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COMMUNICATION

THE SOLID-STATE STRUCTURE OF $K_3C_{60}(THF)_{14}$*

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Abstract—A solution reaction of C_{60} with an excess of potassium metal under sonication yields $K_3C_{60}(THF)_{14}$ (**1**; THF = tetrahydrofuran). Compound **1** forms a polymeric linear chain built-up from one potassium ion bridging between two fulleride ions and thereby sitting above a C–C bond between two pentagons, while the other two potassium ions cap the C_{60} molecule from top and bottom, thereby being located above six-membered rings. The coordination sphere of the potassium centres is completed by THF molecules. The crystal packing reveals a similarity with the face centred cubic lattice of the superconducting K_3C_{60} phase. The solution EPR spectrum of **1** exhibits a sharp signal with $g = 2.0007$ at temperatures between 120 and 330 K.

As a result of superconductivity in alkali metal M_3C_{60} salts, considerable interest has focused on alkali metal fullerides. Several discrete tetrahydrofuran (THF)-solvated alkali metal salts of the C_{60} anions have been described, and $M_3C_{60} \cdot x$THF have been found to serve as excellent precursors to the superconducting M_3C_{60} phases.[1–5] To the best of our knowledge, however, there appears to be no structural analysis of these solution-phase products.

Our interest in the structural elucidation of $K_3C_{60}(THF)_x$ originated from studies of the interaction of potassium with extended π-systems as part of the investigations on the adsorption of potassium on a graphitic surface,[6–8] together with a growing interest in solid-state structures of π-complexes of the heavier congeners of lithium.[9]

EXPERIMENTAL

Preparation of $\frac{1}{\infty}[\{K(THF)_5\}_2(C_{60})\{\mu\text{-}K(THF)_4\}]$ **(1)**

C_{60} (0.25 g, 0.35 mmol) and 0.08 g (2.10 mmol) of potassium metal in 5 cm^3 of tetramethylethylenediamine (tmeda) were treated for 1 h in an ultrasonic bath at 70°C to give a black slurry. Addition of 40 cm^3 of THF and 10 cm^3 of diethyl ether furnished a black–red solution, from which highly air-sensitive black–red crystals could be grown upon slow and stepwise cooling to 2°C.

Crystal structure determination

Empirical formula $C_{116}H_{112}K_3O_{14}$, formula weight 1847.36 g mol^{-1}. A crystal with a size of

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$0.2 \times 0.1 \times 0.25$ mm^3 was mounted on an Enraf–Nonius CAD-4 diffractometer equipped with a low-temperature unit [temperature set to 140(5) K, Mo-K_α radiation, $\lambda = 0.71069$ Å, graphite monochromator]. Cell parameters were determined from 25 high angle reflections in the range $18° < 2\theta < 30°$, $a = 25.051(4)$, $b = 14.033(5)$, $c = 12.905(3)$ Å, $\beta = 93.11(2)°$, $V = 4530(2)$ Å^3, $Z = 2$, $D_{calc} = 1.354$ g cm^{-3}, monoclinic, $C2/m$ (No. 12). Reflections were measured with an intensity-dependent scan time (maximal 50 s), with two-thirds of the time being allocated for the peak scan and one-sixth each for the scan of the left and right background, ω–2θ scan ($3° \leqslant 2\theta \leqslant 50°$), $-29 \leqslant h \leqslant 29$, $0 \leqslant k \leqslant 16$, $0 \leqslant l \leqslant 15$, 3276 reflections measured, 3175 symmetry-independent ($R_{int} = 0.0852$, μ(Mo-K_α) = 2.14 cm^{-1}, $F(000) = 1954$. Crystal orientation was checked every 200 reflections based on the angle determination of three check reflections. A deviation of more than 0.1% led to a new orientation matrix based on the newly centred 25 reflection. The intensities of the check reflections were tested every 2 h for crystal decomposition. No decay was observed. The raw data were corrected for Lorentz and polarization effects. The systematic absences $h+k = 2n+1$ are consistent with the space group $C2/m$. The normalized structure factor amplitudes suggested a centrosymmetric space group. The positions of the potassium atoms were located in a three-dimensional Patterson map (SHELXS-86).[10] Successive calculations of the Fourier and difference-Fourier maps with full-matrix least squares on F^2 (SHELXL-93)[10] gave the remaining non-hydrogen atoms. The hydrogen positions were calculated‡ and added to the model with constant temperature factors.§ Structure refinement was hampered by a heavy disorder in the coordinated THF molecules (see text). No absorption correction, 3163 data, 383

‡ We note that the calculated hydrogen positions on the disordered THF molecules are not very meaningful. However, because of their large number, empirical formula $C_{116}H_{112}K_3O_{14}$, inclusion of the hydrogen atoms subtracts a considerable amount of electron density in this essentially light atom or organic structure and is therefore necessary for an improved structure solution. Omitting the hydrogen atoms leads to an increase in the R_1 value by somewhat more than 0.02.

§ Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-401653, the names of the authors and the journal citation.
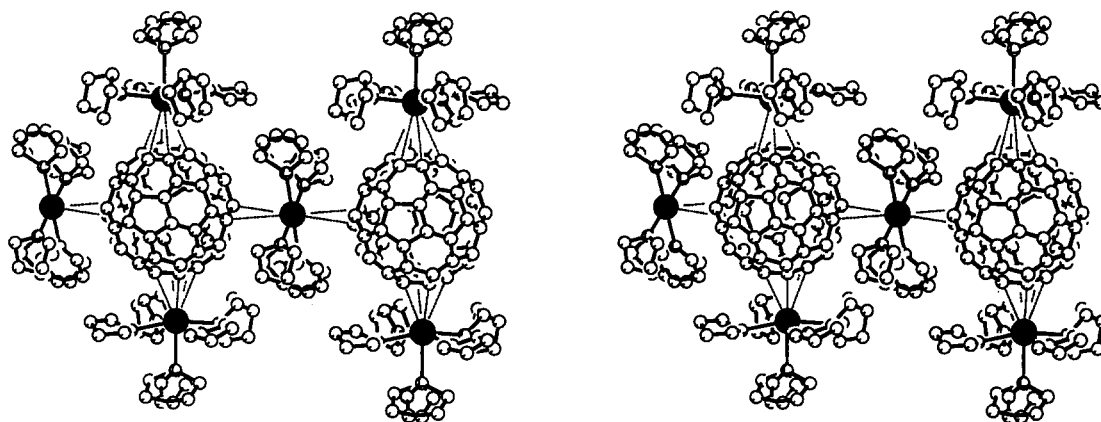
parameters refined, final $R_1 = 0.1152$, $R_{w2} = 0.3023$ and goodness-of-fit $= 1.065$ for 1767 reflections with $I > 2\sigma(I)$ $\{R_1 = (\Sigma \| F_0 | - | F_c \|)/\Sigma | F_0 |$; $R_{w2} = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$; GOF $= [\Sigma[w(F_0^2 - F_c^2)^2]/(n-p)]^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, where $P = (\max(F_0^2 \text{ or } 0) + 2F_c^2)/3$ with $a = 0.2003$ and $b = 5.5774\}$, largest difference peak and hole 0.34, -0.35 e Å^{-3}.

Electron paramagnetic resonance spectra

These were recorded on a Bruker ESP300E system at X-band frequency at temperatures between 120 and 330 K; microwave frequency 9.44 GHz, microwave power $\leqslant 0.5$ mW, modulation frequency 100 kHz, modulation amplitude $\leqslant 0.05$ mT. The g values were determined with an NMR magnetometer and DPPH (DPPH $= 2,2$-Bis-[4-(1,1,3,3-tetramethylbutyl)-phenyl]-1-picryl-hydrazyl) as g marker.

RESULTS AND DISCUSSION

Stirring a suspension of C_{60} in tmeda with a six-fold excess of potassium metal under sonication at 70°C followed by addition of THF and diethyl ether gave a deep black–red solution, from which crystals of the fulleride $(3-)$ salt $\frac{1}{\infty}[\{K(THF)_5\}_2(C_{60})\{\mu - K(THF)_4\}]$ (1) could be grown in good yield upon cooling. Figure 1 shows a stereo section of the linear chain structure of 1, determined by single-crystal X-ray diffraction. Of the three potassium centres per formula unit, one cation [K(2)] is bridging between two buckyballs, thereby sitting above a C—C bond between two pentagons of each C_{60} trianion. The other two potassium centres [K(1)] are symmetry related and cap the fulleride from top and bottom, being positioned above a six-membered ring. The potassium coordination environments are completed by four [K(2)] or five [K(1)] THF molecules, respectively. The potassium ions sit on special positions, with parallel mirror planes passing through K(1) and K(2); in addition K(2) lies on the C_2 axis, which runs perpendicular to the mirror planes. Only a quarter of the buckyball is symmetry independent.

The coordinated THF molecules are disordered. Since the THF rings are neither co-planar nor perpendicular to the respective mirror plane, part of the disorder is crystallographically induced, as the symmetry operation then requires a second position of the ring. The disorder might even be inherent in the structure, as a second crystal measured showed the same phenomenon. From a dynamic viewpoint the disorder may then be ascribed to the absence of strong intermolecular interactions between C_{60} and

Fig. 1. Stereoscopic view of a section of the chain structure (running along 010) of **1** in the crystal (PLUTON).[11] The coordinated THF molecules are disordered.

THF. Attempts to crystallize K_3C_{60} from other solvents such as dimethoxyethane or tetrahydropyrane have failed in our hands. Potassium to THF oxygen distances between 2.61 and 2.74 Å are as seen before,[7,8] while the potassium to carbon contacts (dashed lines in Fig. 1), ranging from 3.292(2) to 3.440(3) Å for K(1)—C, with K(2)—C = 3.642(4) Å, are comparable to the longer K—C_6 contacts observed in [K(THF)$_2$][K(tmeda)][μ-9-tert-butyl-fluorenide]$_2$ (variation 3.09–3.49 Å)[7] or on [K(THF)$_2$(tmeda)][coronene] (variation 3.13–3.55 Å).[8] The longer K—C contacts in **1** indicate a more effective solvation of the potassium ions by four or even five THF molecules when compared to the fluorenide or coronene complex, where tmeda is part of the solvation sphere. In this respect, however, it is, noteworthy that the nucleophilic THF solvent molecules do not displace the cation from the anion, but that some potassium–π interaction is still retained in **1**. The linear K—C_{60} strands can be though of as being surrounded and separated from each other by the THF molecules.

K_3C_{60}(THF)$_x$ has been described as a precursor for the preparation of a superconducting K_3C_{60} material.[1] Indeed, the crystal structure of K_3C_{60}(THF)$_{14}$ already bears some resemblance to the proposed face centred cubic lattice (space group *Fm3m*) for the superconducting K_3C_{60} phase.[12,13] It is noteworthy that one of the lattice constants in **1** (*b*) is already similar to the unit cell size of K_3C_{60} (*a* = 14.24 Å). In addition, both structures exhibit potassium ions in two different environments in a 2:1 ratio. The unit cell of the superconducting K_3C_{60} phase contains eight potassium ions filling the tetrahedral voids and four potassiums in the octahedral openings formed by the packing of the C_{60} moieties.[12] In comparison, the unit cell of **1** contains four capping potassium centres and two

bridging ones. The former will fall into the tetrahedral sites, the latter will occupy the preformed octahedral sites, both of which are created upon the following lattice distortion suggested for the annealing of **1**. Based on Fig. 2, which provides a view of the K—C_{60} unit cell packing, it is proposed that a loss of THF results in a volume reduction along *a* and *c* as the K—C_{60} strands freed from solvent molecules can close the gap. With the face centred C_{60} array already present in the *ab*-plane, every second 'layer' just has to slip half a unit cell along *a* (or *b*) to give the face centred cubic lattice. Thereby, the capping potassium ions [K(1)] move an additional quarter of the unit cell along *b*, together with some adjustment along *a* and *c*, into the tetrahedral sites.
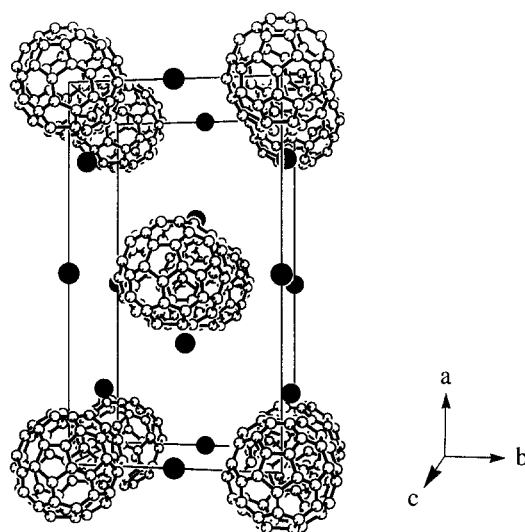

Fig. 2. Packing diagram of the unit cell of **1** with only the K_3C_{60} fragment shown (THF molecules are omitted for clarity).

A sharp EPR signal at $g = 2.0007$ (± 0.0003; peak-to-peak line width $\Delta B_{pp} = 0.1$ mT) is observed at room temperature for the solution of the mother liquor, from which the single crystals of 1 were grown (Fig. 3a). For modulation amplitudes <0.01 mT, two signals can be resolved with $g = 2.0008$ ($\Delta B_{pp} = 0.08$ mT) and 2.0005 ($\Delta B_{pp} = 0.02$ mT) (this small splitting is not visible on the scale used in Fig. 3a). The spectrum did not change for temperatures up to 330 K. In frozen solution, the line is slightly asymmetric ($g = 2.0007$, $\Delta B_{pp} = 0.2$ mT) and two very small additional peaks with a splitting of 1.2 mT were indicated (Fig. 3b). This signal is the same as observed for solutions containing the electrochemically generated C_{60}^{3-} anion, which were exposed to room temperature under inert conditions.[14] Saturated solutions of 1 containing a solid material which precipitated during EPR sample preparation exhibit a broad symmetric line ($g = 1.999$, $\Delta B_{pp} = 3$ mT) superimposed by the narrow line with $g = 2.0007$ of the supernatant solution (Fig. 3c). Corresponding broad lines have been described in the literature for diamagnetically non-diluted solids of alkaline fulleride anions.[3] The features of the EPR spectra described above support their assignment to a spin doublet ground state.[3,5,14] The difficulties concerning their assignment to a

discrete species have been reported in detail in the literature.[14] We can now, however, unequivocally assign the EPR spectra in Fig. 3 to a C_{60}^{3-} anion which is contained in the mother liquor of 1.

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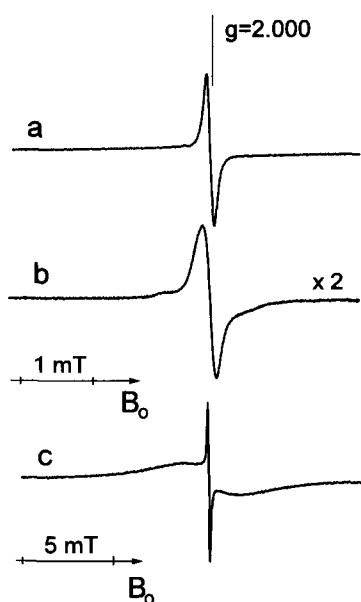

Fig. 3. X-band EPR spectra of a THF solution containing C_{60}^{3-} at $T = 293$ K (a, c) and at $T = 120$ K (b); modulation amplitude 0.05 mT, microwave power 0.5 mW. a and b were taken from a homogeneous solution (liquid and frozen, respectively; 5 mT scans); c additionally contains the solid precipitate (broad line, 20 mT scan). Spectra taken at different frequencies and sweep widths were shifted horizontally to align at $g = 2.000$.

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