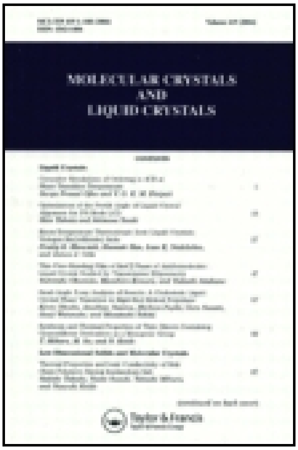

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Synthesis, Spectra and Magnetism of the Charge-Transfer Complex Formed by Fullerene with Decamethylferrocene

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Synthesis, Spectra and Magnetism of the Charge-Transfer Complex Formed by Fullerene with Decamethylferrocene

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A charge-transfer complex of fullerene (C_{60}) with decamethylferrocene (Fc^*) was prepared. The charge-transfer properties were investigated by infrared and electronic spectroscopy and by electron paramagnetic resonance. A complicated reaction was observed. Variable temperature EPR spectral study in the solid state showed that the g-value shifts with peak-width change. A relaxation with degradation process of this charge-transfer complex was proposed. Magnetic studies conducted by SQUID magnetometer showed that the magnetic behavior of these charge-transfer complexes may be described as a superposition of paramagnetic and ferromagnetic components. The coercive forces and residual magnetizations of these complexes measured at low temperature are described herewith.

Keywords: charge-transfer complex; C_{60}; decamethylferrocene; EPR; ferromagnetism

1. INTRODUCTION

The possibility of reducing fullerenes to stable fullerides have led to the preparation of novel molecular materials. Charge transfer compounds of C_{60} have been synthesized which exhibit the important solid-state properties of superconductivity [1] and ferromagnetism [2,3]. The requirement for conventional charge transfer complexes is that the charge transfer complexes should have the partially filled band structure and the segregated stacking of the component

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molecules. The latter requirement is relaxed with increasing dimension of the electronic structure of the charge transfer complex. To design an organic ferromagnet, one of the requirements is that the constituent molecules have degenerate frontier orbitals. With the discovery of fullerenes and the high degeneracy of their LUMO, scientists developed many charge transfer complexes that exhibit surprising solid-state properties. For instance, the recently observed soft ferromagnetism in the [(TDAE)-C_{60}] complex with a Curie temperature T_C of about 16 K, which is the highest transition temperature of a pure organic material [2]. A charge transfer complex of C_{60} with multi-sulphur donors based on the reduction of fullerene was also reported [4,5].

However, due to weak acceptor properties of C_{60}, only a few charge transfer complexes with other donors have been reported so far. The crystal structure of charge transfer complex formed by ferrocene and C_{60}, was reported by Wallton [6]. Bossard [7] reported the one-, two- and three-electron reduction of C_{60} using the electron-reservoir complex $[Fe^I(C_5H_5)(C_6Me_6)]$. In this report, we describe the synthesis and characterization of a new charge transfer complex of C_{60} with decamethylferrocene (**Fc***). The magnetism and electron paramagnetic resonance study were performed over a wide temperature range. It is demonstrated that charge transfer complex of C_{60} shows an interesting behavior at low temperature both in magnetization and EPR spectrum.

2. EXPERIMENTAL

C_{60} was prepared and characterized following the literature procedure [8]. The donor decamethylferrocene (**Fc***) and biferrocene (bifc) were synthesized by the procedure of Rausch [9]. Crystals of the fulleride compounds, $(bifc)_{0.8}C_{60}(CH_3CN)_{0.7}$ and $(Fc^*)_{0.8}C_{60}(CH_3CN)_{0.4}$ were obtained by electrochemical synthesis of the C_{60} charge transfer complex using acetonitrile as a solvent. Elemental analysis and mass spectra confirmed the composition of these compounds. The charge transfer properties were studied by infrared (Bio-Rad FTS-40) and UV/Vis (ShimadzuUVPC-3101) spectrophotometry. Magnetic measurements were carried out on a SQUID magnetometer (MPMS Quantum Design). Variable temperature electron paramagnetic resonance spectra of these complexes were measured by Bruker ECS-106 spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. FT-IR of Charge-Transfer Complex

IR spectra of the complexes were recorded on KBr discs in the range 4000–400 cm^{-1}. The most significant observation is the appearance

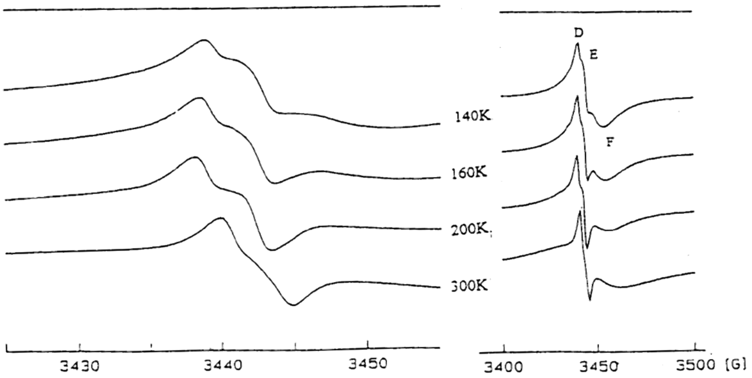

FIGURE 1 Variable temperature EPR spectra of $[\mathbf{Fc}^{*+} - \mathbf{C}_{60}^{-1}]$ complex in 30 gauss range (left) and in 100 gauss range (right).

of the peaks at 527 and 577 cm^{-1} of C_{60} in $[\mathbf{Fc}^{*+} - \mathbf{C}_{60}^{-1}]$ complex, which indicates the formation of the charge transferred species. A new stretching frequency observed at 550 cm^{-1} was assigned to anti-symmetric metal-ligand stretching transition, which only occurs in the oxidized form of $\mathbf{Fc}^{*}$. The slight shift of the anti-symmetric carbon-carbon stretching from 1449 cm^{-1} in free $\mathbf{Fc}^{*}$ to 1464 cm^{-1} in the $[\mathbf{Fc}^{*+} - \mathbf{C}_{60}^{-1}]$ complex was induced by oxidation of $\mathbf{Fc}^{*}$. This indicates that $\mathbf{Fc}^{*+}$ ion exist in the charge transfer complex $[\mathbf{Fc}^{*+} - \mathbf{C}_{60}^{-1}]$.

3.2. EPR Spectra

The variable temperature EPR spectra of $[\mathbf{Fc}^{*+} - \mathbf{C}_{60}^{-1}]$ shown in Figure 1 is the simple Lorentzian form without hyperfine structure. Furthermore, the shape of $[\mathbf{Fc}^{*+} - \mathbf{C}_{60}^{-1}]$ gradually becomes sharp at lowering temperatures.

Based on the temperature dependent EPR spectra of the [PPN-C_{60}] complex reported by Kobayashi [10], we assign the three peaks in Figure 1 as indicated Scheme I.

Peak **D** and **F** are observed due to the formation of free C_{60}^{-1} radical and $[\mathbf{Fc}^{*+} - \mathbf{C}_{60}^{-1}]$ charge transfer complex, respectively. Peak **E** is

$$\underset{\textbf{F}}{[\mathrm{Fc}^{*+}\text{–}\mathrm{C}_{60}^{-1}]} \Leftrightarrow \underset{\textbf{E}}{[\mathrm{Fc}^{*+}\cdots\mathrm{C}_{60}^{-1}]} \Leftrightarrow \underset{\textbf{D}}{[\mathrm{Fc}^{*+}] + [\mathrm{C}_{60}^{-1}]}$$

SCHEME I

assigned to the weak interaction between $\mathbf{Fc}^{*+}$ and $\mathbf{C}_{60}^{-1}$ in the $[\mathbf{Fc}^{*+}\cdots\mathbf{C}_{60}^{-1}]$ complex, which was formed by the degradation of $[\mathbf{Fc}^{*+}-\mathbf{C}_{60}^{-1}]$ complex. The g-value of $[\mathbf{Fc}^{*+}-\mathbf{C}_{60}^{-1}]$ (peak **F**) is 2.007 at 300 K and decreased to 2.0004 as temperature is decreased to 140 K. The g-value of $[\mathbf{Fc}^{*+}\cdots\mathbf{C}_{60}^{-1}]$ (peak **E**) is 2.0006 at 300 K but is invariant as a function of decreasing temperature. The temperature-dependence of the peak-to-peak bandwidth (ΔH_{pp}) of the $[\mathbf{Fc}^{*+}-\mathbf{C}_{60}^{-1}]$ complex decreases from 5.0 G at 300 K to 4.5 G at 140 K. The ΔH_{pp} decreases gradually in $[\mathbf{Fc}^{*+}-\mathbf{C}_{60}^{-1}]$ complex, which is similar with the other charge

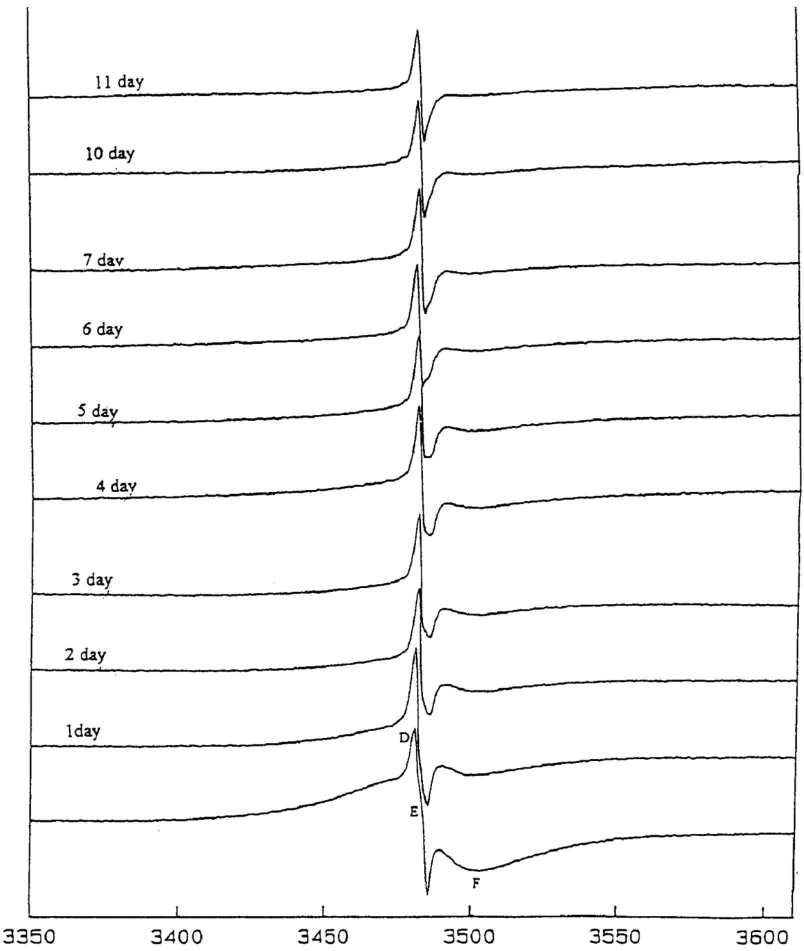

FIGURE 2 Time-dependent EPR spectra of $[\mathbf{Fc}^{*+}-\mathbf{C}_{60}^{-1}]$ complex in 300 G range from freshly prepared to 11 days.

transfer complex of C_{60} reported in literature. This ΔH_{pp} narrowing phenomena probably attributed to the increase in exchange interaction between electronic spins of donor and acceptor at lower temperature.

The time-dependent EPR spectra are shown in Figure 2. The freshly prepared sample shows three absorptions with different half-band widths. The broadest band **F** is due to formation of $[\mathbf{Fc}^{*^+} - \mathbf{C}_{60}^{-1}]$ charge transfer complex. The band decreased greatly within the first day, and then gradually thereon. After 11 days, band **F** had almost disappeared. The only residue was a sharp band **D**, which comes from the free $[\mathbf{C}_{60}^{-}]$ radical. These results indicate that the $[\mathbf{Fc}^{*^+} - \mathbf{C}_{60}^{-1}]$ charge transfer complex is not so stable in room temperature. It may dissociate from strongly coupled charge transfer complexes to weakly interacting salts.

3.3. Magnetic Behavior

Variable temperature magnetic study of $[Fc^{*^+} - C_{60}^{-1}]$ complex was performed over temperature range 4.2 K to 300 K. The plot of magnetic susceptibility (χ_g and χ_g^{-1}) versus temperature is shown in Figure 3.

In the higher temperature range between 100 K and 300 K, the magnetic susceptibility follows Curie-Weiss Law with a Weiss

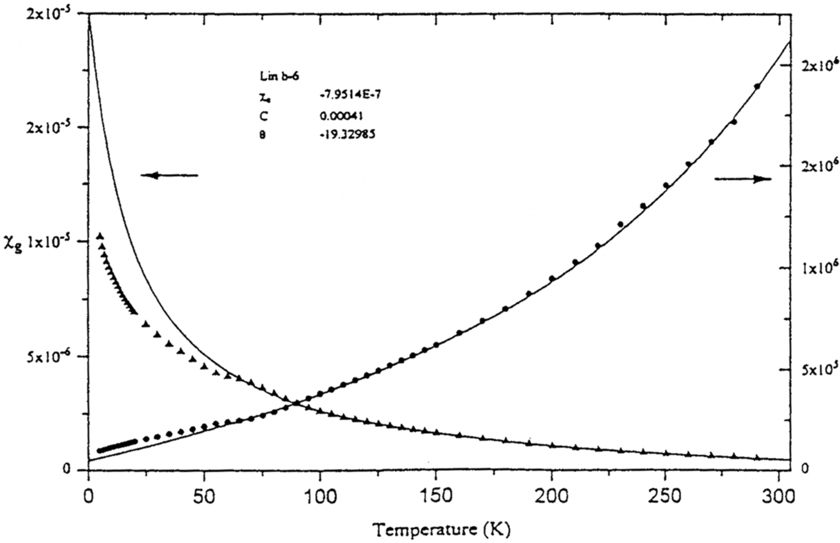

FIGURE 3 Magnetic susceptibility (χ_g) *vs.* temperature and reciprocal magnetic susceptibility (χ_g^{-1}) *vs.* temperature plot for $[Fc^{*^+} - C_{60}^{-1}]$ complex.

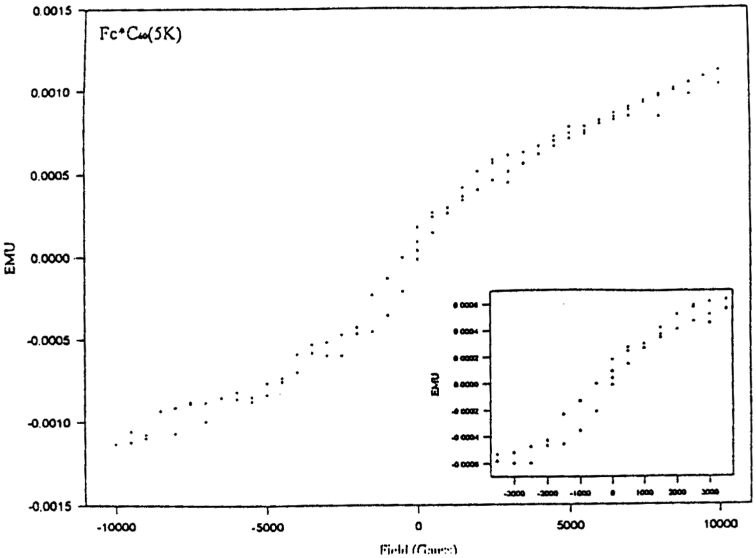

FIGURE 4 Hysteretic curve of $[\mathrm{Fc}^{*^+}\text{–}\mathrm{C}_{60}^{-1}]$ complex at 5 K in the range of –10 kG to 10 kG magnetic field range. The inset shown an enlarged scale diagram.

constant $\theta = -19.3$ K. On the low temperature range, below 100 K, it shows a weak ferromagnetic interaction. To further understand the magnetic behavior of $[\mathrm{Fc}^{*^+} - \mathrm{C}_{60}^{-1}]$ complex, field dependencies of the $[\mathrm{Fc}^{*^+} - \mathrm{C}_{60}^{-1}]$ complex were measured at 5 K and 20 K with the applied field that varied from – 10 kG to 10 kG. A hysteretic curve obtained from $[\mathrm{Fc}^{*^+} - \mathrm{C}_{60}^{-1}]$ is shown in Figure 4. The magnetization at 5 K shows no saturation up to a 10 kG field. A hysteretic behavior is observed both at 5 K, which is of ferromagnetic characteristics.

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