

An unsolvated buckycatcher and its first dianion†

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The X-ray crystallographic study of C₆₀H₂₈ consisting of two tethered corannulene bowls revealed a unique solid-state packing based on tight convex–concave π–π interactions. The controlled reduction of C₆₀H₂₈ 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 buckybawls or fullerene fragments¹) 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.² Thus, utilizing complementarity of the concave surfaces of buckybawls 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 buckybawl, 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 C₆₀ and C₇₀ in the solid state as well as in toluene solutions.^{3a,4} The encapsulation affinity of **1** and its analogue with a saturated linker between two corannulene moieties was further shown by trapping of N@C₆₀⁵ and smaller organic molecules,⁶ as evidenced by structural investigations. However, until now the solid-state structure of a neat buckycatcher has remained unknown.

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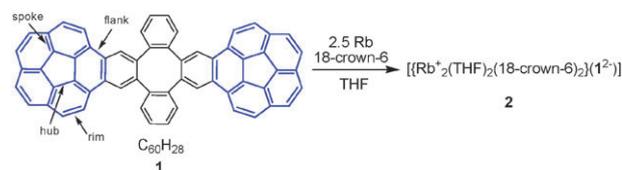
† Electronic supplementary information (ESI) available: Synthetic procedure, X-ray diffraction data and refinement details, and UV-vis and mass spectra. CCDC 973695 and 973696. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc49451a

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 anions⁸ and the more recent crystallographic reports on corannulene anions in the form of their alkali metal ion salts,⁹ 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 C₆₀H₂₈ 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 tetrabenzo-cyclooctatetraene 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**.

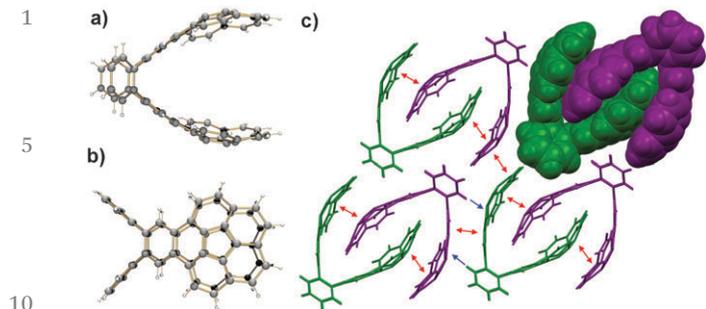


Fig. 1 Side (a) and top (b) views of **1** along with the fragment of its polymeric arrangement ((c) red and blue arrows show, respectively, $\pi \cdots \pi$ and $C-H \cdots \pi$ contacts, one dimer is depicted using a space-filling model).

(11.3–11.5 Å).^{3a,4} 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 $\pi \cdots \pi$ 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 bowls¹⁶ and in the functionalized corannulene cations.¹⁷ 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 $C-H \cdots \pi$ T-shape¹⁸ interactions with the adjacent six-membered rings (Fig. 1c). The corresponding shortest $H \cdots C$ and $H \cdots C_{6(\text{centroid})}$ separations (2.7 and 2.6 Å, respectively) are typical for the intermolecular contacts of this type observed in buckybowls.¹⁶

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.^{9a,19} 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 $[Rb^+_2(THF)_2(18\text{-crown-6})_2(1^{2-})]$ (**2**) which was isolated as a dark green air- and moisture-sensitive solid. The quenching of the solution of **2** with D_2O affords the dideuterio derivative as the major product ($m/z = 752$) (ESI†, Fig. S5), providing the evidence for the existence of dianionic species in the THF solution.

Single crystals of **2** were grown from the THF solution by layering with hexanes at 10 °C as dark-green long needles. Their X-ray diffraction study²⁰ revealed the presence of two types of rubidium ions, Rb1/Rb2 and Rb3 (Fig. 2a). Both cations bear 18-crown-6 ether molecules coordinated by all six O-sites. The apical coordination positions of the Rb3 ions located within the internal cavities of 1^{2-} are additionally occupied by two THF molecules. The corresponding $Rb3 \cdots O_{THF}$ bond lengths are 2.877(5) Å and 3.463(9) Å, whereas the $Rb \cdots O_{\text{crown}}$ 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 perimeter (Fig. 2b). The shortest $Rb \cdots C$ 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 (3.833(5)–4.012(5) Å). Similar binding with close $Rb \cdots C$ distances was observed in the rubidium salt of the corannulene monoanion, $[Rb^+(18\text{-crown-6})(C_{20}H_{10}^-)]$.^{9f} This sandwiching of rubidium cations between dianions 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 $C_5 \cdots C_5$ intercentroid distance (11.8 Å) is notably larger in 1^{2-} than in 1^0 (8.7 Å) and is close to that measured in the adducts of **1** with fullerenes (11.3–11.5 Å).^{3a,4} This can be explained by trapping of a sizable cationic guest and/or electrostatic repulsion of negatively charged arms. The geometry of 1^{2-} is beneficial for reception of a large guest molecule, as observed by encapsulation of the $[Rb(18\text{-crown-6})(THF)_2]^+$ cation between the two concave corannulene surfaces in **2** (Fig. 3b). The $[Rb(18\text{-crown-6})(THF)_2]^+$ ion, trapped by the dianion, shows the set of $C-H \cdots \pi$ interactions with the interior surface of 1^{2-} . The corresponding shortest $H \cdots C$ distance is 2.8 Å. We have recently demonstrated that the $C-H_{(\text{crown})} \cdots \pi$ interactions

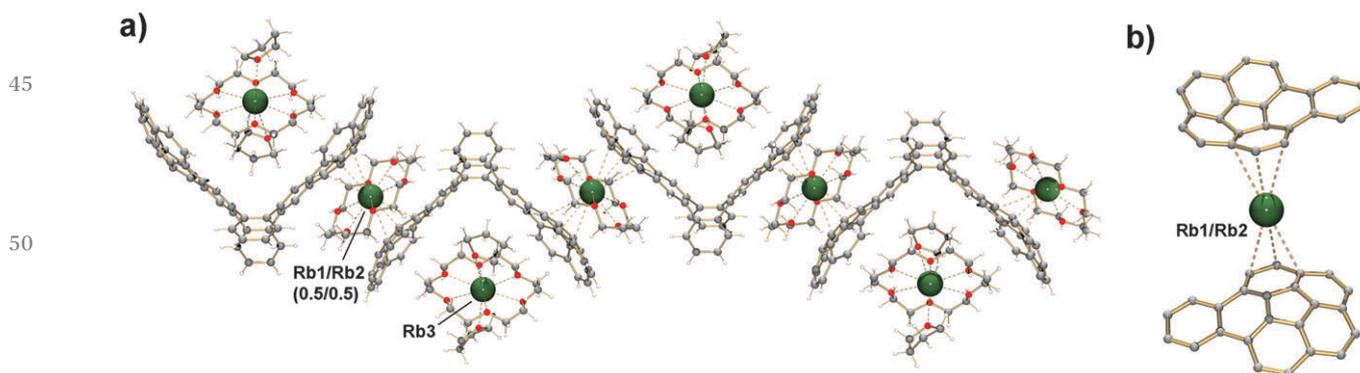


Fig. 2 Fragment of a 1D polymeric chain in **2** (a); sandwiching of Rb1/Rb2 cations ((b) only benzocorannulene fragments with six short $Rb \cdots C$ contacts are shown).

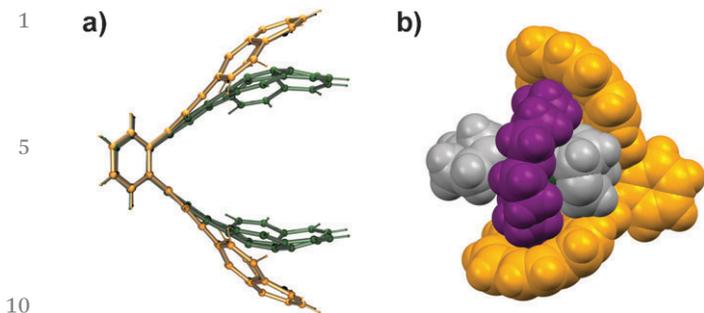


Fig. 3 Superposition of 1^0 and 1^{2-} ((a) green and orange colors are attributed to the neutral ligand and the dianion, respectively); space filling model for the encapsulation of the $[\text{Rb}(18\text{-crown-6})(\text{THF})_2]^+$ cation by 1^{2-} ((b) orange, purple and grey colors show the dianion, crown ether and THF, respectively).

Table 1 Key geometrical parameters of **1** and **2** (in Å)

	1	2
Rim	1.376(2)–1.443(2)	1.371(7)–1.448(6)
Hub	1.413(2)–1.430(2)	1.398(8)–1.432(7)
Spoke	1.371(2)–1.383(2)	1.367(9)–1.410(7)
Flank	1.436(2)–1.472(2)	1.404(6)–1.484(6)
Bowl depth	0.85, 0.90	0.79, 0.81
$\text{C}_5 \cdots \text{C}_5(\text{centroids})$	8.7	11.8

with a polyarene surface can provide a significant contribution to the total bonding energy in the $[\text{Rb}(\text{crown}) \cdots \text{polyarene}]$ system that can be even larger than the metal binding.²¹ The UV-vis spectra of the $\text{C}_{60}\text{H}_{28}^{2-}$ 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 dianions via $\text{C-H}_{(\text{crown})} \cdots \pi$ interactions existing in solution.^{9d}

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 0.79/0.81 Å in 1^{2-} vs. 0.85/0.90 Å in 1^0), whereas the C–C bonds were only slightly affected (Table 1). It should be mentioned that the bowls in 1^{2-} are noticeably flatter than in the corannulene monoanion (0.85 Å).^{9d}

In summary, we have isolated and structurally characterized the first anion of the $\text{C}_{60}\text{H}_{28}$ buckycatcher as well as crystallized the parent molecule under solvent-free conditions without any extraneous 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,^{4,22} we provide the first experimental evidence for the remarkable adjustability 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

- (a) *Fragments of Fullerenes and Nanotubes: Designed Synthesis, Unusual Reactions, and Coordination Chemistry*, ed. M. A. Petrukhina and L. T. Scott, John Wiley & Sons, Hoboken, NJ, 2012; (b) A. Sygula, *Eur. J. Org. Chem.*, 2011, 1611; (c) Y.-T. Wu and J. S. Siegel, *Chem. Rev.*, 2006, **106**, 4843; (d) V. M. Tsefrikas and L. T. Scott, *Chem. Rev.*, 2006, **106**, 4868.
- (a) D. Eisenberg, J. M. Quimby, L. T. Scott and R. Shenhar, *J. Phys. Org. Chem.*, 2013, **26**, 124; (b) D. Eisenberg, J. M. Quimby, D. Ho, R. Lavi, L. Benisvy, L. T. Scott and R. Shenhar, *Eur. J. Org. Chem.*, 2012, 6321; (c) E. Shabtai, R. E. Hoffman, P.-C. Cheng, E. Bayrd, D. V. Preda, L. T. Scott and M. Rabinovitz, *J. Chem. Soc., Perkin Trans. 2*, 2000, 129.
- (a) A. Sygula, F. R. Fronczek, R. Sygula, P. W. Rabideau and M. M. Olmstead, *J. Am. Chem. Soc.*, 2007, **129**, 3842; (b) M. Yanney and A. Sygula, *Tetrahedron Lett.*, 2013, **54**, 2604; (c) A. Sygula and W. E. Collier, in *Fragments of Fullerenes and Carbon Nanotubes*, ed. M. A. Petrukhina and L. T. Scott, John Wiley & Sons, Hoboken, NJ, 2012, p. 1.
- C. Mück-Lichtenfeld, S. Grimme, L. Kobryn and A. Sygula, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7091.
- Y. Yang, P. Feng, A. Sygula, W. Harneit, J.-H. Su and J. Du, *Phys. Lett. A*, 2012, **376**, 1748.
- L. Kobryn, W. P. Henry, F. R. Fronczek, R. Sygula and A. Sygula, *Tetrahedron Lett.*, 2009, **50**, 7124.
- (a) D. Eisenberg and R. Shenhar, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2012, **2**, 525; (b) A. Minsky, A. Y. Meyer, K. Hafner and M. Rabinovitz, *J. Am. Chem. Soc.*, 1983, **105**, 3975; (c) M. Rabinovitz and A. Minsky, *Pure Appl. Chem.*, 1982, **54**, 1005.
- A. V. Zabula and M. A. Petrukhina, *Adv. Organomet. Chem.*, 2013, **61**, 375.
- (a) S. N. Spisak, A. V. Zabula, M. V. Ferguson, A. S. Filatov and M. A. Petrukhina, *Organometallics*, 2013, **32**, 538; (b) A. V. Zabula, S. N. Spisak, A. S. Filatov and M. A. Petrukhina, *Organometallics*, 2012, **31**, 5541; (c) A. V. Zabula, S. N. Spisak, A. S. Filatov and M. A. Petrukhina, *Angew. Chem., Int. Ed.*, 2012, **51**, 12194; (d) A. V. Zabula, S. N. Spisak, A. S. Filatov, V. M. Grigoryants and M. A. Petrukhina, *Chem.–Eur. J.*, 2012, **18**, 6476; (e) A. V. Zabula, A. S. Filatov, S. N. Spisak, A. Y. Rogachev and M. A. Petrukhina, *Science*, 2011, **333**, 1008; (f) S. N. Spisak, A. V. Zabula, A. S. Filatov, A. Y. Rogachev and M. A. Petrukhina, *Angew. Chem., Int. Ed.*, 2011, **50**, 8090; (g) A. S. Filatov, A. V. Zabula, S. N. Spisak, A. Y. Rogachev and M. A. Petrukhina, *Angew. Chem., Int. Ed.*, 2014, **53**, 140.
- A. V. Zabula, A. S. Filatov, J. Xia, R. Jasti and M. A. Petrukhina, *Angew. Chem., Int. Ed.*, 2013, **52**, 5033.
- (a) A. S. Filatov and M. A. Petrukhina, *Coord. Chem. Rev.*, 2010, **254**, 2234; (b) M. A. Petrukhina, *Coord. Chem. Rev.*, 2007, **251**, 1690.
- A. Sygula, in progress.
- $\text{C}_{60}\text{H}_{28}$, $M = 748.82$, triclinic, space group $P\bar{1}$, $a = 9.8507(3)$ Å, $b = 14.1479(4)$ Å, $c = 15.1646(4)$ Å, $\alpha = 105.607(1)^\circ$, $\beta = 102.809(1)^\circ$, $\gamma = 110.367(1)^\circ$, $V = 1788.10(9)$, $Z = 2$, $\mu = 0.605 \text{ mm}^{-1}$, $F(000) = 776$, $T = 100(2)$, 26 110 reflections measured, 6486 unique ($R_{\text{int}} = 0.0257$), $R_1 = 0.0374$, $wR_2 = 0.0930$ for $I > 2\sigma(I)$. CCDC 973696.
- Previous computational studies located four distinct gas-phase conformers of **1** with very similar energies (ref. 4).
- M. A. Petrukhina, K. W. Andreini, J. Mack and L. T. Scott, *J. Org. Chem.*, 2005, **70**, 5713.
- A. S. Filatov, L. T. Scott and M. A. Petrukhina, *Cryst. Growth Des.*, 2010, **10**, 4607.
- A. V. Zabula, S. N. Spisak, A. S. Filatov, A. Y. Rogachev and M. A. Petrukhina, *Angew. Chem., Int. Ed.*, 2011, **50**, 2971.
- C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
- M. Baumgarten, J. L. Gherghel, M. Wagner, A. Weitz, M. Rabinovitz, P.-C. Cheng and L. T. Scott, *J. Am. Chem. Soc.*, 1995, **117**, 6254.
- $\text{C}_{98}\text{H}_{104}\text{O}_{15.5}\text{Rb}_2$, $M = 1700.75$, triclinic, space group $P\bar{1}$, $a = 9.3921(2)$ Å, $b = 16.1731(3)$ Å, $c = 28.6015(5)$ Å, $\alpha = 80.358(1)^\circ$, $\beta = 89.767(1)^\circ$, $\gamma = 80.008(1)^\circ$, $V = 4216.81(14)$, $Z = 2$, $\mu = 2.048 \text{ mm}^{-1}$, $F(000) = 1780$, $T = 100(2)$, 56 730 reflections measured, 14 310 unique ($R_{\text{int}} = 0.0663$), $R_1 = 0.0655$, $wR_2 = 0.1739$ for $I > 2\sigma(I)$. CCDC 973695.
- S. N. Spisak, N. J. Sumner, A. V. Zabula, A. S. Filatov, A. Y. Rogachev and M. A. Petrukhina, *Organometallics*, 2013, **32**, 3773.
- Y. Zhao and D. G. Truhlar, *Phys. Chem. Chem. Phys.*, 2008, **10**, 2813.