An unsolvated buckycatcher and its first dianion†

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The X-ray crystallographic study of C_{60}H_{28} consisting of two tethered corannulene bowls revealed a unique solid-state packing based on tight convex–concave π–π interactions. The controlled reduction of C_{60}H_{28} resulted in the isolation and structural characterization of its dianion in the form of the rubidium salt that shows an entrapment of counterions by an anionic pincer.

Design of extended π-systems utilizing bowl-shaped polyarenes (also known as buckybowl or fullerene fragments) as functional building units has received increased attention in recent years. The length and nature of the linkage between the curved fragments is varied to alter their electronic coupling and supramolecular behaviour and to give new carbon-rich compounds with novel functions. Thus, utilizing complementarity of the concave surfaces of buckybowl and the convex surfaces of fullerenes, the first efficient molecular receptors for fullerenes have been synthesized by Sygula’s group by employing one of the smallest buckybowl, corannulene, as a pincer.3

A buckycatcher (1, Scheme 1), constructed from the tetrabenzo-cyclooctatetraene tether and two corannulene pincers, was shown to exhibit a remarkable affinity toward both C_{60} and C_{70} in the solid state as well as in toluene solutions.3b,c The encapsulation affinity of 1 and its analogue with a saturated linker between two corannulene moieties was further shown by trapping of N@C_{60} and smaller organic molecules, as evidenced by structural investigations. However, until now the solid-state structure of a neat buckycatcher has remained unknown.

The addition of extra electrons to polyarenes is known to serve as an effective method to alter their chemical and physical properties.7 In contrast to the structural investigations of planar polyarene anions and the more recent crystallographic reports on corannulene anions in the form of their alkali metal ion salts,7 the related solid-state studies on other curved polyarenes with an open carbon surface are limited only to the reduced fragment of nanotubes.10 In this work we report the first successful crystallographic investigation of the dianion of 1 in the form of its rubidium salt as well as of the parent unsolvated buckycatcher.

For the crystal growth of 1 we selected a convenient and efficient gas-phase deposition procedure11 to avoid the encapsulation of solvent molecules into the crystal lattice of 1, always observed upon crystallization from the solution.12 A very slow deposition of 1 at 300 °C in vacuo over two months afforded the yellowish crystals of C_{60}H_{28} without any guest molecules.

The X-ray crystallographic study13 of 1 revealed the formation of dimeric subunits of two concave–concave conformers14 of 1 geared in a head-to-head fashion by a pair of concave–convex π–π stacked corannulene pincers from two neighbouring molecules (Fig. 1).

The linkage of corannulene fragments with a tetrabenzyocyclooctatetraene tether in 1 results in the significant elongation of rim and flank bonds at the site of fusion (1.442(2) Å vs. 1.376(2)–1.388(2) Å and 1.472(2) Å vs. 1.439(2)–1.447(2) Å, respectively). The remaining C–C bonds and bowl depths (0.85 and 0.90 Å) are almost equidistant compared with those measured in corannulene.15 The intramolecular separation between the centroids of the five-membered rings in 1 (8.7 Å) is significantly smaller than in its adducts with fullerenes.

Scheme 1 Buckycatcher 1 (corannulene moieties are shown in blue) and its controlled rubidium reduction with the formation of salt 2.
(11.3–11.5 Å). This shows the flexibility of 1 in adapting its geometry for the effective trapping of sizeable guest molecules.

The open space between two corannulene arms of C_{60}H_{28} in the crystal is occupied by the corannulene fragment of a neighbouring molecule (Fig. 1c). The resulting centrosymmetric dimer is glued by tight convex-concave π···π contacts between each pair of corannulene bowls (3.6–3.9 Å). Similar interactions were previously observed in the crystals of curved polyarenes with deeper bowls and in the functionalized corannulene cations. The dimers in 1 are additionally linked into a 2D network by convex–convex interactions of the pincer bowls (3.3–3.8 Å) as well as by weaker contacts between the naphthalene rings of a linker (3.5–3.8 Å). The H-atoms of the remaining benzene rings in a linker show intermolecular C–H···π T-shape interactions with the adjacent six-membered rings (Fig. 1c). The corresponding shortest H···C and H···C_{centroid} separations (2.7 and 2.6 Å, respectively) are typical for the intermolecular contacts of this type observed in buckybowls.

In the next step, the reduction of 1 with alkali metals has been studied. We have seen that the addition of the group 1 metals readily generates an intense green solution followed by the formation of a purple solution in a fashion similar to that observed during the first reduction steps of corannulene. Higher reduction stages are observed upon a prolonged reaction time and can be detected by UV-vis spectroscopy (see ESI† for details). Although we were unable to crystallize the highly reduced products so far, the controlled reduction of 1 to the dianion (Scheme 1) and its subsequent crystallization as the rubidium salt (ESI† Scheme S2) have been accomplished. The reduction of C_{60}H_{28} with 2.5 eq. of rubidium metal in THF in the presence of the 18-crown-6 ether gave the product [Rb₃(THF)₂−(18-crown-6)(C_{60}H_{28})] with close Rb–OTHF bond lengths 2.877(5) Å and 3.463(9) Å, whereas the Rb–O_{crown} separations fall in the range of 2.725(9)–2.904(9) Å.

The Rb1/Rb2 counterions are sandwiched between the convex faces of corannulene moieties with a notable shift to their bowl perimeters (Fig. 2b). The shortest Rb···C distances measured are 3.308(5)–3.602(5) Å, whereas the remaining exo-contacts between the cation and C-atoms of the benzene ring are significantly longer. Similar binding with close Rb···C distances was observed in the rubidium salt of the corannulene monoanion, [Rb(18-crown-6)(C_{60}H_{28})] This sandwiching of rubidium cations between diatoms in the crystal lattice of 2 led to the formation of zigzag polymeric chains, propagating in the c-direction (Fig. 2a).

The dianion in 2 shows a concave–concave orientation of corannulene fragments, similarly to a neutral ligand (Fig. 3a). However, the intramolecular C_{centroid}···C_{centroid} intercentroid distance (11.8 Å) is notably larger in 1⁻ than in 0 (8.7 Å) and is close to that measured in the adducts of 1 with fullerenes (11.3–11.5 Å). This can be explained by trapping of a sizable cationic guest and/or electrostatic repulsion of negatively charged arms. The geometry of 1⁻ is beneficial for reception of a large guest molecule, as observed by encapsulation of the [Rb(18-crown-6)(THF)]⁺ cation between the two concave corannulene surfaces in 2 (Fig. 3b). The [Rb(18-crown-6)(THF)]⁺ ion, trapped by the dianion, shows the set of C···H···π interactions with the interior surface of 1⁻. The corresponding shortest H···C distance is 2.8 Å. We have recently demonstrated that the C–H(crown)···π interactions
with a polycyclene surface can provide a significant contribution to the total bonding energy in the [Rb(crown)-polyarene] system that can be even larger than the metal binding.

The UV-vis spectra of the C_{60}H_{28}^{2-} anion in THF show that the presence of crown ether results in a hypsochromic shift (9 nm) of the most intense absorbance maxima (ESI, Fig. S4). This can also be related to the association of crown ether with corannulene moieties of the diions via C-H-crown-π interactions existing in solution.

The addition of two electrons to the buckycatcher along with the coordination of rubidium ions resulted in the flattening of the corannulene cores (bowl depths 0.79/0.90 Å in 1–1', whereas the C-C bonds were only slightly affected (Table 1). It should be mentioned that the bowls in 1–1' are noticeably flatter than in the corannulene monoanion (0.85 Å).

In summary, we have isolated and structurally characterized the first anion of the C_{60}H_{28} buckycatcher as well as crystallized the parent molecule under solvent-free conditions without any extra-aneous molecules. This carbon-rich compound in its neutral and anionic forms exhibits a sufficient flexibility required for a versatile host, as it can readily adjust its pincer opening according to the size of the encapsulated guests. While the flexibility of the buckycatcher has been previously postulated based on computational studies, we provide the first experimental evidence for the remarkable adjustable nature of the tether of 1. This study expands on the coordination and supramolecular limits of carbon-rich aromatic receptors and opens new perspectives for investigation of their highly reduced forms and aggregates with different counterions.

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Notes and references


12 A. Sygula, in progress.

13 C_{60}H_{28}, M = 748.82, triclinic, space group PI, a = 8.9807(3) Å, b = 14.1790(4) Å, c = 15.1646(4) Å, α = 110.65(1)°, β = 102.809(1)°, γ = 110.367(1)°, V = 1788.10(9) Å^3, Z = 2, μ = 0.605 mm^-1, F(000) = 776, T = 100(2), 26 110 reflections measured, 6486 unique (R(int) = 0.0257), R1 = 0.0374, wR2 = 0.0930 for I > 2σ(I). CCDC 973696.

14 Previous computational studies located four distinct gas-phase conformers of 1 with very similar energies (ref. 4).


20 C_{54}H_{16}O_{15}Rb_{2}, M = 1700.75, triclinic, space group PI, a = 9.3921(2) Å, b = 16.1731(3) Å, c = 28.6015(5) Å, α = 80.385(1)°, β = 89.767(1)°, γ = 80.089(1)°, V = 4216.81(14) Å^3, Z = 2, μ = 2.048 mm^-1, F(000) = 1780, T = 100(2), 56 730 reflections measured, 14310 unique (R(int) = 0.0663), R1 = 0.0655, wR2 = 0.1739 for I > 2σ(I). CCDC 973695.
