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Novel Cesium Contact Ion Multiples with Tetraphenylethanediyl and 1,1,4,4-Tetraphenylbutadiene-2,3-diyl π-Dianions: Crystallization and Structure

Hans Bock,* Tim Hauck, and Christian Näther

Chemistry Department, University of Frankfurt, Marie-Curie-Strasse 11,
60439 Frankfurt, Germany

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Summary: Organocesium compounds, which are still a rarity, are easily prepared using a droplet of liquid cesium and occasional ultrasonic surface reactivation. Despite their extreme air sensitivity, structure analysis has been achieved under a cooled-N_2 *flow both for the black coordination polymer (tetraphenylethanediyl)dicesium bis(diglyme) (*$[(Ph_2C{-}CPh_2)^{2-}(Cs^+(diglyme)_2]_\infty$*), which exhibits the expected cyanine distortion with the molecular halves* $^-C(C_6H_5)_2$ *twisted by 76° around the central CC single bond of 1.51 Å length, and for the violet-blue coordination polymer (1,1,4,4-tetraphenylbutadiene-2,3-diyl)tetracesium bis(diglyme) bis(2-methoxyethanolate) (*$[(Ph_2C{=}(CHCH){=}CPh_2)^{2-}(Cs^+(diglyme))(Cs^{+-}OCH_2CH_2OCH_3)_2]_\infty$*), which shows a bond alternancy change relative to the hydrocarbon,* $>C{=}C(H){-}(H)C{=}C< + 2e^- \rightarrow >C^-{-}C(H){=}(H)C{-}^-C<$.

The ever-increasing structure reports of alkali-metal−organic species and especially of lithium, sodium, and potassium compounds have considerably improved a rationalization of their physical and chemical properties.[1,2] In contrast, a search in the Cambridge Structural Database[3] showed that out of the total of about 140 entries for ion multiples with contacts $M^+\cdots C^{\delta-}$ only two concern Cs^+ countercations.[4,5]

This may be due to their extreme air and moisture sensitivity, which makes their preparation difficult, as well as to their resulting low synthetic importance.[5] However, the Cs atom exhibits an extremely low first vertical ionization potential of only 3.89 eV, and its cation has the largest radius ($r_{Cs^+} = 1.67$ Å) of all nonradioactive alkali metals.[6] Because of our interest in the structural details of organocesium compounds, we have developed a simple technique for the reduction of π-hydrocarbons in aprotic ether solution using a Cs metal droplet above its melting point and, if necessary, surface reactivation by occasional brief ultrasonic sound irradiation.[7] As examples, the low-temperature single-crystal structures of (tetraphenylethanediyl)dicesium bis(diglyme), $[(H_5C_6)_2C{-}C(C_6H_5)_2{}^{2-}(Cs^+(H_3COCH_2CH_2OCH_2CH_2OCH_3)_2]_\infty$[8] (Figure 1), and of (1,1,4,4-tetraphenylbutadiene-2,3-diyl)tetracesium bis(diglyme) bis(2-methoxyethanolate), $[(H_5C_6)_2C{=}(CHCH){=}(C_6H_5)_2{}^{2-}(Cs^+H_3COCH_2CH_2OCH_2CH_2OCH_3)_2(Cs^{+-}OCH_2CH_2OCH_3)_2]_\infty$[9] (Figure 2), are reported.

In the structure determined for the black crystal[8] (Figure 1A), the Cs^+ countercations show interactions with four phenyl rings of two different tetraphenylethanediyl dianions as well as with the three oxygens

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(1) Interactions in Crystals. 86. Part 85: Näther, C.; Bock, H.; Claridge, R. F. C. *Helv. Chim. Acta*, in press, and literature cited therein.

(2) (a) Bock, H.; Ruppert, K.; Näther, C.; Havlas, Z.; Hermann, H.-F.; Arad, C.; Göbel, I.; John, A.; Meuret, J.; Nick, S.; Rauschenbach, A.; Seitz, W.; Vaupel, T.; Solouki, B. *Angew. Chem.* **1992**, *104*, 565; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 550. (b) Weiss, E. *Angew. Chem.* **1993**, *105*, 1670; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501. (c) Schade, C.; von Rague-Schleyer, P. *Adv. Organomet. Chem.* **1987**, *27*, 169. Setzer, W. N.; von Rague-Schleyer, P. *Adv. Organomet. Chem.* **1985**, *24*, 353. (d) Bock, H. *Mol. Cryst. Liq. Cryst.* **1994**, *240*, 155; *Jahrb. Dtsch. Akad. Naturforsch. Leopoldina* **1992**, *38*, 221. (e) Bock, H.; Näther, C.; Havlas, Z.; John, A.; Arad, C. *Angew. Chem.* **1994**, *106*, 931; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 875. (f) Bock, H.; Hauck, T.; Näther, C.; Rösch, N.; Staufer, M.; Häberlen, O. D. *Angew. Chem.* **1995**, *107*, 1439; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1353. See also references cited therein for each.

(3) Cambridge Structural Database, Version V5.09; search Jan 1995. For Cs contact ion multiples with heteroelement interactions $Cs^+\cdots X^-$ the total of 122 000 CSD entries produced 216 hits. Not yet included is, for example, the structure of $CsC(SiMe_3)_3 \cdot 3.5C_6H_6$ by: Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, D. J. *Angew. Chem.* **1995**, *107*, 756; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 687.

(4) (a) $[Cs^+C_{60}{}^{\bullet -}]$: Zhou, O.; Fischer, J. E.; Coustel, N.; Kycia, S.; Zhu, Q.; McGhie, A. R.; Romanow, W. J.; McCauley, J. P.; Smith, A. B.; Cox, D. E. *Nature* (*London*) **1991**, *351*, 462. (b) $[Cs^{+-}C(C_6H_5)_3(H_3C)_2NCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)_2]_\infty$: Hoffmann, D.; Bauer, W.; Schleyer, P. v. R.; Pieper, U.; Stalke, D. *Organometallics* **1993**, *12*, 1193. (c) $[Cs^+(carbazol)^-(H_3C)_2NCH_2N(CH_3)(CH_2CH_2N(CH_3)_2]_2$: Gregory, K.; Bremer, M.; Schleyer, P. v. R. *Angew. Chem.* **1989**, *101*, 1261; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1224. Preparations have been achieved (a) by reduction with cesium metal vapor in a sealed tube or (b, c) by transmetalation using $CsOC(CH_3)_3$.

(5) The well-known "cesium effect" in macrocyclic syntheses (cf. e.g. Dietrich, B.; Viout, P.; Lehn, J. M. *Macrocyclic Chemistry*; VCH Verlag: Weinheim, Germany, 1993; pp 114−118) has, to the best of our knowledge, not yet extended to organocesium derivatives.

(6) Cf.: Bock, H.; Ruppert, K. *Inorg. Chem.* **1992**, *31*, 5094 and references cited therein.

(7) General procedure for Cs metal reduction of π-hydrocarbons in aprotic ether solution: About 2 mmol each of Cs metal and compound are placed under argon together with 20 mL of diglyme, freshly distilled from Na/K alloy, in a carefully dried Schlenk trap. After 3 days most of the metal has vanished and, after the deeply colored solution has been covered four times with 5 mL layers of *n*-hexane, after 6 days the highly air-sensitive crystals are harvested under argon.

(8) Crystal data for (tetraphenylethanediyl)dicesium bis(diglyme): $a = 15.237(1)$ pm, $b = 18.256(1)$ pm, $c = 13.919(1)$ pm, $\beta = 100.13(1)°$, $V = 3811.4$ Å^3 ($T = 200$ K), monoclinic, $C2/c$, $Z = 4$, $\mu = 1.95$ mm^{-1}, $R(2715\ F_o > 4\sigma(F_o)) = 0.0534$, wR2 = 0.1258 for all 3125 reflections. Bond distances (Å) and angles (deg): C1−C2, 1.51(1); C1−C11, 1.45(1); C2−C21, 1.43(1); C11−C1−C11A, 1.27(1); C21−C2−C21A, 1.23(1); Cs1−O1, 3.06(1); Cs1−O2, 3.19(1); Cs1−O3, 3.00(1); Cs1−C26, 3.45(1); Cs1−C16, 3.48(1); Cs1−C15, 3.50(1); Cs1−C12, 3.53(1); Cs1−C11, 3.55(1); Cs1−C13, 3.55(1); C26C−Cs1, 3.57(1); Cs1−C14; 3.57(1), Cs1−C25, 3.58(1); C12B−Cs1, 3.58(1); C13B−Cs1, 3.73(1); C25C−Cs1, 3.83(1).

(9) Crystal data for (1,1,4,4-tetraphenylbutadiene-2,3-diyl)tetracesium bis(diglyme) bis(2-methoxyethanolate): $a = 10.180(1)$, $b = 10.545(1)$ pm, $c = 12.622(1)$ pm, $\alpha = 97.05(1)°$, $\beta = 95.61(1)°$, $\gamma = 106.19(1)°$, $V = 1279.0$ Å^3 ($T = 150$ K), triclinic, $P1$, $Z = 1$, $R(5628\ F_o > 4\sigma(F_o)) = 0.0352$, wR2 = 0.0928 for all 7323 reflections. Bond distances (Å) and angles (deg): C1−C2, 1.452(4); C1−C1A, 1.382(6); C2−C10, 1.444(4); C2−C20, 1.460(4); C1A−C1−C2, 1.293(4); C10−C2−C20, 1.213(2); Cs1−O4A, 2.825(2); Cs1−O3, 3.099(3); Cs1−O2, 3.149(3); Cs1−O1, 3.240(3); Cs1−C2A, 3.269(3); Cs1−O5, 3.353(3); Cs1−C10A, 3.464(3); Cs1−C11, 3.533(3); Cs1−C20A, 3.612(3); Cs1−C1A, 3.694(3); Cs1−C21, 3.707(4); Cs2−O4A, 2.890(3); Cs2−O4, 2.922(3); Cs2−O5, 3.206(3); Cs2−C2, 3.251(3); Cs2−O2A, 3.328(3); Cs2−C1, 3.487(3); Cs2−C25, 3.560(3); Cs2−C1, 3.719(3); Cs2−C20, 3.573(3); Cs2−C10, 3.576(3).

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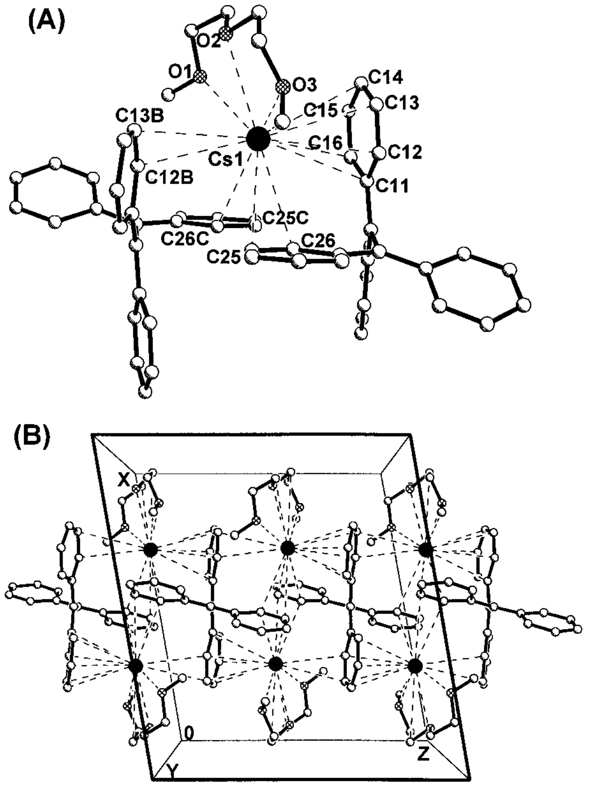

Figure 1. Single-crystal structure of (tetraphenylethanediyl)dicesium bis(diglyme) at 200 K:[8] (A) Cs$^+$ coordination to one diglyme solvent ligand and to two twisted tetraphenylethanediyl dianions ($d(^-C-C^-) = 1.51$ Å, $\omega(C_2{}^-C-C^-C_2) = 76°$); (B) unit cell (monoclinic, $C2/c$, $Z = 4$) in y direction.

of one diglyme molecule, forming a distorted polyhedron around the 15-fold-coordinated Cs$^+$ center. In the dianion, the $(H_5C_6)_2C^-$ halves are twisted by 76° around a single $>^-C-C^-<$ bond, elongated from 1.36 Å in the neutral hydrocarbon to 1.51 Å, i.e. by 0.15 Å (!). This is in close analogy to the disodium–diethyl ether salt,[2a,10] representing another impressive example of a large cyanine distortion.[2a] The contact distances Cs$^+\cdots$O$^{\delta-}$ vary from 3.48 to 3.83 Å, and the Cs$^+\cdots$O contacts are 3.04, 3.06, and 3.19 Å, with the longest one to the central oxygen of the diglyme ligand. The η^6 coordination of Cs$^+$ to the phenyl ring at a centroid distance of 3.24 Å is slightly unsymmetrical, with closer contacts to the meta and para positions. The bridging of two different dianions by each Cs$^+$ cation on both sides of their horizontal $(H_5C_6)_2C^-$ planes leads to a linear one-dimensional coordination polymer with intriguing intermolecular lattice packing (Figure 1B).

For the violet-blue single crystal of the other and in some aspects analogous coordination polymer, the structure determination[9] (Figure 2) reveals the following features: the butadiene dianion is perturbed to a but-2-ene-1,4-diyl π-system with the bond alternation in the neutral molecule[11] converted by addition of two electrons, $>C{=}C(H){-}(H)C{=}C< + 2e^- \rightarrow >^-C-C(H){=}(H)C-C^-<$, and the negative charges delocalized into the phenyl rings:[2a,11] The central CC bond is shortened by 0.06 Å to 1.38 Å, and the outer ones are

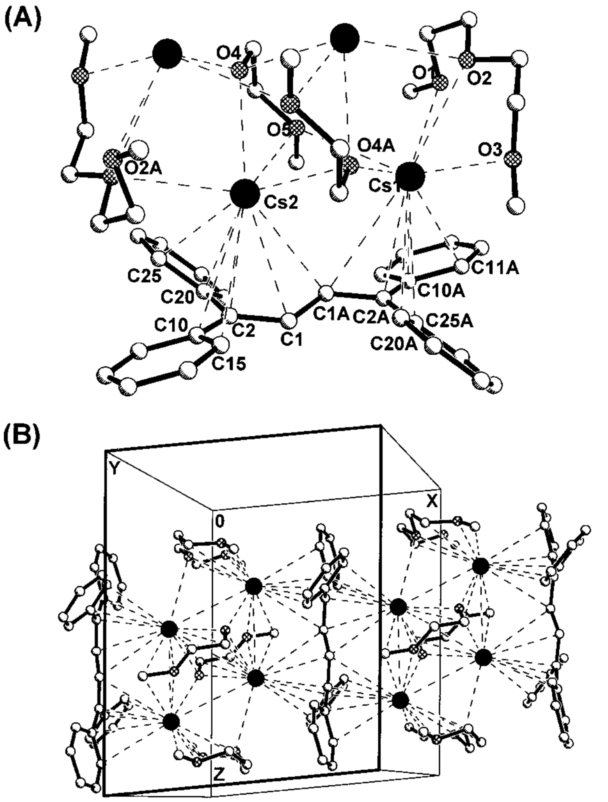

Figure 2. Single-crystal structure of (1,1,4,4-tetraphenylbutadiene-2,3-diyl)tetracesium bis(diglyme) bis(2-methoxyethanolate) at 150 K:[9] (A) Cs$^+$ coordination to one diglyme solvent ligand, two anions $^-OCH_2CH_2OCH_3$ (from diglyme decomposition), and one skeletal half of the tetraphenylbutadienediyl dianion; (B) unit cell (triclinic, $P\bar{1}$, $Z = 4$) in y direction.

elongated by 0.09 Å to 1.45 Å. Each Cs$^+$ cation is η^6- or η^7-bonded to one dianion, η^3-bonded to one diglyme molecule, and η^2-bonded to two 2-methoxyethanolate anions resulting from reductive ether fragmentation by Cs metal, which are shared with to other Cs$^+$ cations of adjacent subunits (Figure 1A, dashed lines). The coordination spheres of both cations differ slightly, despite comparable contact distances: Cs$^+\cdots$O(diglyme) is between 3.10 and 3.33 Å, Cs$^+\cdots{}^-$O is 2.83 Å, and Cs$^+\cdots$C$^{\delta-}$ between 3.49 and 3.72 Å, with the shortest distances of only 3.25 and 3.27 Å to the C2 centers bearing the highest negative charge.[2a,11] Two but-2-ene-1,4-diyl dianions are bridged by four Cs$^+$ cations, which enclose the additional anions $^-OCH_2CH_2OCH_3$ (Figure 2B).

In summary, a simple procedure allowed us to grow crystals of organocesium compounds under argon and aprotic conditions. Their structures can be determined under a cooled-N$_2$ flow. Due to the negative reduction potential of Cs metal (−2.92 V[6]) dianions of hydrocarbons such as tetraphenylethene and 1,1,4,4-tetraphenylbutadiene thus generated show severe cyanine and charge localization distortions, which can be compared to literature values especially for Li$^+$,[2a,11,12] Na$^+$,[2a,12,13] or K$^+$ [2a,11,13] analogues. A preliminary overview would suggest that Cs$^+$ centers due to their large ionic radii tend to crystallize in multihapto- and multiion-coordinated, linear polymeric aggregates and that the bor-

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(10) Bock, H.; Ruppert, K.; Merzweiler, K.; Fenske, D.; Goesmann, H. *Angew. Chem.* **1989**, *100*, 1715; *Angew. Chem., Int. Ed. Engl.* **1989**, *18*, 1684.

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(12) Bock, H.; Hauck, T.; Näther, C. Unpublished results.

(13) Bock, H.; Näther, C.; Ruppert, K.; Havlas, Z. *J. Am. Chem. Soc.* **1992**, *114*, 6907.

derline between monomeric and higher order complexes frequently is around Li^+/Na^+ or Na^+/K^+.[11,13]

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Supporting Information Available: Tables giving details of the crystal structure determinations, including bond lengths and angles, atomic coordinates, and anisotropic displacement parameters for the two compounds discussed in this paper (22 pages). Ordering information is given on any current masthead page.

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