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Single Crystals of Rb_4C_{60}: Synthesis and Structure Determination

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Single crystals of Rb_4C_{60} were obtained at 973 K in a closed niobium ampule, and the structure was determined by X-ray diffraction ($I4/mmm$, $Z = 2$, $a = b = 11.9783(17)$ Å, $c = 11.035(2)$ Å, and $V = 1583.3(4)$ Å^3). The refinement was successful without any bond distance restraint and resulted in average C$-$C bond lengths of $d(6{:}6) = 1.383(5)$ Å and $d(5{:}6) = 1.453(5)$ Å. $C_{60}{}^{4-}$ is rotationally disordered and has the shape of a distorted truncated icosahedron (D_{2h}). Using the new structural data, density functional theory calculations obtain a metallic ground state.

Since the beginning of research on alkali-metal fullerides, the molecular structure of the anions $C_{60}{}^{n-}$ ($n = 1-6$) as the fundamental building blocks was of particular interest.[1] A first structure determination was reported for the superconducting compound K_3C_{60} ($T_c = 19.3$ K) using synchrotron powder X-ray diffraction data.[2] Later, the isolation of single crystals of $[PPN^+]_2[C_{60}{}^{2-}]$ [PPN^+ = bis(triphenylphosphine)iminium ion] led to a full structural characterization of a fulleride anion.[3] The use of a cryptand made it possible to isolate even the highly reduced $C_{60}{}^{4-}$ from solution, but a structure determination was not reported.[4] Therefore, knowledge about the molecular structure is based mainly on the powder X-ray diffraction studies on Cs_4C_{60}.[5] Here we report the synthesis of single crystals of Rb_4C_{60} and present a structure determination conducted on a conventional in-house X-ray diffractometer at 293 K as well as first-principles band-structure calculations using the newly refined data.

Black rodlike single crystals of Rb_4C_{60} were obtained at 973 K in a closed niobium ampule (for details, see the Supporting Information). The structure refinement used the proposed model of K_4C_{60},[6] which assumed an orientational disorder of the $C_{60}{}^{4-}$ anion in the crystal structure (space group $I4/mmm$, $Z = 2$, $a = b = 11.9783(17)$ Å, $c = 11.035(2)$ Å, and $V = 1583.3(4)$ Å^3). In this model, the spherical anion adopts two different orientations with the same probability. In orientation A, the C1$-$C1′ bond is parallel to the *b* axis (Figure 1), whereas in orientation B, the bond is parallel to the *a* axis. Overlaying both orientations results in a 4-fold screw axis parallel to the *c* axis. Furthermore, the anisotropic displacement parameters were set as equal for C1 to C3 and for C4 to C9. No other constraints, concerning, e.g., the bond lengths, were used as common for the structure refinement of alkali-metal fullerides using powder X-ray diffraction data. The cell parameters are in agreement with the ones previously reported from powder X-ray diffraction data,[7] and the improved parameter-to-data ratio allows for a stable refinement and a better structural model.

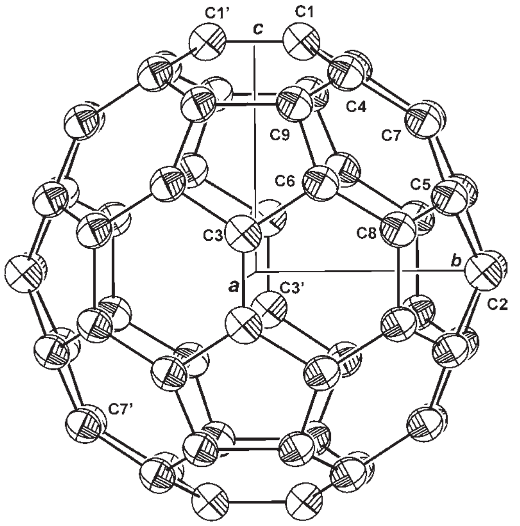

Figure 1. Structure of $C_{60}{}^{4-}$ in Rb_4C_{60} as an ORTEP presentation (50% probability level). The carbon atoms of the asymmetric unit are labeled, and the relative orientations of the unit cell axes to the fulleride anion are given (orientation A).

The structure of $C_{60}{}^{4-}$ is shown in Figure 1. The 60 three-bonded carbon atoms form a distorted truncated icosahedron

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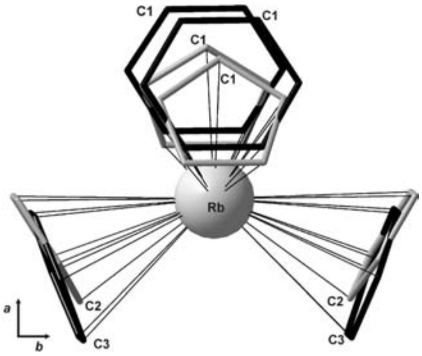

Figure 2. Coordination sphere of rubidium (pentagons in gray and hexagons in black). Each of the four surrounding fulleride ions is only presented by polygons of both orientations. The drawn Rb−C distances vary from 3.137(15) to 3.759(16) Å.

with 20 hexagons and 12 pentagons as faces (point group D_{2h}). The C−C bonds belonging to two hexagons [d(6:6), e.g., C6−C8] range from 1.38(3) to 1.43(2) Å with an average of $d(6:6) = 1.42(2)$ Å. For the bonds included in a hexagon and a pentagon [d(5:6), e.g., C6−C9], the distances vary between 1.42(1) and 1.47(3) Å, resulting in an average of $d(5:6) = 1.44(2)$ Å. Because there are no sufficiently precise structural data of pure C_{60} crystals available, we use for comparison the average distances obtained from single-crystal structure determinations of adducts.[1] For the neutral C_{60} molecule in adducts, the mean values for the two different bond types of $d(6:6) = 1.389$ Å and $d(5:6) = 1.449$ Å are well separated and hardly vary with a change of the cocrystallization agent.[8,9] In agreement with density functional theory (DFT) calculations,[10] we observe for $C_{60}{}^{4-}$ an elongation of d(6:6), which can be interpreted as a weakening of the double bonds due to the extra charges.

For quantification of the distortion of fulleride anions, several methods were suggested. One is to determine the difference between the longest and shortest diameters in the molecule, which are $d(C3-C3') = 7.13(2)$ Å and $d(C7-C7') = 7.07(2)$ Å, giving $\Delta = 0.064$ Å (the DFT result for D_{2h} symmetry is $\Delta = 0.096$ Å[10]). Following a more sophisticated method, the ideal crystallographic positions of the carbon atoms were calculated from the two average distances d(5:6) and d(6:6), describing an undistorted truncated icosahedron.[11,12] Then, the difference of the positional parameters was determined and the norm of the distortion vector calculated. We obtained for Rb_4C_{60} a value of 0.179 Å (the DFT result is $\Delta = 0.124$ Å[10]). Both methods suggest for $C_{60}{}^{4-}$ a static distortion of the ideal shape. However, in terms of the estimated standard deviations of the bond lengths, no conclusive statement can be made, similar to reports on $C_{60}{}^{2-}$[13] and $C_{60}{}^{3-}$[14] anions.

The results are in agreement with the structural data of Cs_4C_{60} determined by neutron powder diffraction data,[5] which reports for the d(5:6) and d(6:6) distances at 293 K the mean values 1.44(3) and 1.41(2) Å, respectively, and for the shortest diameter $d = 6.99$ Å.

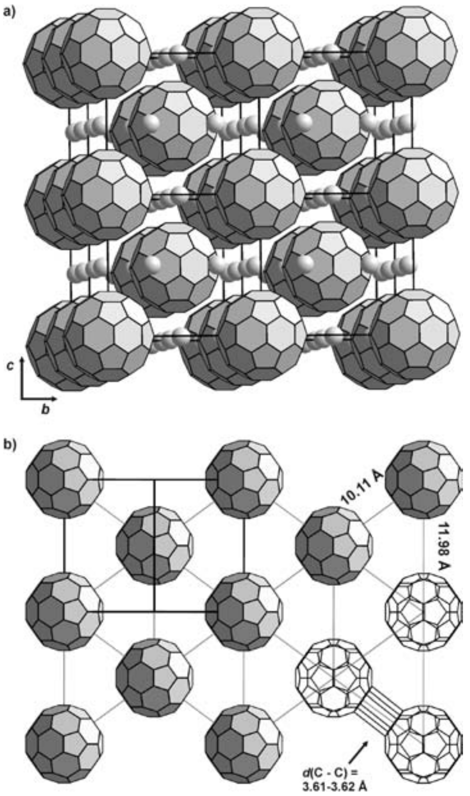

Figure 3. Crystal structure of Rb_4C_{60} (orientational disorder is not shown): (a) body-centered-cubic packing of fulleride anions in a 2 × 2 × 2 supercell (outlined); (b) pseudohexagonal layer of fulleride anions (view direction 0−11) with distances between the centroids (gray) and the shortest intermolecular C−C distances (the unit cell is shown in black).

Each rubidium ion in Rb_4C_{60} is surrounded by four $C_{60}{}^{4-}$ anions in a tetrahedral fashion (Figure 2). The Rb−C distances vary from 3.137(15) Å (Rb−C2) to 3.759(16) Å (Rb−C8) with a gap until 4.034(17) Å (Rb−C1). The coordination takes place via a pentagonal or a hexagonal face, depending on the orientation of the particular fulleride anion. In the case of C1-containing hexagons, only four short contacts are found, whereas for all other arrangements, all carbons atoms of the polygon are included. This leads to a variable coordination number for rubidium between 18 and 22.

The coordination sphere of a fulleride anion consists of 16 rubidium ions forming 80 contacts and 8 + 2 + 4 surrounding $C_{60}{}^{4-}$ anions (centroid distances: 10.108, 11.035, and 11.978 Å). The resulting tetragonal body-centered-cubic crystal structure is shown in Figure 3a. Focusing on the shortest intermolecular distances, pseudohexagonal layers of fulleride anions can be defined as shown in Figure 3b. The shortest intermolecular C−C contacts (3.61−3.62 Å) are found between opposite hexagonal faces, which form an oblique hexagonal prism. This is longer than the typical van der Waals contacts observed for neutral $C_{60}-\pi$ system complexes ($C_{60}\cdot 4C_6H_6$, $d = 3.27-3.21$ Å; $C_{60}\cdot C_{60}H_{28}\cdot 2C_7H_8$, $d = 3.128$ Å).[15,16]

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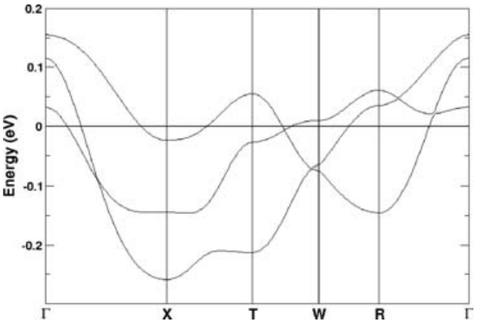

Figure 4. Band structure of Rb_4C_{60} close to the Fermi level. The bands at the Fermi level belong only to the carbon 2p orbitals pointing radially outward (see the Supporting Information).

Using this new structural data, we analyzed the electronic structure for an ordered model (space group *Immm*) by employing the full potential local orbital code FPLO.[17] The resulting band structure is shown in Figure 4. The three bands (t_{1u} band complex) crossing the Fermi level are made from 60 carbon 2p orbitals. The width of the t_{1u} band is 0.42 eV, which is smaller compared to that of K_4C_{60} (0.56 eV).[18] The metallic state is contrary to the insulating state observed experimentally.[19] Possible Jahn−Teller distortion or an underestimation of the strong Coulomb correlations (*U*) within DFT were suggested to cause these conflicting results.[20]

The collected single-crystal X-ray diffraction data on the alkali-metal fulleride Rb_4C_{60} allow, for the first time, the full refinement of all carbon atom positions along with two different anisotropic displacement parameters for two types of carbon atoms (C1−C3 and C4−C9). An elongation of the carbon double bonds [*d*(6:6)] in the hexagonal faces is observed in comparison with the neutral C_{60} molecule. Using the new structural data, DFT calculations obtain a metallic ground state.

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Supporting Information Available: Crystallographic data of Rb_4C_{60}, distribution and list of bond distances in $C_{60}{}^{4-}$, and experimental details on the preparation. This material is available free of charge via the Internet at http://pubs.acs.org.

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