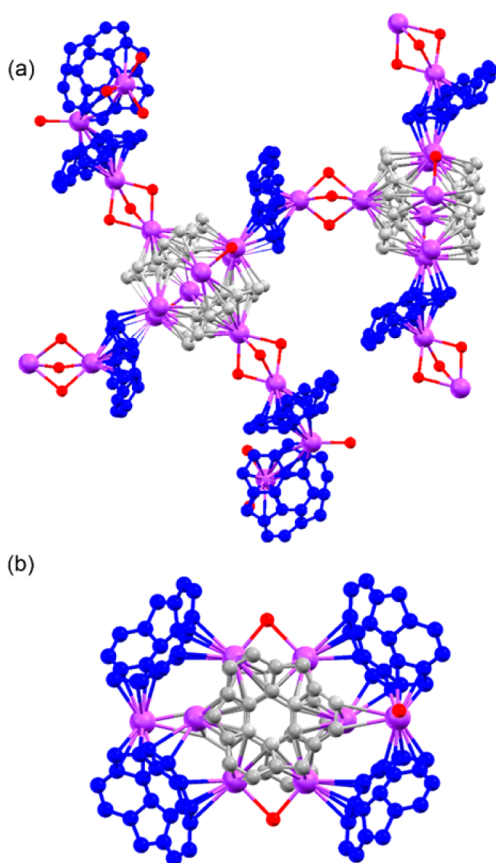
**Figure 2.** (a) Space filling and (b) ball-and-stick representations of a sandwich built by sumanenyl trianions with K<sup>+</sup> ions (purple). O atoms of THF are red, all H and C atoms of THF are removed for clarity. (c) Space-filling model of the K<sub>6</sub>-core of the sandwich (top-view) overlaid with one sumanenyl trianion and (d) surrounded by four sumanenyl dianions and two THF molecules (only O atoms are shown).

encapsulating six potassium cations (Figure 2c) between the convex faces of two triply charged bowls. The K<sup>+</sup>···C distances for the sandwiched potassium ions range over 2.967(5)–3.343(5) Å (K<sup>+</sup>···C<sub>η<sup>5</sup></sub> distances, 2.967(5)–3.275(5) Å, and K<sup>+</sup>···C<sub>η<sup>6</sup></sub> distances, 3.141(5)–3.343(5) Å). Notably, these K<sup>+</sup>···C separations are comparable to those measured in the potassium salt of the corannulene dianion (3.052(4)–3.378(4) Å).<sup>20</sup> The distances between K<sup>+</sup> ions within the belt comprised of six metal ions are 3.712(5) and 3.771(5) Å. For comparison, the K<sup>+</sup>···K contacts in the recently isolated mixed metal sandwiches formed by corannulene tetraanions, [(C<sub>20</sub>H<sub>10</sub><sup>4-</sup>)(LiK<sub>5</sub>)<sup>6+</sup>(C<sub>20</sub>H<sub>10</sub><sup>4-</sup>)]<sup>2-</sup> and [(C<sub>20</sub>H<sub>10</sub><sup>4-</sup>)(Li<sub>3</sub>K<sub>3</sub>)<sup>6+</sup>(C<sub>20</sub>H<sub>10</sub><sup>4-</sup>)]<sup>2-</sup> are longer (3.858–4.485 and 4.310 Å, respectively).<sup>13a</sup>

The internal cavity of each bowl at the outside of the triple-decker sandwich is filled by an additional potassium ion that exhibits interactions with 15 carbon atoms of three Cp-like moieties on the concave surface of sumanenyl trianion (Figure 1e). The interaction of this K<sup>+</sup> ion with three five-membered

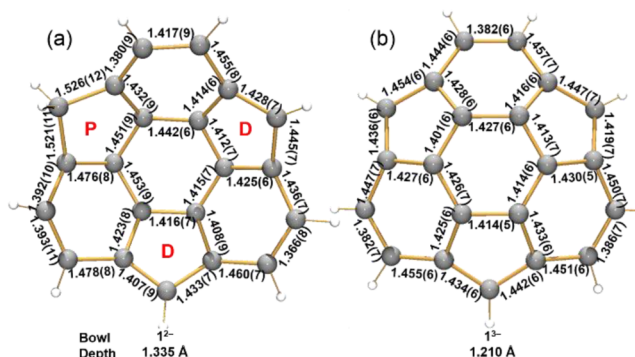
rings of  $1^{3-}$  is slightly asymmetric with the distances to the centroids measured at 2.906(5), 2.912(5), and 3.081(5) Å. The corresponding K...C distances for these three five-membered rings range over 2.945(4)–3.386(5), 2.942(4)–3.395(5), and 3.074(4)–3.615(5) Å. On average, they are shorter than average of two K...C distances to the rim of the six-membered rings of  $1^{3-}$  (3.543(5), 3.747(5), and 3.775(5) Å).

Each concave-trapped  $K^+$  ion has three coordinated THF molecules, which are shared with the neighboring  $K^+$  ion (Figure 2b). The resulting  $[K_2(THF)_3]^{2+}$  dications act as bridges connecting the triple-decker sandwiches in one direction in the solid state structure of **2**. Additionally, at the sandwich periphery the encapsulated potassium ions exhibit close contacts (3.006(5)–3.270(5) Å) with sumanenyl dianions and two THF molecules (Figure 2d), expanding the solid state structure into other dimensions (Figure 3).



**Figure 3.** Fragments of an extended solid state structure of **2** based on sumanenyl di- (blue) and trianions (gray) with  $K^+$  ions (purple). Only O atoms of THF are shown (red). All H atoms are removed for clarity.

The X-ray crystallographic characterization of **2** provides the first structural information on the  $C_{21}H_{10}^{2-}$  dianion ( $1^{2-}$ ) and allows us to compare the geometrical parameters of sumanenyl di- and trianions (Figure 4). The formation of both di- and trianions is accompanied by a noticeable curvature increase of the bowl core (Figures S2 and S3). The average bowl depth calculated for the nondisordered  $1^{2-}$  anion is 1.335 Å vs 1.115 Å for neutral  $C_{21}H_{12}$  bowl.<sup>18</sup> The sumanenyl trianion in **2** is more shallow (1.210 Å) than dianion, probably as a result of push–pull effects of multiple metals coordinated inside and outside of the bowl.

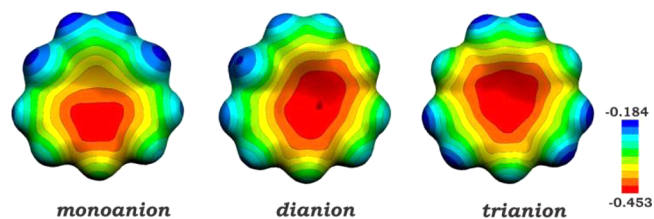


**Figure 4.** Ball-and-stick representation of sumanenyl di- (a) and trianion (b) with corresponding bowl depths and C–C distances (in Å).

Considering other geometrical changes of the sumanenyl trianion: average rim C–C bond distances within the five-membered rings become significantly shorter (1.439(7) Å) than those in the parent sumanene (1.547(4) Å), while spoke C–C bond distances become longer (1.423(7) Å vs 1.395(4) Å). The corresponding hub C–C bonds decrease from 1.430(4) Å in neutral sumanene (**1**) to 1.409(7) Å in  $1^{3-}$ . The rim C–C bonds of peripheral six-membered rings are shortened, while all other C–C bond are elongated.

In contrast to the sumanenyl trianion, the dianion has two types of five-membered rings that are clearly different (those are abbreviated as P and D, Figure 4). The rim C–C bonds of  $1^{2-}$  are much shorter in the deprotonated (D-type) Cp-rings (aver. 1.428(7) Å) vs 1.524(12) Å in the protonated (P-type) ring, but they are all shorter than those in sumanene (1.547(4) Å, Figure S3), indicating some charge redistribution over the doubly charged bowl. The spoke C–C bond distance in the five-membered rings of  $1^{2-}$  is different, too: 1.418(7) Å vs 1.454(9) Å (for D and P rings, respectively), but they are longer than those in neutral sumanene (1.395(4) Å). Overall, the geometric changes for sumanenyl dianion follow the trends observed more clearly for trianion.

In order to provide better understanding of the unique structural features of the title product **2**, theoretical modeling at the DFT level of theory was performed for mono-, di-, and trianions of sumanene (see Supporting Information). In contrast to corannulene anions, where charge is fully delocalized over the surface, the  $C_{21}H_{11}^-$  and  $C_{21}H_{10}^{2-}$  species show remarkable localization of the negative charge in the deprotonated five-membered rings (Figure 5, for NBO atomic charge distribution see Supporting Information). This finding is in excellent agreement with coordination behavior of sumanenyl dianions, observed in the X-ray crystal structure of **2**. The latter showed that only two out of three five-membered rings are active in interactions with  $K^+$  ions (Figure 3b). At the same time, the negative charge in  $C_{21}H_9^{3-}$  is completely delocalized over the



**Figure 5.** Molecular electrostatic potential (MEP) maps of sumanenyl anions.



bowl core. This makes sumanenyl trianion very similar to tetraanions of corannulene, for which the formation of sandwich aggregates having alkali metal belts symmetrically encapsulated between two highly charged polyaromatic decks was experimentally confirmed.<sup>12,13</sup> As consequence of such delocalization in  $C_{21}H_9^{3-}$ , there should be no preference given to any site of the sumanene core when interacting with alkali metal cations. The staggered mutual orientation of two sumanene bowls and symmetric encapsulation of six  $K^+$  ions in the sandwich aggregates found in crystal structure of **2** (Figure 2) clearly supports this conclusion.

In conclusion, the first isolated product of sumanene metalation with potassium reveals the strong tendency of the sumanenyl trianions to self-assemble in the solid state forming a novel triple-decker organometallic sandwich with six  $K^+$  ions encapsulated between the convex faces of two bowls. This remarkable supramolecular product also exhibits a rare involvement of all 15 C atoms of three Cp-rings on the concave bowl surface of  $1^{3-}$  in metal binding. This work provides the first demonstration of an outstanding ability of highly charged sumanenyl trianion to bind multiple metal ions on the concave and convex surfaces, opening the door to the expansion of organometallic chemistry of this unique bowl.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06662.

Experimental details,  $^1H$  NMR data, X-ray structural information (PDF), and calculation details CIF file for **2** (CIF)

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### Notes

The authors declare no competing financial interest.

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