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Triple-Decker Type Coordination of a Fullerene Trianion in $[K([18]crown\text{-}6)]_3[\eta^6,\eta^6\text{-}C_{60}](\eta^3\text{-}C_6H_5CH_3)_2$—Single Crystal Structure and Magnetic Properties**

Thomas F. Fässler,* Rudolf Hoffmann,
Stefan Hoffmann und Michael Wörle

Dedicated to Professor Hans-Herbert Brintzinger
on the occasion of his 65th birthday

Molecular conductors are promising candidates for high-temperature superconductors because large phonon frequency bands with little dispersion and hence a large density of state at the Fermi level (E_F) are possible. The alkali metal–fullerides A_3C_{60} (A is the alkali metal) are a fascinating class of compounds showing superconductivity up to 40 K.[1, 2] The trianions of the C_{60} fullerenes play a deciding role in understanding the superconductivity, and, therefore, the nature of the electronic ground state of $[C_{60}]^{3-}$ and its intermolecular interactions are of particular interest. The LUMO of a C_{60} molecule with I_h-symmetry is threefold degenerate, has t_{1u}-symmetry, and can be occupied by up to six electrons. In A_3C_{60} compounds these orbitals form a small electronic band which is half filled with electrons and is responsible for the metallic conductivity (Figure 1). The occupation of the molecular LUMOs of C_{60} by a further three electrons is expected to result in energetically low-lying quartet (^{4}A) and doublet states (^{2}H and ^{2}T). The doublet states are Jahn–Teller-unstable systems and structural distortion is possible (Figure 1).[3–5] In spite of these interesting findings, there is still not a single crystal structure determination of a binary superconducting phase. Overlapping reflections, in refinements based upon X-ray and neutron powder diffraction studies, give plenty of scope for discussion as to the nature of the conformational disorder found in the K_3C_{60} fullerene molecules.[6–8]

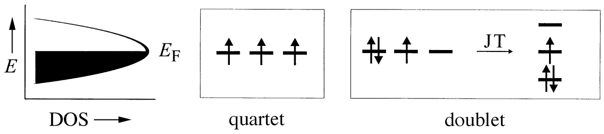

Figure 1. The three fold degenerate HOMO of the $[C_{60}]^{3-}$ ions with I_h symmetry (center) and the resulting density state (DOS) of the corresponding half-filled band in K_3C_{60} (left). In the doublet states, Jahn–Teller (JT) distortion is possible (right).

In the course of our investigations of soluble Zintl ions of the carbon group,[9, 10] we recently reported the reduction of C_{60} with potassium in DMF and the crystallization of a fullerene dianion with cryptands. In $[K([2.2.2]crypt)]_2[C_{60}](C_6H_5CH_3)_4$ (**2**),[11] following the principle of spherical close packing, the $[C_{60}]^{2-}$ units form layers which are separated from each other by bulky $[K^+([2.2.2]crypt)]$ ions (Figure 2a and b).[12] In attempting to prepare homoatomic anions of the heavier homologues of the carbon group by a one-pot synthesis, we chose to try the reduction of the elements tin and lead with alkali earth metals in the molten crown ether [18]crown-6.[13–16] Using fullerenes in this synthetic procedure has now enabled us to perform a single crystal structure determination of a salt containing two ordered C_{60} trianions. We now report the synthesis, and structural and magnetic properties of the complex $[K([18]crown\text{-}6)]_3[C_{60}](C_6H_5CH_3)_2$ (**1**).

Potassium dissolves in the molten crown ether [18]crown-6 at 313 K to give a deep blue solution. Carbon is added to the melt in the form of C_{60}. After the blue coloration disappears, DMF is added to the reaction mixture. Crystals of the title compound are then obtained by layering extracts of the reaction mixture with toluene [Eq. (1)]. The crystals are black cuboids which when crushed have a red hue.

$$C_{60} \xrightarrow[\text{DMF, toluene}]{\text{[18]crown-6, K}} [K([18]crown\text{-}6)]_3[C_{60}](C_6H_5CH_3)_2 \quad \mathbf{1} \qquad (1)$$

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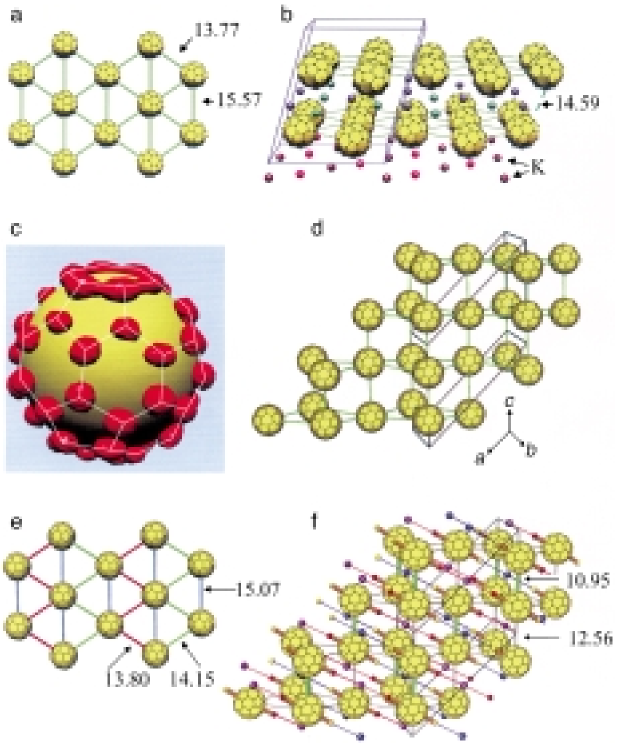

Figure 2. a) View of the distorted hexagonal arrangement of the fullerene molecules in the crystal structure of **2**. b) Arrangement of the fullerene molecules in **2**; instead of the [K([2.2.2]crypt)] units only the K atoms (spheres) are shown. c) Three dimensional view of an equal electron density surface in the area of the fullerene molecule in **1** from Fourier calculations. The white lines show the C_{60} polyhedron. The uppermost six atoms coordinate to the K atom (see also Figure 3a). d) Distorted primitive hexagonal arrangement of the fullerene units in **1**. Angles between the centers of the fullerene molecules in the plane perpendicular to the *c*-axis: 57.8°, 56.9°, and 65.3°. e) A layer of fullerene molecules in **1** in a plane perpendicular to the *c*-axis. f) Crystal structure of **2**. Instead of the [K([18]crown-6)] units only the K atoms (spheres) are shown (K1 = blue, K2 = violet, K3 = red, and K4 = yellow). The K–K separations are shown as thin lines to show the packing more clearly.

The results of the single crystal structure analysis at 110 K are shown in Figures 2c–f and 3.[17] The asymmetric unit contains one half of the C_{60} molecule and four K atoms. Consideration of the site symmetry at special positions comes to three K atoms per C_{60} molecule and, thus, a threefold negative charge on the C_{60} anion. The potassium atoms are each bound to the six O atoms of the crown ethers. Two of the potassium atoms additionally coordinate to two opposing hexagonal faces of the C_{60} polyhedron, the other two potassium atoms each coordinate to two toluene molecules (Figure 3a).

Of the K atoms coordinated to the fullerene anion, K3 has six bonds to the C atoms which are of almost equal length (two of 3.279, two of 3.257, and two of 3.238 Å). K4 is shifted from the axis running through the center of the hexagon in the direction of the 5:6-ring connection (two bonds of 3.386, two of 3.261 and two of 3.138 Å; the shortest bonds are shown in Figure 3a as solid lines). The asymmetric coordination of the K atoms is also shown by the angle between the hexagonal face of the fullerene and the plane through the six O atoms of the crown ether; the angles for K3 and K4 are 1.3° and 9.7°, respectively. The toluene molecules which complete the 'sandwich' coordination of the other two potassium atoms, K1 and K2, bind as η^3-ligands with three noticeably shorter K–C bond lengths (3.230(8) – 3.517(5) Å compared to the three longer ones, 3.738 – 4.054 Å). The coordination of potassium by aromatic systems is known.[18] The shortest K–C bond length in **1** is shorter than the K–C bonds in potassium complexes with η^6-coordinated neutral aromatic molecules. In $[K^+(\text{dibenzo}[18]\text{crown-6})](\eta^6\text{-}C_6H_6)$, the K–C bond lengths are in the range 3.29 – 3.50 Å[18] and, in potassium complexes with cyclophane-like fullerene (dibenzo[18]crown-6) ligands, which have well defined distances between the C_{60} hexagon and the oxygens of the crown ether after covalent connection of the crown ether unit to the fullerene molecule, the shortest distance is 3.42 Å.[19] The shorter K–C bond lengths in **1** arise from the greater charge on the fullerene and from steric factors. The convex surface of the fullerene allows a closer approach of the C_{60} and the K atom of the $[K^+([18]\text{crown-6})]$ unit, relative to planar aromatic hydrocarbons.

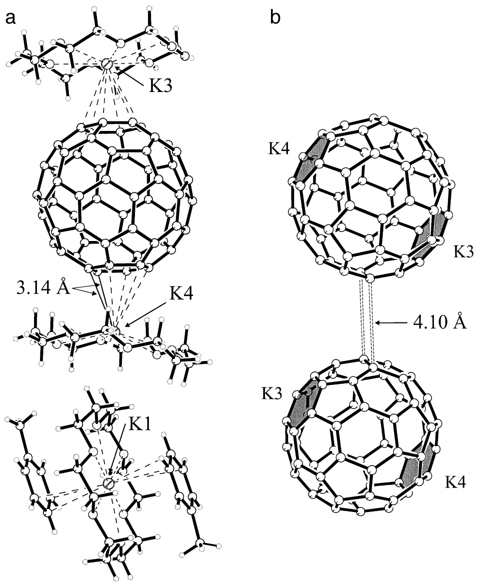

Figure 3. a) Relative arrangements of a $[K([18]\text{crown-6})]_2[\eta^6,\eta^6\text{-}C_{60}]$ (above) and a $[K([18]\text{crown-6})](\eta^3\text{-}C_6H_5CH_3)_2$ unit (below; see also the crystal packing diagram in Figure 2f). b) Arrangement of two fullerene molecules along the *c*-axis. The broken lines indicate the shortest intermolecular C–C separations (see also the separations marked in green in Figure 2f).

A comparison of the coordination of the potassium atoms in **1** and in the superconducting phase K_3C_{60}, a cubic face-centered lattice of fullerene molecules in which the potassium atoms occupy the octahedral and tetrahedral holes, is of particular interest. In a model of K_3C_{60}, in which there are two orientational disorders of the C_{60} molecule, the potassium atom in the tetrahedral hole is surrounded by four hexagonal faces belonging to the four nearest neighboring C_{60} molecules. The K–C bond lengths for this potassium (3.27 Å) are similar to those in **1**. The K–C bond lengths for the K atoms in the octahedral holes are 3.69 Å.[6, 20, 21]

The packing diagrams in Figures 2d–f show a situation analogous to the close packing of spheres, with layers of C_{60} molecules lying parallel to the *b*-axis and perpendicular to the *c*-axis. The distances between the centers of the fulleride anions in one layer are 13.80 (2 ×), 14.15 (2 ×), and 15.07 Å

(2 ×) and these correspond approximately to the separations in the layers of compound **2.** In **2** the stacking of the layers of fulleride ions resembles a hexagonal closest-packed array (Figure 2a and b), while in **1** the layers lie directly above each other, building a slightly distorted primitive hexagonal array (figure 2d and f). The layers are slightly puckered, resulting in shorter and longer distances between the ions. The shortest distance between fulleride centers (10.95 Å) is noticeably shorter than that in **2** (Figure 2b), but clearly longer than those of the cubic face-centered frameworks of the superconducting alkali metal intercalation complexes A_3C_{60} (10.07 (K_3C_{60}) to 10.25 Å (Rb_2CsC_{60})).[2]

The C_{60} anions of the title complex are ordered; this can be seen in the three-dimensional distribution of the electron density around the centers of the atom positions in the fullerene molecules (Figure 2c). The two different C–C bond lengths (6:6 and 5:6 ring connections) in C_{60} were, in each case, refined together and they converge to 1.380(5) and 1.460(5) Å, respectively. These bond lengths almost correspond to the values determined for a neutral C_{60} molecule.[22–24] A 'leveling out' of the two different bond lengths, as is the tendency in other ions,[25] is not seen in this case.[17]

The EPR spectra of freshly prepared microcrystalline powders show a broad isotrope signal at $g = 2.001$ (line width 4.08 mT) at room temperature, which indicates localization of the electrons.[26] A simulation of the signal[27, 28] allows identification of a second small line of lower intensity at $g = 2.000$ (line width 0.80 mT). Similar spectra are also obtained from binary phases from nominal compositions of A_3C_{60} (A = K – Cs)[29] and from electrochemically formed anions.[30, 31] The EPR spectra of $C_{60}{}^{n-}$ ions ($n = 1-3$) are the subject of much discussion.[32] There are other cases in which an obscured, sharp signal of lower intensity is found next to a broad line. Up to now it was not clear if this line is from a second spin state or from a fullerene carrying a different charge. Recently, it was suggested, for the monoanion $C_{60}{}^{-}$, that this small line arises from the formation of a fullerene dioxo radical through oxidation by oxygen.[33, 34] In the spectrum of **1** we observe that the intensity of the sharp line increases when the probe is exposed to air.

The paramagnetic properties were confirmed by temperature-dependent susceptibility measurements. The magnetic behavior follows the Curie – Weiss law; analysis of the data in the temperature range 80 – 280 K afforded the parameters $C = 0.373(3)$ emu K mol^{-1}, $\theta = -4.0(5)$ K, and $\chi_0 = 200 \times 10^{-6}$ emu mol^{-1} (Figure 4).[35] The calculated magnetic moment of 1.73 μ_B corresponds to an isolated spin doublet ($S = ½$). In agreement with these results the shortest intermolecular C–C separations indicate that only very weak interactions between the ions can be expected and show that the title complex has a diluted magnetic spin system. It is interesting to note that, in **1**, the carbon atoms of two different fullerene molecules lie only 4.10 Å apart (Figure 3b), the result of a type of [2+2] cycloaddition of the 5:6 ring connection. An analogous situation occurs in RbC_{60}, which can be described as a one dimensional polyfulleride formed by the [2+2] cycloadditions of the 6:6 ring connections of the fullerene molecules.[36, 37]

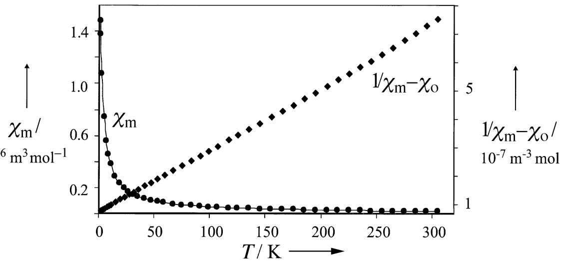

Figure 4. The temperature-dependence of the molar magnetic susceptibility χ_m (●) and the reciprocal temperature-dependent contribution $1/(\chi_m - \chi_0)$ (◆).

Generally, investigations of the electronic states of C_{60} trianions are difficult because, in solution the anions disproportionate and thus do not necessarily all have the same charge, and in the solid state either the exact composition or the complete structure is not known.[30, 31, 38–40] The efficient synthesis of single crystal samples of the title complex, a molecular species containing $[C_{60}]^{3-}$ ions, has enabled an extensive study of the structure – property relationships in fulleride trianions to be performed. The investigations of the magnetic properties show that, in this compound, the majority of the trianions are in the doublet state. A partial disproportination into anions carrying two and four negative charges, as demonstrated for the [K([2.2.2]crypt)] salts of $[Sn_9]^{3-}$ and $[Pb_9]^{3-}$,[41] can be ruled out.

Experimental Section

To perform the reduction in liquid [18]crown-6 at 313 K [18]crown-6 (800 mg, 3.00 mmol) and potassium (98 mg, 2.5 mmol) were weighed into a 20 mL Schlenk tube. The mixture was heated to 313 – 323 K so that the crown ether only just melted. C_{60} (100 mg, 0.14 mmol) was added to the intense blue melt and the mixture was stirred for 1 h. After cooling, DMF (3.0 mL) was added and the mixture sonicated for 15 min. The resulting dark red solution was filtered and layered with toluene (4.5 mL). The product crystallized over the course of 2 weeks.

Alternatively, the reduction can be carried out in DMF. Potassium (21.6 mg, 0.56 mmol) and C_{60} (100 mg, 0.14 mmol) were weighed into a 20 mL Schlenk tube. DMF (4 mL) was added and the mixture stirred at room temperature for approximately 14 h. During this time the color of the solution changed from green through violet to red. The red solution was filtered onto [18]crown-6 (202 mg, 0.75 mmol), sonicated for 30 min, and layered with toluene (5 mL). Over 2 weeks, the product precipitated as black rectangular cuboids. The yield from the second method is 145 mg (57.1 % from C_{60}). Elemental analysis ($C_{110}H_{88}O_{18}K_3$, 1815.19 g mol^{-1}): calcd (found) [%]: C 72.79 (71.33), H 4.89 (5.18), K 6.46 (6.39).

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[17] X-Ray analysis of **1**: A crystal with dimensions $0.50 \times 0.30 \times 0.25$ mm^3 was, after removal of solvent, washed with toluene and mounted in a glass capillary. Cell constants at 110 K: $a = 32.306(7)$, $b = 15.065(3)$, $c = 23.493(5)$ Å, $\beta = 133.44(3)^\circ$, $V = 8303$ Å^3; space group $C2/m$ (Nr. 12), $Z = 4$, $\rho_{\text{calcd}} = 1.452$ g cm^{-3}. Data collection: STOE-IPDS diffractometer, $\text{Mo}_{\text{K}\alpha}$ radiation, $2\theta_{\text{max}} = 48.22^\circ$ (image plate separation 80 mm, angle of rotation 0.7°, 257 frames). 24011 Reflections, of which 6445 were independent ($R_{\text{int}} = 8.8\%$). $R_1 = 8.23\%$ and $wR_2 = 21.36\%$ for 4679 reflections with $I > 2\sigma(I)$; $R_1 = 11.21\%$ and $wR_2 = 23.83\%$ for all reflections; 626 parameters of which 49 were coupled. When all fullerene parameters were independently refined, six longer (1.62–1.64 Å, 5:6 ring connections) and twelve shorter C–C bond lengths (1.31–1.35 Å, 6:6 ring connections) were found. The parameters correlate with this model, thus the refinement with coupled bond length parameters was favored. Few residual electron density maxima (< 1.47 e Å^{-3}) above the faces of the C_{60} polyhedra suggest that, besides the main orientation, a much smaller population of a second molecule, which is rotated by 90° about the K3–K4 axis of the main species, is also present. The molecule with this secondary orientation breaks the mirror plane. A refinement of two further fullerene molecules as well as the main species is not possible because of the correlation between the parameters. A twinned model fitting the data in an analogous manner does not lead to any improvement in the refinement. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138621. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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