

Structural and Electronic Ordering Phenomena in Fullerides.

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The chemistry of fullerenes offers a lot of potential that still remains but partially exploited. With respect to the field of solid state chemistry of fullerenes, their ability to easily form anions and to develop covalent intermolecular bonds is particularly interesting. In most cases, the resulting anions are open shell species, which gives rise to a variety of fascinating electronic effects in fulleride based extended solids, such as superconductivity or ferromagnetism. The mechanisms behind these collective properties are not yet fully clarified, however, have been tentatively associated with certain local electronic structures. For C_{60} , and also for many other highly symmetric fullerene cages, the frontier orbitals are highly degenerate, which upon reduction may get unequally occupied. Such a scenario inevitably should result in a Jahn-Teller effect (JT), which is assumed to play a crucial role in the fulleride properties.

Single-crystal X-ray structure determination is the most definitive experimental technique for detailed structural analysis and exploration of fulleride properties in the solid state. Nevertheless the progress in this field has been slowed by the difficulty in the synthesis of high quality single crystals. As a rule the fulleride crystals are frequently twinned and suffer from orientational disorder of the sphere-like C_{60} anions. To broaden the basis for in depth studies of the interesting physics and chemistry of fullerides, we have started a project aiming at the synthesis and characterization of diverse fullerides that are stable at room temperature and form structures containing ordered anions. Using different cationic building blocks, it is possible to generate low dimensional structures that allow for direct fulleride–fulleride interactions, resulting in interesting collective electronic states.

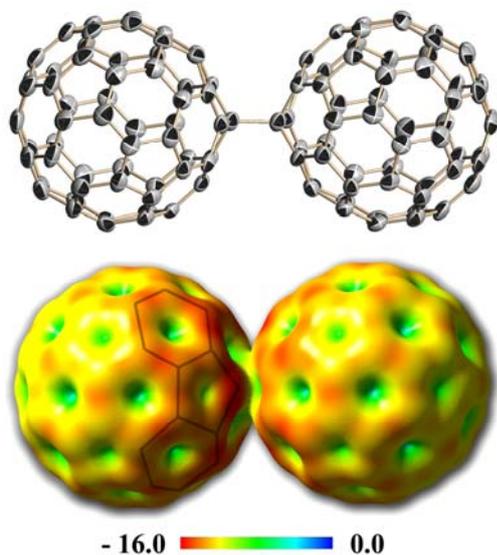


Figure 1: (top) *ORTEP*-presentations of an ordered dimer at 125 K in $[K(\text{dibenzo-18-crown-6})]_4 (C_{60})_5 \cdot 12\text{THF}$. Ellipsoids are shown at the 50% probability level. (bottom) Electrostatic potential of an isosurface of the electron density of the dimer in the singlet state in the *trans*-conformation (DFT, B3LYP, 6-31G basis set). The electrostatic potential distribution within the dimer shows that the negative charge is predominantly distributed over the fluorene fragments (two hexagons fused with a pentagon), mainly driven by the aromatization of the pentagon in the fluorene fragments. Thus, the slight advantage of the *anti*- as compared to the *gauche*-conformation, resulting from the specific charge distribution displayed within the dimer, seems to generate significant selectivity during crystallization, which is in contrast to the earlier claim that C_{60} dimers should exist as a mixture of the *anti*- and *gauche*-conformations.

We have demonstrated the efficiency of the “break-and-seal” approach for the synthesis of high quality fulleride single crystals, allowing the investigating of structural transformations in fulleride solids. Using a $[K(\text{dibenzo-18-crown-6})]_4 (C_{60})_5 \cdot 12\text{THF}$ single crystal, the ordering of the fullerene species along with the partial dimerization of two fullerene ion-radicals into $(C_{60})_2^{2-}$ dimers has been monitored while cooling.[1] For the first time, a crystal structure containing a fully ordered C_{60} dimer dianion has been obtained, thus allowing for an analysis of the molecular geometry and electronic structure. The negative charge within the dimer dianion is localized on a fluorene fragment adjacent to the sp^3 -hybridized C-atoms and not delocalized over the entire C_{60} cage (Figure 1). Remarkably, the fullerene molecules in this structure are present in three different bonding states: uncharged C_{60} , anion-radicals $C_{60}^{\cdot -}$ and dianions $(C_{60})_2^{2-}$, which is without precedent in fullerene chemistry.

Temperature-dependent measurements of the magnetic susceptibility at different magnetic fields confirm the phase transition observed crystallographically, and allow an unambiguous charge assignment to the different C_{60} species in the $[K(\text{dibenzo-18-crown-6})]_4(C_{60})_5 \cdot 12\text{THF}$.

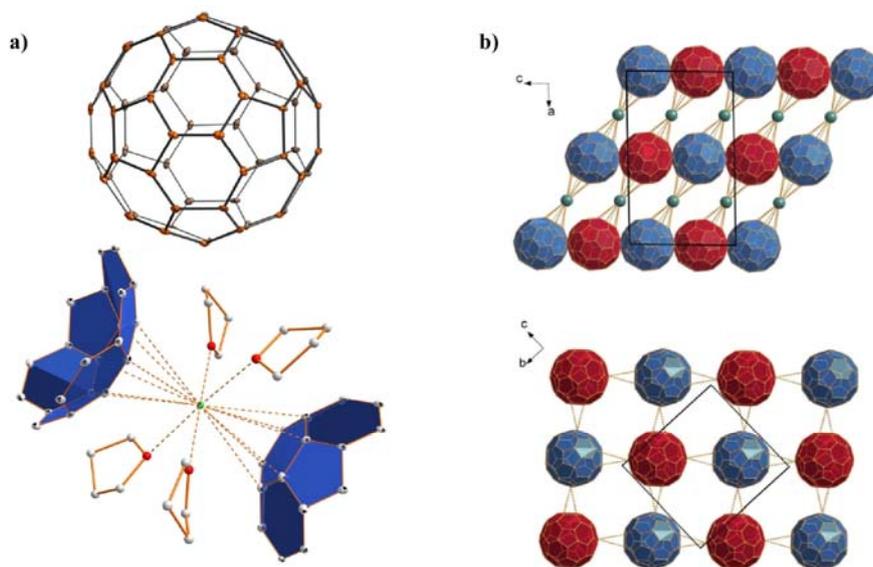


Figure 2: **a)** (top) ORTEP plot of the C_{60} anion radical in $[Cs(\text{THF})_4]C_{60}$ at 50 K. Displacement ellipsoids are drawn at 50% probability level. (bottom) Sandwich-like $[Cs(\text{THF})_4(\eta^6-C_{60})_{2/2}]$ fragment showing Cs^+ coordinated by four THF and two $C_{60}^{\cdot-}$ molecules. Hydrogen atoms are omitted for clarity. Only sumanene fragments of C_{60} are presented. **b)** (top) Projection of the crystal structure along [010] showing C_{60} -Cs individual chains (coded by blue and red colors) and layers of $C_{60}^{\cdot-}$. The unit cell is shown in black. THF molecules are omitted for clarity. (bottom) C_{60} layer with square shaped arrangement of the fullerene molecules. The short intermolecular $C \cdots C$ contacts of less than 3.3 Å are marked by dashed lines.

Recently we have demonstrated the synthesis of fully ordered $[Cs(\text{THF})_4]C_{60}$ single crystals, which have allowed us to monitor for $C_{60}^{\cdot-}$ the structural and electronic implications of the JT theorem, in particular to directly observe the transition from static to a dynamic JT effect.[2] The anionic and cationic building units in $[Cs(\text{THF})_4]C_{60}$, are the radical anion $C_{60}^{\cdot-}$ and cationic $[Cs(\text{THF})_4]^+$, where four THF molecules act as monodentate ligands forming a square-planar complex. Each fullerene anion is twofold coordinated by Cs, resulting in a linear chain of alternating cations and anions (Figure 2). The packing of the respective chains gives a square 2D-fullerene net, where each $C_{60}^{\cdot-}$ has four fullerene neighbors with short center-to-center intralayer distances of about 9.94 Å, while the shortest interlayer separation is substantially larger and amounts to 13.09 Å. Two of the coordinated THF molecules partially protrude into inter-fullerene voids, preventing the anion radicals from dimerization. Such an atypical square-shaped organization of fullerene anion radicals with short inter fullerene contacts have been regarded sufficient to manifest 2D-metallic behavior.

The precise structural information as obtained from 50 K diffraction data clearly gives evidence for a static JT distortion of C_{60} fullerene in $[Cs(\text{THF})_4]C_{60}$. An inspection of bond lengths in $C_{60}^{\cdot-}$ reveals a significant degree of deviation from the ideal I_h symmetry, indicating some systematic symmetry reduction as required in terms of the JT theorem. The deviations of the 6:6 carbon-carbon bond lengths as compared to unperturbed C_{60} was found to be systematic, and is fortunately not biased by the crystallographic site symmetry of $C_{60}^{\cdot-}$ (C_1). Relative to neutral C_{60} , the average length of the 6:6 bonds is increased from 1.383 Å to 1.396 Å whereas the average of 5:6 bond lengths is reduced from 1.453 Å to 1.449 Å. These changes are consistent with the nature of the now partially occupied t_{1u} LUMO of C_{60} which is antibonding with respect to 6:6 bonds and bonding with respect to 5:6 bonds.

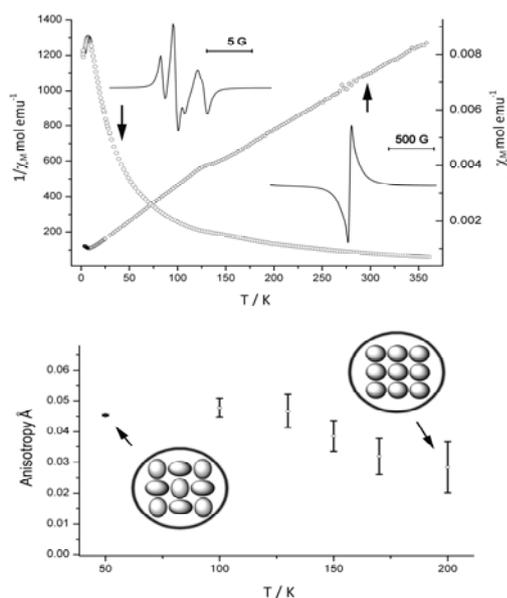


Figure 3: Observation of the transition from static to dynamic Jahn-Teller effects in $[\text{Cs}(\text{THF})_4]\text{C}_{60}$. (top) Temperature dependence of the molar magnetic susceptibility (χ_M) and inverse molar magnetic susceptibility ($1/\chi_M$) of $[\text{Cs}(\text{THF})_4]\text{C}_{60}$. Insets show the EPR lines for LT and HT phases. (bottom) The temperature dependence of the global anisotropy of C_{60}^- cage. Circle insets show schematically the relative direction of elongation in the fullerene cages within the square fullerene layer. For an evaluation of the degree of ellipsoidal distortion from the ideal sphere the anisotropy effect has been considered as a difference between longest and shortest carbon-to-carbon diameters. The anisotropy value of about 0.04 Å lays between the values experimentally found for pristine C_{60} (0.02 Å) and C_{60} dianion (0.07 Å).

The structural findings have been corroborated by temperature dependent magnetic susceptibility and EPR measurements. Magnetic measurements were performed in the 2–360 K range. Over the ranges 15–90 K and 160–360 K, the molar magnetic susceptibility can be fitted by the Curie–Weiss law $\chi_M = C/(T-\theta) + \chi_0$ with a constant $\chi_0 = 2 \times 10^{-4} \text{ emu mol}^{-1}$. The θ value was found to be -17 K for low-temperature region (LT), and -23 K for the high-temperature region (HT). The C value of 0.27 emu K mol⁻¹, which corresponds to the contribution of about 75% of the spins from the total amount of C_{60} , remain the same for both phases. The EPR spectrum of the HT phase shows a broad isotropic signal with a peak-to-peak line width of about ca. 150 G ($g = 2.0002$) which decreases dramatically to ca. 6 G for the LT phase (75 K) and shows a remarkable anisotropy. Such a behavior is associated with a transition from static to dynamic JT effects. The anisotropic nature of the spectrum of the LT phase indicates evidence for static C_{60}^- distortion from I_h symmetry whereas for the HT phase the effect appears to be dynamic on the EPR time scale, and an isotropic signal is observed. Due to dynamic averaging of ellipsoidal JT structures the anisotropy collapses and gives effective icosahedral symmetry (pseudorotation). Although the static-to-dynamic transition is well accepted, no direct evidence of this transformation in fullerides has been reported so far. The structural transformations in the system were analyzed in the phase transition region by means of X-ray crystallography. Neither irregular changes in the lattice parameters, nor in the relative position and orientation of individual molecules have been observed. However, a detailed analysis reveals that fullerene molecules undergo remarkable deformations and assume an ellipsoidal form at low temperature. The results of anisotropy changes are visualized in Figure 3, showing the transition to occur at the same temperature range found by magnetic measurements. The anisotropy factor of about 0.030 Å found for the HT phase is close to the anisotropy factor observed for pristine C_{60} . Decreasing the temperature causes an increase in the anisotropy in the interval of 130–160 K to ca. 0.048 Å which remains constant during further cooling.

The quality of the single crystals obtained has allowed the direct monitoring of phase transitions by means of X-ray analysis. The high quality X-ray data provide structural information sufficient to confirm charge distribution and even JT distortion in the C_{60} anion radical.

References:

- [1] N.V. Kozhemyakina, K.Yu. Amsharov, J. Nuss and M. Jansen Chem. Eur. J. **17**, 1798–1805 (2011).
- [2] K. Yu. Amsharov, Y. Krämer and M. Jansen Angewandte Chemie **123**, 11844–11847 (2011).