

Preliminary communication

The first example of η^8 coordination of lithium cations with a cyclooctatetraene dianion: crystal structure of $\text{Li}_2(\text{dibenzo}[a,e]\text{cyclooctatetraene})(\text{TMEDA})_2$

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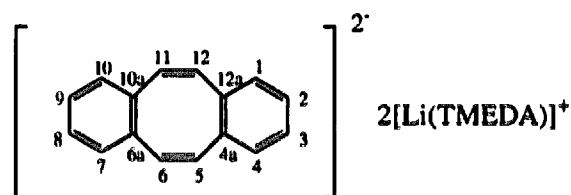
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Abstract

The reported crystal structure of $\text{Li}_2(\text{dibenzo}[a,e]\text{cyclooctatetraene})(\text{TMEDA})_2$ represents the first crystal structure of a dilithio cyclooctatetraene dianion, and the first example of η^8 coordination of a lithium cation with the cyclooctatetraene system.

Keywords: Lithium; Cyclooctatetraene; Ion triplets

The paramount importance of aromaticity in organic chemistry has led to considerable interest in the structure of cyclooctatetraene (COT) and its aromatic dianion (COT^{2-}). The planarization of the COT^{2-} framework, relative to the non-planar, neutral COT, represents a textbook example for the application of the Hückel $4n + 2$ rule. It is therefore not surprising that several X-ray diffraction studies on the complexes of COT and its derivatives with both alkali [1] and transition metals (see for example Ref. [2]) have been reported. However, only limited information on organolithium complexes of COT is available. A search of the Cambridge Structural Database [3] reveals only two such studies, and they are mixed complexes of COT with lithium and samarium [4] or cerium [5]. Moreover, in both cases the lithium cation exhibits a rather unexpected coordination with the COT unit, unlike the η^8 coordination of the heavier alkali metal ions. Herein we present the results of the first crystal structure determination of a dilithiated COT system, $\text{Li}_2(\text{dibenzo}[a,e]\text{cyclooctatetraene})(\text{TMEDA})_2$, which also represents the first example of η^8 coordination of lithium cations with the COT dianion.



The dilithio salt of dibenzo[a,e]cyclooctatetraene (1) was formed on contact of lithium metal with a solution of 1 [6] in dry THF (the dianion of 1 was previously studied by NMR, see Ref. [7]). Some hexane and TMEDA were added to the dark solution, and the mixture was filtered and refrigerated at -20°C (crystals of dilithio-1 could also be obtained from the THF-hexane solution without the addition of TMEDA; however, they were not stable at room temperature, presumably due to the loss of THF). The resulting dark red crystals were separated and a crystal suitable for X-ray analysis was sealed in a glass capillary tube; all manipulations were performed under a dry argon atmosphere.

Crystal data: $\text{Li}_2\text{C}_{28}\text{H}_{44}\text{N}_4$, $M = 450.57$, monoclinic, space group $C2/m$, $a = 12.6629(7)$, $b = 13.6833(8)$, $c = 8.3417(10)$ Å, $\beta = 108.829(7)^\circ$, $V = 1368.0(4)$ Å³, $Z = 2$, $D_c = 1.094$ g cm⁻³, $F(000) = 492$, $T = 297$ K, $R = 0.056$, $R_w = 0.069$ for 1144 observed data having $2 < \theta < 75^\circ$ and $I > 1\sigma(I)$. Three quad-

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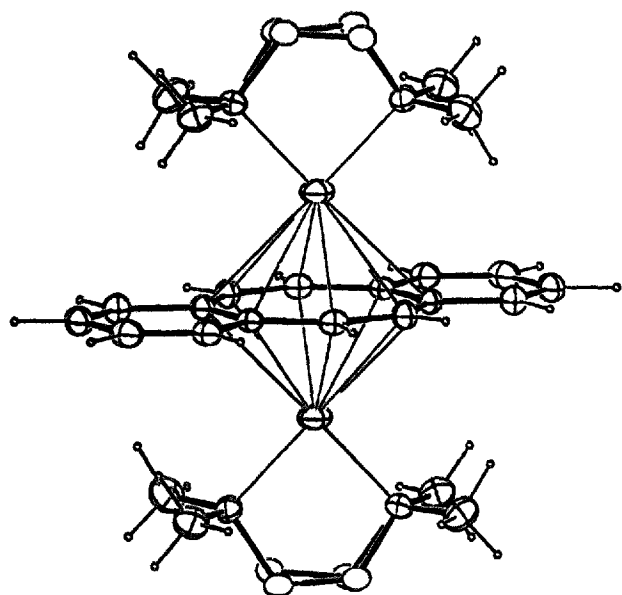


Fig. 1. ORTEP view of $\text{Li}_2(\text{dibenzo}[\text{a,e}]\text{cyclooctatetraene})(\text{TMEDA})_2$. Both half-populated sites of the disordered ethylene units within TMEDA molecules shown, with their hydrogen atoms omitted for clarity.

rants of intensity data were collected using a dark red crystal mounted in a capillary, on an Enraf-Nonius CAD4 diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) and a graphite monochromator. Redundant data were averaged ($R_i = 0.020$) to yield 1473 unique data. TMEDA carbon atom C9 is disordered into two positions separated by approximately 0.8 \AA ; these sites were treated as half-populated. H atoms were refined isotropically, except for those of the methyl groups and disordered CH_2 group, which were placed in calculated positions.

The structure of dilithio-1 is presented in Fig. 1, while selected bond lengths and angles are presented in Table 1. The molecule has crystallographic C_{2h} symmetry.

Table 1
Selected C–C and Li–C distances (\AA) and angles ($^\circ$) for dilithio-1 with estimated standard deviations in parentheses

C1–C2	1.356(3)	C5–C6	1.417(3)
C1–C12a	1.425(3)	C6–C6a	1.407(3)
C2–C3	1.401(5)	Li–C4a	2.727(3)
C3–C4	1.365(4)	Li–C5	2.604(4)
C4–C4a	1.448(3)	Li–C6	2.607(4)
C4a–C5	1.405(3)	Li–C6a	2.736(3)
C4a–C12a	1.450(4)		
C12a–C1–C2	125.1(3)	C4a–C5–C6	140.9(2)
C1–C2–C3	119.2(2)	C5–C6–C6a	141.0(2)
C2–C3–C4	118.5(2)	C6–C6a–C7	114.7(2)
C3–C4–C5	125.1(3)	C6–C6a–C10a	128.5(2)
C4–C4a–C5	115.1(2)	Li–C5–C6	74.3(1)
C4–C4a–C12a	115.3(3)	Li–C5–C6–C6a	50.0(1)

In analogy to the other COT^{2-} systems studied, the two-electron reduction of 1 leads to planarization of the molecular skeleton. In fact, since the $\text{C}_{16}\text{H}_{12}$ unit lies in a crystallographic mirror plane, the dianion is perfectly planar. Of course, due to benzannelation, the central eight-membered ring does not form a regular octagon; the two benzannelated carbon–carbon bonds are significantly longer [$1.450(4) \text{ \AA}$] than the six remaining carbon–carbon bonds [$1.405(3)$ – $1.417(3) \text{ \AA}$]. The two lithium cations, each solvated by a single TMEDA molecule, are symmetrically located over and under the center of the eight-membered ring within a distance of $1.923(4) \text{ \AA}$ from its plane. The two cations define the C_2 crystallographic axis of symmetry with the overall arrangement representing a perfect ion triplet structure that is predicted to be of lowest energy for a dianion/ 2metal^+ system based on electrostatics [8]. The TMEDA has its central ethylene carbon atoms disordered into two half-populated sites.

While this same arrangement is observed for the crystals of dipotassium and dirubidio salts of COT [1], it is not the case when lithium cations have been involved. In the first example of COT–lithium coordination, the lithium cation is η^2 bound to the COT^{2-} moiety in a mixed complex of COT with lithium and samarium [4]. In the second example the lithium cation is solvent-separated from an anionic sandwich complex of $[\text{Ce}(\text{COT})_2]^-$, although the same anionic sandwich prefers η^8 binding with either sodium or potassium cations [5,9]. These results prompted the conclusion that the coordination of the alkali metal cation with the COT unit depends on the size and/or polarizability of the cation [5]. However, the results reported herein show that lithium can also be bound in an η^8 fashion to the COT dianion. The C–Li distances in dilithio-1 are in the range $2.604(4)$ – $2.736(3) \text{ \AA}$, and are thus slightly longer than the typical distances for lithium cations bound to the π -faces of five- and six-membered rings [10]. The elongation may safely be explained on the basis of the electrostatic model, since delocalization of the negative charge beyond the eight-membered ring decreases charge density, and therefore decreases the attraction between the cations and the organic dianion.

Acknowledgements

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