

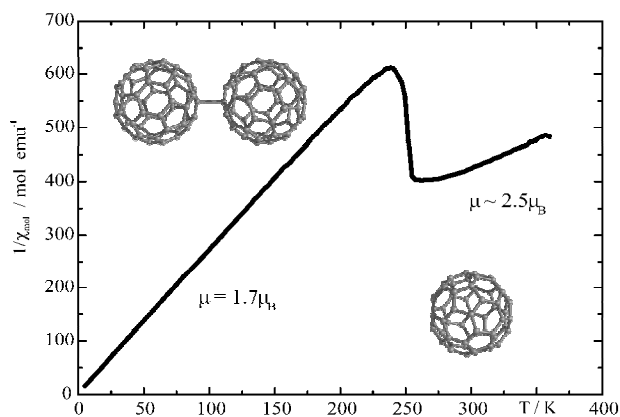
## Structural Response of Fullerenes on Reduction

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Due to the high molecular point group symmetries of  $C_{60}$  and  $C_{70}$  ( $I_h$  and  $D_{5h}$ , respectively) their lowest unoccupied molecular orbitals exhibit a high degree of degeneration. Thus, the reduction of this fullerenes is expected to lead to pronounced structural responses in the resulting fulleride-anions. Therefore we started systematic studies in the synthesis and structural characterization of compounds containing mono- and dianionic  $C_{60}^-$  and di- and trianionic  $C_{70}$ -fullerides prepared by chemical and electrochemical means.

**$C_{60}$ -fulleride monoanions** were prepared by electrochemical reduction of  $C_{60}$  in the presence of  $Ph_4P-Cl$  as well as by chemical reduction of  $C_{60}$  with  $Cr(C_7H_8)_2$ . The product of electrochemical reduction,  $(Ph_4P)_2(C_{60})Cl$ , suffers from rotational disorder of the fulleride sublattice. Bis(toluene)chromium fulleride,  $Cr(C_7H_8)_2C_{60}$ , crystallizes cubic and is constituted of dynamically disordered fulleride anions and bis(toluene)chromium(I) cations in an CsCl arrangement. The magnetic moment  $\mu = 2.5 \pm 0.2 \mu_B$  corresponds to two electron spins per formula unit. At 250K a reversible phase transition occurs, leading to a jump of the magnetic moment to  $\mu = 1.72 \pm 0.01 \mu_B$  (see fig. 1). EPR measurements confirm the single unpaired electron spin per formula unit to be localized at the chromium site ( $g_{iso} = 1.9870$ ). High resolution synchrotron powder diffraction studies of the low temperature phase as well as the phase transition itself confirm the lock-in of the rotational disorder of the  $C_{60}$ -monoanions and the formation of closed shell, dumb-bell shaped  $(C_{60})_2^{2-}$  dimers in the low temperature phase (see fig. 1).



**Fig. 1:** Magnetic susceptibility and molecular structure of  $[Cr(C_7H_8)_2]C_{60}$  for high and low temperature phase

**$C_{60}$ -fulleride dianions** were prepared by either direct reduction of  $C_{60}$  with alkaline-earth metals in liquid ammonia or ion-exchange of  $K_2C_{60}$  with properly loaded cationic ion-exchange resins in liquid ammonia. Due to the low temperature of crystallization the crystal structures of  $AC_{60} \cdot nNH_3$  ( $A=Ba, Co, Mn, Ni, Zn, Cd$ ) do not show any disorder in the fulleride sublattice. Except the Ba compound,  $[A(NH_3)_6]C_{60} \cdot 6NH_3$  crystallize triclinic. The crystal structures may be deduced from the *fcc* structure of pristine  $C_{60}$ , placing the hexamine-metal-complexes in the 'octahedral voids'.

Individual distances of the carbon atoms and the center of gravity give no significant hint to an aspherical distortion of the  $C_{60}$  dianion. A detailed analysis of the carbon-carbon bond lengths points, even in case of the triclinic com-

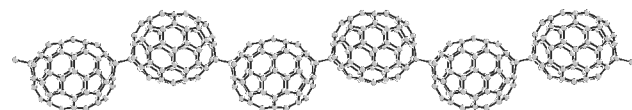
pounds, to a local, non crystallographical, molecular point group symmetry of  $D_{3d}$  ( $A=Ba, Co, Ni, Zn, Cd$ ) and  $D_{2h}$  ( $A=Mn$ ). In comparison to the neutral molecule, the bond-length alternation ( $d_{65}-d_{66}$ ) of the  $C_{60}$ -dianions is reduced and splits into four sets. *Local-Ansatz* calculations of the three different electron configurations of  $D_{3d}$  symmetric  $C_{60}^{2-}$ , i.e.  $^1D_0$ ,  $^3P_1$  and  $^1S_0$ , show the energetic differences to vary within the methodological error. On the other hand, the experimental bond-length alternations are in good agreement with those found for the  $^1S_0$  configuration. Thus, the electronic groundstate of  $C_{60}$  dianions in  $AC_{60} \cdot nNH_3$  is a singlet spin-state. The proposed Jahn-Teller-effect does not manifest in an aspherical distortion of the fulleride dianion but in an anisotropic bond length alternation pattern, i.e. it is of **local character**.

**$C_{70}$ -fulleride di- and trianions** were prepared by direct reduction of  $C_{70}$  with alkaline-earth metals in liquid ammonia and crystallized in sealed tubes under autogenous pressure at ambient temperature. The crystal structures of  $[Sr(NH_3)_8]C_{70} \cdot 3NH_3$ ,  $[Ba(NH_3)_9]C_{70} \cdot 7NH_3$  and  $[Sr(NH_3)_8]_3(C_{70})_2 \cdot nNH_3$  ( $n=20-22$ ) consist of polymeric anionic chains  $^1_\infty[C_{70}^n]$  ( $n=2, 3$ ; see fig. 2), arranged as distorted hexagonal packings of rods.

In contrast to high-pressure fullerene polymers and simple binary fullerides, the  $C_{70}$  fulleride-ions of these polymer chains are linked not in a two-bond cyclobutane like arrangement, but by solely one carbon-carbon single bonds located at the pentagons of each  $C_{70}$  cap, close to the former fivefold axis of the neutral monomer. Furthermore, the  $C_{70}$  trianionic polymer chains realize two different, diastereomeric schemes of intercage connection with syndiotactic arrangement following AABB.

Quantum chemical investigations of  $C_{70}^{2-}$  and  $[C_{70}(CH_3)_2]^{2-}$  as a model system for the  $C_{70}$  dianionic polymer chain and neutral  $C_{70}$  as reference system show different structural responses of  $C_{70}$  on reduction for  $C_{70}^{2-}$  and  $[C_{70}(CH_3)_2]^{2-}$ : structural changes in  $C_{70}^{2-}$  appear exclusively in the phenylene type belt at the small equator while any structural changes in  $[C_{70}(CH_3)_2]^{2-}$  are located in the caps in the vicinity of the five-fold axis. In contrast to  $C_{70}^{2-}$ , the optimized structure of  $[C_{70}(CH_3)_2]^{2-}$  resembles the experimental structure of the dianionic polymer chain at bond-length differences less than 2 pm, already at the HF-SV level. Analyzing the bonding properties of  $[C_{70}(CH_3)_2]^{2-}$  by means of electron localization function (ELF) calculations, the phenylene type belt resembles the characteristics of aromatic systems. The features found close to the caps correspond to conjugated olefines. Finally, the ELF in the vicinity of the intercage bonds represents carbon-carbon single bonds and slightly carb-anionic character, respectively. Thus, the preservation of the aromatic character of the phenylene type belt at the small equator of the  $C_{70}$  cage is the driving force to a highly local structural response of  $C_{70}$  and the formation of  $^1_\infty[C_{70}^n]$  ( $n=2, 3$ ) polymeric chains.

In conclusion, the **structural response** of  $C_{60}$  and  $C_{70}$  fullerenes on reduction to mono-, di- and trianionic fullerides exhibits a broad variety but is always of **highly localized character**.



**Fig. 2:** Polymeric anionic chains  $^1_\infty[C_{70}^{2-}]$  in  $AC_{70} \cdot nNH_3$