

FERROCENE DERIVATIVE IN 1,3 DIPOLAR CYCLOADDITION REACTION TO FULLERENE C₆₀

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Abstract

Properties of FeC₆₀ solid samples were investigated by X-ray diffraction, ⁵⁷Fe Mössbauer spectroscopy and magnetic measurements in order to examine interaction of iron with fullerene. FeC₆₀ samples were prepared by decomposition of adduct based on the fullerene and ferrocene derivative. The samples exhibited superparamagnetic properties originating from an interaction between FeC₆₀ complexes within nanoparticles. Each nanoparticle consisted of hundreds to thousands complexes. The results of experiments are compared with theoretical studies using PM3 method based on the Neglect of Diatomic Differential Overlap approximation.

Keywords: ferrocene derivative C₆₀ cycloadduct, fullerene, magnetic properties, thermal stability

Introduction

Chemically stable C₆₀ doped with metals, located inside (endohedral compounds) or outside (exohedral) the fullerene cage, has been prepared and studied by electron spin resonance (ESR) [1, 2], X-ray diffraction [3, 4], extended X-ray absorption [5, 6], photoelectron [7] and Mössbauer spectroscopy [5, 8, 9]. The existence metal-C₆₀ complexes in the gas phase has also been confirmed [10, 11].

The aim of our work was to prepare the fullerenes with transition metal atoms attached externally, directly to the C₆₀ cage. Such a compound may prove to be a new magnetic material due to an interaction between fullerene π -electrons and d -electrons localized at the metal site adopting various spin states. We report investigations on the fullerene adduct with iron. This paper is a continuation of our earlier studies [12–15] on the preparation of exohedral FeC₆₀ complex with ferrocene (Fn→C₅H₅FeC₅H₅) as iron source. We have applied the 1,3 dipolar cycloaddition process of ferrocene nitrile oxide FcCN⁺O⁻ (Fc→C₅H₅FeC₅H₄) to fullerene. In this reaction the 6–6 bonds, common to two six-membered rings in C₆₀ are attacked, resulting in a monoadduct C₆₀ONCFc or a diadduct C₆₀(ONCFc)₂. During the process fullerite

becomes contaminated by hydrocarbon impurities originating from the ferrocene derivative. The organic groups can be removed by annealing of the monoadduct though iron remains in C₆₀ matrix. We tried to estimate geometry and heat of formation of the FeC₆₀ complexes, their total spin, dipole moment and charge distribution around Fe nucleus on the basis of semi-empirical quantum chemical calculation. The results of the theoretical analyses are listed in [13, 16].

Final product FeC₆₀ was used for magnetic measurements. The experimental results are compared with the quantum chemical calculation using the PM3 method implemented in the commercially available package [17].

Experimental results and discussion

Synthesis and identification of C₆₀ONCFc adduct

1,3-Dipolar cycloaddition of ferrocene nitrile oxide FcC≡N⁺O⁻ to fullerene employed to synthesize fullerene derivative proceeds according to the following scheme:



The synthesis is described in details in [16]. The product C₆₀ONCFc was separated by a chromatography method using silica gel column with toluene as an eluent.

It is expected that in this reaction the molecule of ferrocene is bound to the fullerene at the 6–6 ring junction by isoxazoline (–C=N–O–) ring. Number and positions of the ¹H and ¹³C NMR lines support the proposed structure. The structure of the fullerene monoadduct C₆₀ONCFc optimized with use of method PM3 is presented in Fig. 1.

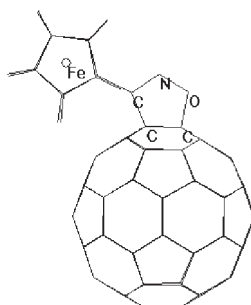


Fig. 1 Idealized structure of C₆₀ONCFc monoadduct constructed with PM3 model

Thermal and structural investigations

Thermal experiments were performed using a DuPont Instruments apparatus applying DSC and TG methods. The measurements were carried out under helium atmosphere with the flow rate of 25 mL min⁻¹ at 10°C min⁻¹ heating rate. Figure 2 presents the characteristic process of the C₆₀ monoadduct thermal decomposition. From DSC and TG plots it is visible that decomposition involves several endothermic and exothermic processes. The first endothermic process was registered at temperatures of

100±200°C and was connected with 8% mass loss. We ascribe this effect to evaporation of toluene and ferrocene derivative not bound to C₆₀. The next exothermic effect, in the temperature interval 270÷400°C originates from decomposition of the monoadduct. The observed 15% mass loss corresponds to 18% mass loss that should be expected if C₃H₅ and C₃H₄CNO of the C₆₀ONCFc monoadduct completely evaporated. The difference of 3% in the mass loss is probably caused by evaporation of free ferrocene derivative at the temperature close to 200°C. The presence of exothermic peak, instead of the expected endothermic one due to breaking of the C₆₀-Fc oxime bonds indicates that the freed organic fragments dimerize or polymerize still in the measuring pan. Further experiments proved that during the decomposition process most of iron remains in the C₆₀ matrix.

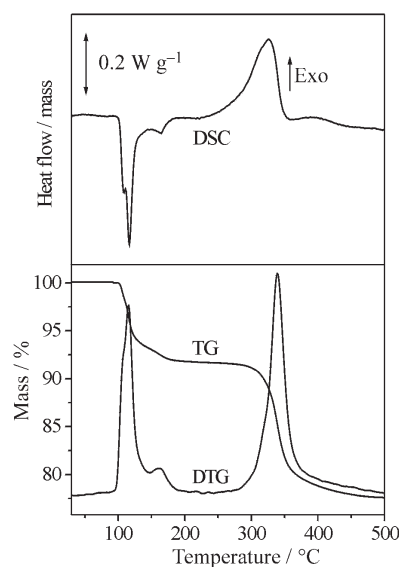


Fig. 2 TG and DSC results on C₆₀ONCFc monoadduct, showing the mass loss and endothermic and exothermic effects during decomposition

The dried powder of the fullerene monoadduct C₆₀ONCFc was investigated by X-ray diffraction analyses using Siemens D500 diffractometer. The reflections could be indexed in terms of a monoclinic lattice with following parameters: $a=1.873$ nm, $b=1.414$ nm, $c=1.419$ nm, $\beta=108.3^\circ$. The unit cell $V=3.758$ nm³ are sufficient to accommodate four C₆₀ONCFc molecules if the ferrocene fragments were directed towards the interstitial sites. Fragment of pseudo-hexagonal plane of the proposed monoclinic lattice in [111] direction is shown in Fig. 3.

The crystalline structure has not been changed by annealing the sample to 200°C in spite of the observed mass loss, that points out that the volatile molecules could probably be located between the crystalline grains, but did not constitute the unit cell.

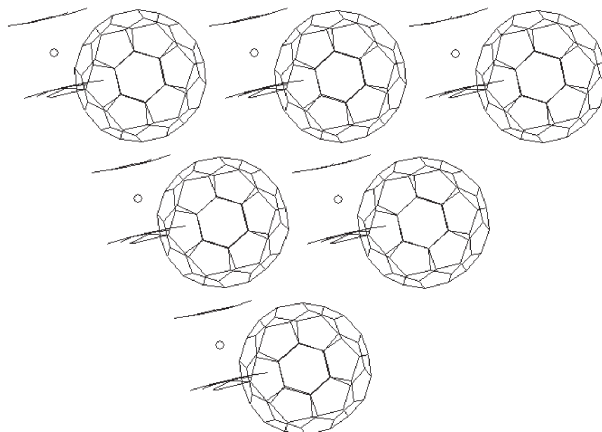


Fig. 3 Pseudohexagonal plane of monoclinic lattice of C₆₀ONCFc in [111] direction

After annealing to 400°C when most of the volatile compounds evaporated, the samples adopted the face centered cubic lattice with the lattice constant larger by about 1% than of pure C₆₀. Increase of the lattice constant may result from iron atoms dispersed between fullerenes. There were no diffraction lines that could be ascribed to iron, iron oxide or carbide clusters. Iron concentration in fresh sample and after decomposition was determined by X-ray fluorescence method, it was found to be 1Fe/60C and 0.85Fe/60C respectively.

In samples heated to 400°C we were unable to detect either ¹H NMR or IR absorption lines, that could be ascribed to residual hydrocarbon groups.

Mössbauer spectroscopy

The Mössbauer effect was measured in standard transmission geometry using constant acceleration spectrometer coupled to a 50 mCi ⁵⁷Co/Rh source. The Mössbauer spectrum was approximated by Lorentzian lines to determine Mössbauer parameters: isomer shift (*IS*) and quadrupole splitting (*QS*). *IS* depends on *s* electrons density in the nucleus region and the *QS* is determined by gradient of the electric field that is generated by the charge distribution around Fe nucleus thus supply information on the type of the chemical bond of Mössbauer atom (Fe). In the fresh sample, a single quadrupole doublet was observed with *IS*=0.418 mm s⁻¹, *QS*=2.336 mm s⁻¹ and line widths of 0.254 mm s⁻¹ at the temperature 300 K. These values are very close to those found in pure ferrocene [8, 18] and are consistent with the double oxidation of the iron and a low symmetry of the electric field gradient at the nuclei. This result suggests that the charge distributions at Fe nucleus in ferrocene and in the monoadduct are similar. That is because the cyclopentadien rings (C₅H₅) well shield iron from the influence of the surroundings. In order to confirm the notion we have performed a semi-empirical quantum calculation using the PM3 model and found that, in both compounds, the charge distribution has a similar symmetry and density.

Magnetic properties

Magnetic properties of Fe_xC₆₀ samples prepared by various methods are similar [19, 20] therefore, we will summarize here the precise discussion of the observed effects presented in [20].

The magnetic measurements were performed in various magnetic fields up to 15 kOe and temperatures from 4.2 to 300 K (Fig. 4, inset) on samples cooled at $H=0$ and in magnetic field. The magnetization (M) reaches saturation in magnetic field above 5 kOe. The results may be fitted by the Langevin function, if it is assumed that the samples consist of particles having large magnetic moments with the Curie constant $C \approx 2000$ emu K mol⁻¹ Oe⁻¹. It ensures to determine the magnetic moment of individual particle and average size of single particle therefore the number of FeC₆₀ complexes in the particle. The similar number of FeC₆₀ complexes and number of Bohr magnetons μ_B in the particle suggest that each complex has the magnetic moment of approximately one μ_B both at low and high temperature. It suggests that there exist interaction between complexes within the particles that aligns their magnetic moments.

The temperature dependence of the magnetic susceptibility χ in zero field cooled (ZFC) samples diverges from that observed in field cooled (FC) samples at low temperatures (Fig. 4). It follows from this result that the external magnetic field easily induces changes in the orientation of the particles' magnetic moment only at high temperatures. However, there is temperature below which the anisotropy field of the particles blocks reorientation of the magnetic moments thus magnetic moment can be frozen in the samples. The anisotropy constant has been determined to be $K \approx 4.9 \cdot 10^3$ erg cm⁻³.

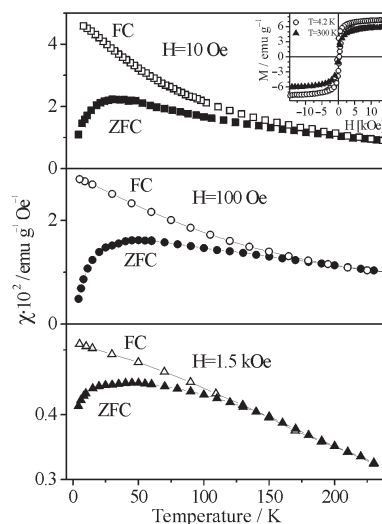


Fig. 4 Temperature dependence of the magnetic susceptibility χ of the FeC₆₀ samples cooled in zero magnetic field (ZFC) and in magnetic field (FC). The inset shows the magnetic field dependence of the magnetization (M) of the sample measured at $T=4.2$ and 300 K

The values of Curie constant and the anisotropy constant K are typical a superparamagnet at room temperature [20].

In order to verify a possibility of ferromagnetic ordering in the fullerenes containing iron we have applied the open-shell unrestricted Hartree–Fock approximation to optimize a few hypothetical exohedral FeC₆₀ complexes. The data in detail were reported previously [13, 16]. The calculations indicate that because of the charge shift from fullerene to iron the complexes exhibit large dipole moments, regardless of their geometry and that nonzero spin density is not confined to Fe d -orbitals but extends over the C₆₀ molecules. The interaction between FeC₆₀ complexes in the solid can be responsible for the ferromagnetic ordering of magnetic moments within large particles and to the superparamagnetic behavior of the samples.

Conclusions

We produced fullerite with iron by decomposition of the fullerene adduct based on metallocenes. The obtained FeC₆₀ complexes had a long range ferromagnetic order in ensemble of nanometric magnetic particles with large magnetic moments.

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This work was supported by State Committee for Scientific Research Grant No 2 P03B 061 19.

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