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Synthesis and Crystal Structure of a New C_{60}^{2-} Fulleride: $[K(DB24C8)(DME)]_2C_{60}\cdot DME$

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The "break-and-seal" approach was applied to synthesize the new fulleride $[K(DB24C8)(DME)]_2C_{60}\cdot DME$ by reacting fullerene C_{60} with potassium and dibenzo-24-crown-8 (DB24C8) in dimethoxyethane (DME). Single crystals were grown from solution by the modified "temperature difference method", single-crystal X-ray analysis was performed revealing the structure [$C2/c$, $Z = 4$, $a = 31.133(4)$, $b = 15.127(2)$, $c = 21.433(3)$ Å, $\beta = 117.506(3)°$, $R_1 = 0.056$, $wR(\text{all}) = 0.171$, 8459 independent reflections]. Due to crystal symmetry, the C_{60}^{2-} anion is disordered between two well distinguishable orientations. The distribution of the bond lengths within the fullerene is discussed and attributed to a Jahn–Teller distortion.

Introduction

The electronic structure of C_{60} fullerene, exhibiting the conspicuously high point group symmetry of I_h, is singular for its highly degenerate frontier orbitals. The two lowest unoccupied molecular orbitals may accommodate as many as twelve additional electrons. Each of the resulting anions C_{60}^{n-} is featuring some specific chemical and physical properties, in their respective compounds. However, because of open-shell configurations, manifold low-lying, slightly separate states, and Jahn–Teller instabilities involved, the underlying electronic structures are hard to cope with. In particular in the case of C_{60}^{2-} all attempts to unambiguously define the electronic ground state have failed, so far.[1] The threefold degenerate LUMO, occupied by two electrons, is very much reminiscent of the situation encountered for a carbon atom, suggesting that Hund's rule will be obeyed and that C_{60}^{2-} might display a triplet ground state. However, for a molecule one would rather expect that the system stabilizes by lifting the degeneracy of the unequally occupied orbitals, according to the Jahn–Teller theorem. Among the symmetry reduced structures allowing the degeneracy of the t_{1u} orbital to be lifted, the D_{5d} and D_{3d} structures have been identified as possible minima, and the D_{2h} structure as a saddle point of the associated potential energy surface.[2] Still singlet or triplet ground states are possible. Experimental studies as well as theoretical analyses have ended up with contradictory results. Although, the C_{60}^{2-} fullerides, for which measurements of the magnetic susceptibilities have become available, can be regarded "magnetically dilute", never the full as expected magnetic moment has been found,[3,4] or they even proved to be diamagnetic.[5,6] Also, with respect to a global geometric distortion of the fulleride molecule, predicted to generate a prolate ellipsoid, the experimental findings have remained unsettled for a long time. However, revising and reanalyzing a set of crystal structures previously determined with high accuracy[7–12] have revealed a preferred characteristic distortion pattern. The overall symmetry of C_{60}^{2-}, e.g. in $[Ba(NH_3)_7]C_{60}\cdot NH_3$,[8] is reduced to D_{3d} by elongating a specific subset of C–C bonds shared by two hexagons.[13] This distortion pattern was validated by quantum mechanical calculations, identifying a singlet ground state. However, further experimental data is needed in order to corroborate the picture as derived from the based on alkaline earth or transition metal fullerides ammoniates.

Moving to thermally more stable fullerides of bulky cations, synthesized from conventional organic solvents, might afford materials that allow for structure determinations of high accuracy. In pursuing this objective we have synthesized a new $[K(DB24C8)(DME)]_2C_{60}\cdot DME$ fulleride along the "break-and-seal" approach reported elsewhere.[14]

Results and Discussion

The title compound $[K(DB24C8)(DME)]_2C_{60}\cdot DME$ has been obtained according to the "break-and-seal" procedure[14] by reacting fullerene C_{60} with potassium and dibenzo-24-crown-8 (DB24C8) in dimethoxyethane (DME) as red-brown, plate-like crystals, which are sensitive to air.

$[K(DB24C8)(DME)]_2C_{60}\cdot DME$ crystallizes in the monoclinic space group $C2/c$ (no. 15) with four formula units per unit cell. Potassium atoms are coordinated by the crown-ether as well as by one solvent molecule, forming complex

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cations $[K(DB24C8)(DME)]^+$ (Figure 1, above). The crown-ether, being too large for potassium, is twisted around the K-atom, whereby all eight oxygen atoms of the crown-ether coordinate the potassium atom at distances 2.800(3), 2.808(3), 2.810(4), 2.817(4), 2.818(3), 2.833(4), 2.904(3) and 3.233(3) Å. Additionally, the metal atom is coordinated by two oxygen atoms of the solvent at 2.935(3) and 2.954(2) Å, the solvent molecule being in *cis*-conformation (Figure 1, above). The structure contains two $[K(DB24C8)(DME)]^+$ units per fullerene, thus, the resulting charge of C_{60} is –2 (Figure 1, below), and one additional solvent molecule (DME) which is not coordinated to potassium. This second DME molecule is "isolated" and adopts a *trans*-conformation. Figure 2 shows the arrangement of the three building units within the unit cell.

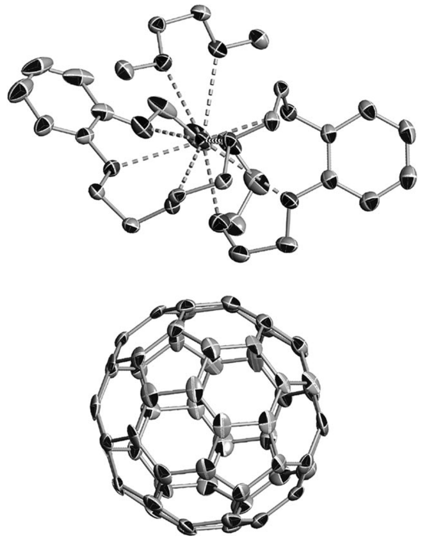

Figure 1. Fragment of the crystal structure showing the coordination of the potassium atom by one solvent molecule and crown-ether (dotted lines, above) together with one of two possible orientations of the next neighbouring fullerene (below). Displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted.

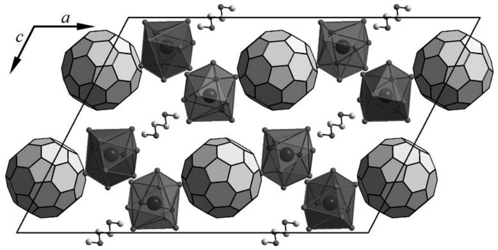

Figure 2. Projection of the crystal structure of $[K(DB24C8)(DME)]_2$-C_{60}·DME along [010], with margins of the unit cell given. For clarity, only one orientation of the fullerene is displayed, the carbon atoms of the crown-ether and the DME coordinated to potassium are omitted. The coordination of potassium by 10 oxygen atoms (8 from DB24C8, and 2 from DME) is shown as a polyhedron.

The C_{60}^{2-} units are arranged in hexagonal layers parallel to the *a*–*b* plane, forming distorted trigonal prisms (Figure 3, left). The fulleride anions and the potassium cations develop a pseudo binary topology which is reminiscent to the CdI_2 type of structure, where C_{60}^{2-} occupy the positions of cadmium, and potassium those of iodine (Figure 3, right). In this layered structure, fully occupied and vacant layers of octahedral sites alternate. Each C_{60}^{2-} anion is thus enclosed in an octahedron built of the potassium centered complexes. The non coordinated DME solvent molecules are located in the remaining octahedral voids (Figure 2).

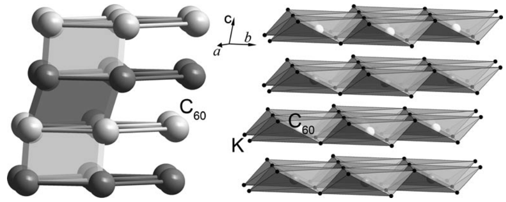

Figure 3. Packing of the fullerene molecules, emphasizing the approximate hexagonal primitive, triangular arrangement of C_{60} (left). Polyhedral representation of the K_2C_{60} partial structure, emphasizing the analogy to CdI_2 (right).

The C_{60}^{2-} anions were found to be statically disordered, due to their location on a special crystallographic position (4*e*: 0, *y*, 1/4), with the orientation of the crystallographic and molecular C_2 axes not matching. This disorder can be best and fully described by two orientations related to each other by the crystallographic C_2 axis (Figure 4). As stated in the experimental section, in a first step to localize the atoms of the fulleride anion a predefined C_{60} unit was imported as a rigid body. Nevertheless, the refinement of the structure could be done without using any constraints and restraints. This has allowed to analyse the intramolecular fulleride bond lengths, applying some sense of proportion, however.

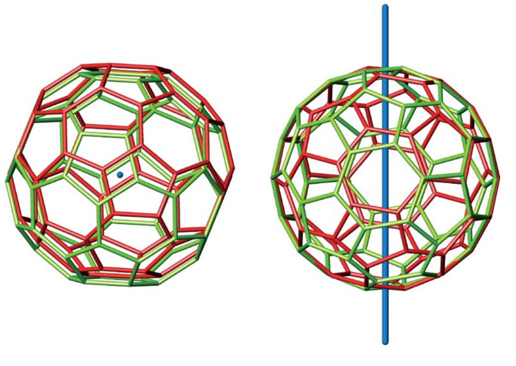

Figure 4. Fragment of the crystal structure showing two orientations of the C_{60}^{2-} anion (red, green), caused by the twofold rotation axis C_2 (blue). Left: view along [010]; right: view along [001].

In Figure 5 a histogram is shown, representing the spread of the C–C distances in C_{60}^{2-}. One can clearly identify a dip in the distribution separating the shorter bonds between edge sharing hexagons [(6,6)-bonds] from those shared by hexagons and pentagons [(6,5)-bonds]. The frequency distribution of 1:2 fits well to the numbers of (6,6)-bonds (30) and (6,5)-bonds (60) present.

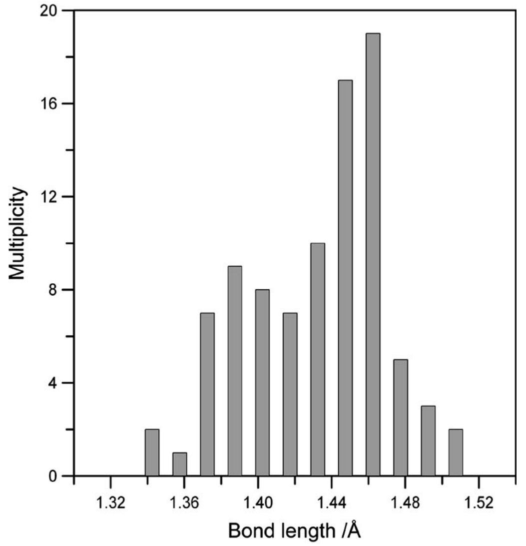

Figure 5. C–C bond length distribution within the fulleride anion C_{60}^{2-} in $[K(DB24C8)(DME)]_2C_{60}\cdot DME$.

When examining the C–C bond lengths as determined for C_{60}^{2-} in $[Ba(NH_3)_7]C_{60}\cdot NH_3$[8] with high accuracy, it has turned out that the C_{60}^{2-} displays a specific symmetry reduction from I_h to D_{3d},[13] just a minimal step needed for lifting the degeneracy of the t_{1u} orbital of the undistorted molecule. Thus, this has been the first observation of a static Jahn–Teller distortion in a C_{60}^{n-} anion. The C–C bonds split up into four inequivalent types, which are represented in Figure 6 by different colours (blue, yellow, red, green). In the case of $[Ba(NH_3)_7]C_{60}\cdot NH_3$, the red ones are elongated most, the yellow and green bonds in a moderate manner, and the blue ones are not significantly changed. This distortion pattern has been confirmed by HF and DFT type quantum chemical calculations, at the same time confirming an electronic singlet ground state.[13]

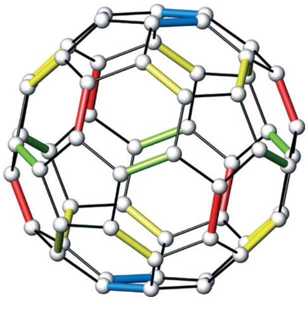

Figure 6. Positions of the symmetry inequivalent (6,6)-bonds in C_{60}^{2-} for the D_{3d} representation. The four different types are represented by different colours.

Unfortunately the crystal structure analysis presented here is not of sufficient precision to directly allow the identification of the distortion pattern. Therefore, the bond lengths of the four symmetry equivalent subsets in D_{3d} (Figure 6) were averaged for all ten possible orientations of the unique (threefold) axis. The result is summarized in Figure 7. Indeed, there are two orientations (no. 3 and no. 8) that match the previous experimental and theoretical findings, in particular with respect to the most elongated bonds (printed in red, Figure 7). The variations in the remaining subsets (yellow, green, blue) are less significant as can also been seen by comparison with the calculated values (Figure 7). This situation of finding two orientations with approximately fulfilling D_{3d} symmetry was encountered earlier in $[Mn(NH_3)_6]C_{60}\cdot 6NH_3$,[11,13] and can be rationalized either by assuming an incoherent superposition of two orientations of the C_3 axis in the crystal structure or by assuming a lower point group symmetry D_{2h} which would be in full accordance with the overall distortion pattern since the orientations 3 and 8 are related by a twofold rotation axis. While D_{3d} is a maximal subgroup of I_h, symmetry reduction to D_{2h} proceeds in two maximal steps from $I_h \rightarrow T_h \rightarrow D_{2h}$. Such a symmetry reduction to D_{2h} is lifting the orbital degeneracy as well.

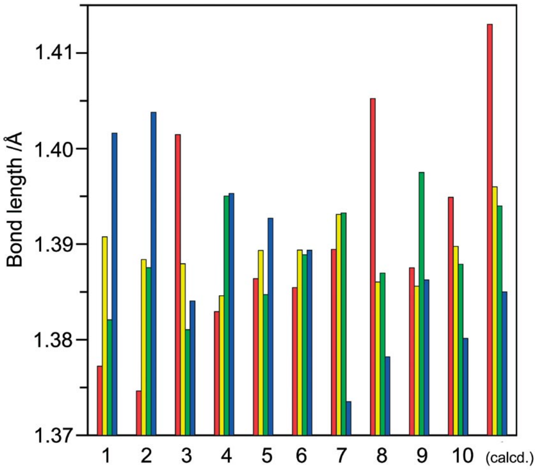

Figure 7. Averages of in D_{3d} symmetry equivalent subsets of C–C bond lengths for all possible orientations (1–10) of the unique threefold axis, and the respective bond length variations as obtained from quantum chemical calculations at 0 K.[13,20]

Conclusions

A new C_{60}^{2-} fulleride has been synthesized and structurally characterized. A comprehensive analysis of the intramolecular bond lengths distributions has revealed a symmetry reduction to point group D_{3d}, lifting the degeneracy of the frontier orbitals in the sense of a Jahn–Teller distortion. We have ventured to extract systematic trends in the intramolecular C–C bond lengths from the rather "noisy" experimental data, because the findings could be backed by independent experimental data from other systems and by calculations.

Experimental Section

Synthesis: All experiments, including the purification of the starting compounds, were conducted in an all-glass apparatus using the "break-and-seal" technique described elsewhere.[14]

48.2 mg (6.9×10^{-5} mol) of ground C_{60} ("MER Corporation", USA, 99.9%) were reacted with 93.0 mg (20.8×10^{-5} mol) of dibenzo-24-crown-8 (DB24C8, "Fluka", 98 %) and an excess of metallic potassium ("Merk", cubes kept under protective liquid, for synthesis) in form of potassium mirror in 30 mL of dimethoxyethane (DME, "Reagentplus", ≥ 90 %).

Unlike the procedure described in ref.[14] where crystals were grown from the primary solution after adding octane by the modified "temperature difference method", in the present work, after keeping the primarily obtained solution for two days, big red-brown thin platelet-like crystals were observed at the bottom of the ampoule where it was stored, while the solution still had remained with its original intense color.

Structure Determination: For X-ray diffraction experiments, a red-brown, plate-like crystal was selected from the mother liquor (in air), transferred to highly viscous oil, and mounted onto a kapton loop (MicroMounts™, MiTeGen, Ithaca, USA). The intensity data of the single crystal were collected with a Smart APEX II diffractometer (Bruker AXS, Karlsruhe, Germany) with Mo-K_α radiation (0.71073 Å) at 100 K.[15] Data reduction was carried out with the Bruker Suite software package,[16] absorption correction was applied using SADABS.[17] The systematic extinctions observed (*hkl*: $h + k = 2n$; and *h*0*l*: h, $l = 2n$) make the two space groups *Cc* (no. 9) or *C*2/*c* (no. 15) possible, from which *C*2/*c* has turned out to be the correct one during structure refinement. The structure was solved by direct methods and refined by full-matrix least-squares fitting with the SHELXTL software package.[18]

The positions of the potassium atom, the oxygen atoms of the crown and those of the solvent molecules could be taken from the structure solution. The missing carbon atoms of the crown and the solvent were found from a subsequently calculated difference Fourier map. For C_{60}, only some of the carbon positions could be localized in the difference Fourier map. Therefore, the missing fullerene C-positions were "imported" as a "rigid body" with the FRAG command (SHELXTL[18]).

Table 1. Crystallographic data for $[K(DB24C8)(DME)]_2C_{60}\cdot DME$.

Chemical formula	$C_{120}H_{94}K_2O_{22}$
Temperature [K]	100(2)
Formula weight	1966.15
Crystal system	monoclinic
Space group (no.), *Z*	*C*2/*c* (15), 4
Lattice constants [Å]	$a = 31.133(4)$ $b = 15.127(2)$ $c = 21.433(3)$ $\beta = 117.506(2)$
Volume [Å^3]	8953(2)
Density (calculated) [g cm^{-3}]	1.459
Crystal size [mm^3]	0.32 × 0.28 × 0.06
Colour	red-brown
Diffractometer	Smart APEX II, Bruker AXS
X-ray radiation, λ [Å]	Mo-K_α, 0.71073
Monochromator	graphite
Absorption coefficient, μ [mm^{-1}]	0.190
2θ range [°]	2.94 to 51.32
Index range	$-37 \le h \le 37$ $-18 \le k \le 18$ $-26 \le l \le 26$
Absorption correction	multi-scan, SADABS[17]
Reflections collected	33955
Independent reflections, R_{int}	8459, 0.065
Number of parameters	922
$R_1[F^2 > 2\sigma(F^2)]$, $wR(F^2)$	0.056, 0.171
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	0.57, –0.35

It turned out that the orientation of the fullerene obtained after refinement did not match the C_2 site symmetry of the special position (4*e*: 0, *y*, 1/4) occupied by C_{60}^{2-}, and a superposition of two units was generated automatically. In an alternative description, the structure was refined in *Cc* assuming twinning with the twofold axis as the twinning element. However, no improvement of the fit between observed and calculated structure factors was obtained, consequently the disorder is local and static.

For the final structure refinement (in *C*2/*c*), all non-hydrogen atoms, including the carbon atoms of the fullerene, were refined independently and treated with anisotropic displacement parameters, without any restraints or constraints. The positions of the hydrogen atoms were calculated geometrically, and their isotropic displacement parameters were restrained to 1.2 times the value of the respective attached carbon atom. Experimental details on the crystallographic data and data collection are given in Table 1, atomic parameters and displacement parameters were deposited in a data base.[19]

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[1] P. D. W. Boyd, P. Bhyrappa, P. Paul, J. Stinchcombe, R. D. Bolskar, Y. Sun, C. A. Reed, *J. Am. Chem. Soc.* **1995**, *117*, 2907–2914.
[2] N. Koga, K. Morokuma, *Chem. Phys. Lett.* **1992**, 191–196.
[3] P. Bhyrappa, P. Paul, J. Stinchcombe, P. D. W. Boyd, C. Reed, *J. Am. Chem. Soc.* **1993**, *115*, 11004–11005.
[4] Th. F. Fässler, A. Spiekermann, M. E. Spahr, R. Nesper, *Angew. Chem.* **1997**, *109*, 502–504; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 486–488.
[5] M. Khaled, R. T. Carlin, P. C. Trulove, G. R. Eaton, S. S. Eaton, *J. Am. Chem. Soc.* **1994**, *116*, 3465–3474.
[6] D. V. Konarev, S. S. Khasanov, G. Saito, I. I. Vorontsov, A. Otsuka, R. N. Lyubovskaya, Yu. M. Antipin, *Inorg. Chem.* **2003**, *42*, 3706–3708.
[7] P. Paul, Z. Xie, R. Bau, P. D. W. Boyd, C. A. Reed, *J. Am. Chem. Soc.* **1994**, *116*, 4145–4146.
[8] K. Himmel, M. Jansen, *Inorg. Chem.* **1998**, *37*, 3437–3439.
[9] K. Himmel, M. Jansen, *Chem. Commun.* **1998**, *11*, 1205–1206.
[10] K. Himmel, M. Jansen, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1–3.
[11] K. Himmel, M. Jansen, *Eur. J. Inorg. Chem.* **1998**, 1183–1186.
[12] H. Brumm, M. Jansen, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1433–1435.
[13] G. Stollhoff, M. Jansen, R. Ahlrichs, *Science*, manuscript submitted.
[14] N. V. Kozhemyakina, J. Nuss, M. Jansen, *Z. Anorg. Allg. Chem.* DOI: 10.1002/zaac.200900283.
[15] G. Cakmak, J. Nuss, M. Jansen, *Z. Anorg. Allg. Chem.* **2009**, *635*, 631–636.
[16] *Bruker Suite*, Version 2008/3, Bruker AXS Inc., Madison, USA **2008**.
[17] G. M. Sheldrick, SADABS–*Bruker AXS area detector scaling and absorption*, Version 2008/1, University of Göttingen, Germany **2008**.
[18] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[19] CCDC-735151 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[20] G. Stollhoff, *J. Chem. Phys.* **1996**, *105*, 227–234.

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