

Synthesis of Cocrystallite with Biferrocene and C₆₀

Tomohiko Ishii, Naoko Aizawa, Ryo Kanehama, Masahiro Yamashita, Hiroyuki Matsuzaka, Hitoshi Miyasaka, Takeshi Kodama, Kouichi Kikuchi, Isao Ikemoto, Yoshihiro Iwasa* and Tomoyuki Mochida**

Department of Chemistry, Tokyo Metropolitan University

Fax: 81-426-77-2525, e-mail: mail@tishii.com

*Department of Physical Materials Science, Japan Advanced Institute of Science and Technology

Fax: 81-761-51-1149, e-mail: iwasa@jaist.ac.jp

**Department of Chemistry, Toho University

Fax: 81-47-472-4406, e-mail: mochida@toho-u.ac.jp

A new cocrystallite, which contains C₆₀ and metal complex of biferrocene (biFc), is prepared and characterized. The electronic feature of the cocrystallite is discussed as possible candidates for ferroelectric magnet, based on the coexistence of a dipole moment and a magnetic spin in the mixed-valence state of biferrocenium (biFc)⁺ salt.

Key words: biferrocene, mixed-valence, magnetism, fullerene, crystal structure

1. INTRODUCTION

Fullerene C₆₀ is quite exceptional molecule because of its high symmetry (12 pentagons and 20 hexagons arrayed in a 'soccer ball'-like structure which belongs to the icosahedral point group, *I_h*) and its large abundance and variety of solid state properties in intercalation compounds (e.g. superconductivity [1] and ferromagnetism [2]). The C₆₀ is attracting much attention, not only due to its unique molecular structure, but also due to its chemical properties. A variety of C₆₀ derivatives have been synthesized and amongst them the 'host-guest' compounds of fullerene and other metal complexes have been discovered.

The facile electron-accepting ability it possesses is one of the most remarkable points. Considering that C₆₀ has a first reduction potential similar to that of an electron acceptor in photosynthetic models, C₆₀ itself is predicted to be an electron acceptor by the artificial photosynthetic model. However, very few compounds that consist of charge transferred C₆₀ have been reported up to now. The (TDAE)⁺(C₆₀)⁻ (TDAE = tetrakis(dimethylamino)ethylene) compound [3] is one of the exception in which the charge has transferred from the TDAE molecule to C₆₀, but the origin of the ferromagnetic interaction between radical spins on (TDAE)⁺(C₆₀)⁻ have not fully been explained so far. Recently, Pd [4], Cu [4], Ag [5] and Ni [6] complexes of octaethylporphyrin cocrystallites with C₆₀ were observed to form solids with a remarkably close contact between the curved π surface of the fullerene and the planar π surface of the porphyrin. Significant strong intermolecular interaction has also been observed in the cobalt complex of tetra(bis-*tert*-butylphenyl)porphyrin (TBP) cocrystallized with C₆₀ [7]. Unfortunately, any proofs of the charge transfer between the porphyrin and C₆₀ molecules in these cocrystallites have not been obtained yet.

One of our research targets is to realize molecular magnets accompanying ferroelectric functions. For

example, a mobile electron in a molecule should lead to the coexistence of an electronic polarity and a magnetic moment, which can be coupled through electron-lattice interactions. As one of the candidates involving such a system, we focus on a biferrocenium ((biFc)⁺; [(η^5 -C₅H₅)Fe(η^5 -C₅H₄)₂)⁺) charge transfer salts (Fig. 1); they are representative mixed-valence compounds showing rapid intramolecular electron transfer (>10⁸ Hz), the electronic state of which have been investigated extensively by means of Mössbauer spectroscopy [8]. A new idea we propose here is to focus on intramolecular electron transfer process as the valence tautomerization should accompany the inversion of a large molecular polarity. Thus the charge transfer complexes of bimetalloenes should be interesting, also in view of a ferromagnetic metallocenium-TCNQ salts [9]. The solid-state properties of charge transfer complexes of various biferrocenium derivatives [10, 11] have been investigated in order to realize molecular magnets with dielectric functions based on intramolecular electron transfer.

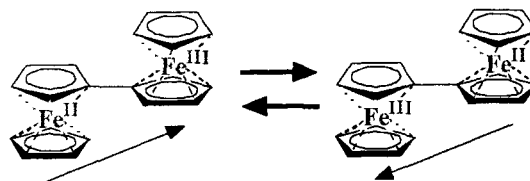
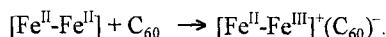


Figure 1. Valence tautomerization coupled with electron transfer in biferrocenium (biFc) salts. The arrows below the molecule denote the electric polarity.

Here we report on the synthesis and the electronic structure of metal complexes of biferrocene

cocrystallized with C_{60} in order to create a new charge transfer salt of $(\text{biFc})^+(\text{C}_{60})^-$ having a charge fluctuation in the cocrystallite, *i.e.*,



The valence tautomerization coupled with electron fluctuation in biferrocenium is supposed to be very influenced in order to make d- π interaction between ferromagnetic d-electrons and conducting π -electrons. Synthesis and crystal structural analysis of cocrystallite of C_{60} with biferrocene have been carried out. We also describe the electronic structure on the basis of the Raman spectrum measurement.

2. EXPERIMENTAL, RESULTS AND DISCUSSION

The compound reported here was obtained in a form suitable for single-crystal X-ray diffraction.

2.1 The cocrystallite of biferrocene with C_{60} , $(\text{biFc}) \cdot 2\text{C}_{60} \cdot 2\text{C}_6\text{H}_5\text{CH}_3$

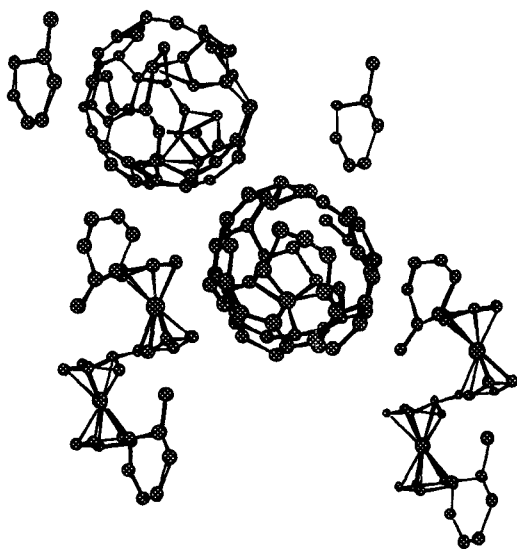


Figure 2. A drawing of the interaction of the two fullerene C_{60} and biferrocenium molecules in $(\text{biFc}) \cdot 2\text{C}_{60} \cdot 2\text{C}_6\text{H}_5\text{CH}_3$.

The unit cell in this compound consists of two C_{60} molecules, one biferrocene and two molecules of toluene, as shown in Fig. 2 for $(\text{biFc}) \cdot 2\text{C}_{60} \cdot 2\text{C}_6\text{H}_5\text{CH}_3$. Unfortunately, the C_{60} cage is disordered even at 83 K in this compound, suggesting that the intermolecular interaction between C_{60} and biferrocene molecules. Within this unit cell in Fig. 2, the fullerene is too far from the atoms of the biFc for any covalent bonding between them. The shortest distance from the carbon atoms on biFc to the those on C_{60} is 3.470 Å.

Two ferrocene portions in the biferrocene molecule in the cocrystallite are observed as the similar shapes among their interatomic distances among C-C and C-Fe elements, suggesting that there are fully averaged structures between two valence tautomerization states, *i.e.* $\text{Fe}^{\text{II}}-\text{Fe}^{\text{III}}$ and $\text{Fe}^{\text{III}}-\text{Fe}^{\text{II}}$. The distances from the

central iron atoms to the carbon atoms on cyclopentadiene ring span the range 1.925-2.321 Å. Since these structural data are almost the same to that observed in the pristine biferrocene molecules, it is expected that such a valence tautomerization and the charge fluctuation are observed in the cocrystallite.

Table 1. Summary of crystallographic data for the complex.

$\text{biFc} \cdot 2\text{C}_{60} \cdot 2\text{C}_6\text{H}_5\text{CH}_3$	
Chemical formula	$\text{C}_{154}\text{H}_{34}\text{Fe}_2$
Formula weight	1995.66
Crystal system	Triclinic
Space group	P1 (#1)
a/Å	13.9409(4)
b/Å	16.1822(8)
c/Å	9.884(1)
α°	90.427(4)
β°	103.955(4)
γ°	113.470(3)
$V/\text{Å}^3$	1971.5(2)
T/K	83
Z	1
μ/mm^{-1}	1.681
No. of reflections measured (total, unique)	15674, 8413
Observed reflects ($I > 3\sigma(I)$)	1412
R1 (obs. data)	0.087
wR2	0.149

The introduction of localized magnetic moments of d-electrons in the complexes may give rise to an interaction between the conduction π -electrons of C_{60} and the magnetic moments of d-electrons. We have predicted that the localized d-spins on biferrocenium are coupled to each other via the π -d interaction in the cocrystallite of C_{60} . In order to discuss the possibility of the π -d interaction of these cocrystallites, Raman spectrum measurement was carried out. The result for the Raman spectrum is shown in Fig. 3.

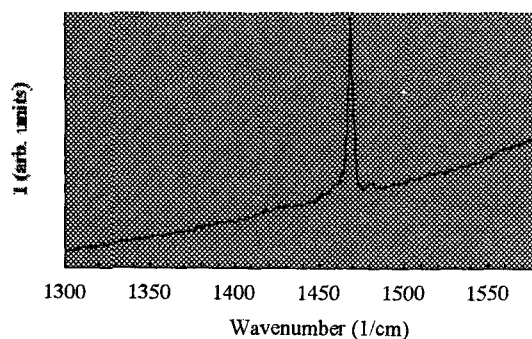


Figure 3. Raman spectrum of $(\text{biFc}) \cdot 2\text{C}_{60} \cdot 2\text{C}_6\text{H}_5\text{CH}_3$

In the Raman spectrum, a strong and sharp signal at

around 1470 cm^{-1} can be observed. This signal denotes that the typical neutral C_{60} molecule, suggesting that there is no charge transferred between biFc and C_{60} molecules. It is supposed that very few electrons are transferred from biferrocene to C_{60} molecules. The composition of the biferrocene to the C_{60} molecules is determined to be 1:2 in the cocrystallite $(\text{biFc})\cdot 2\text{C}_{60}\cdot 2\text{C}_6\text{H}_5\text{CH}_3$. The rate of the charge transferring from biferrocene per a C_{60} molecule is still less than that of the cocrystallites in which the composition of the metal complex to the C_{60} molecule is 1:1. As shown in Fig. 4, the distances between C_{60} molecules are quite short, suggesting that there is the possibility of the existence of the π conducting pass through the C_{60} column. As a result, there is the possibility of the significant magnetism caused by the d- π interaction between the conducting π -electrons on C_{60} column and the magnetic d-electron on mixed-valence molecules of biferrocene. Temperature dependence of the magnetic susceptibility and the electrical conductivity measurement of the compound are now in progress.

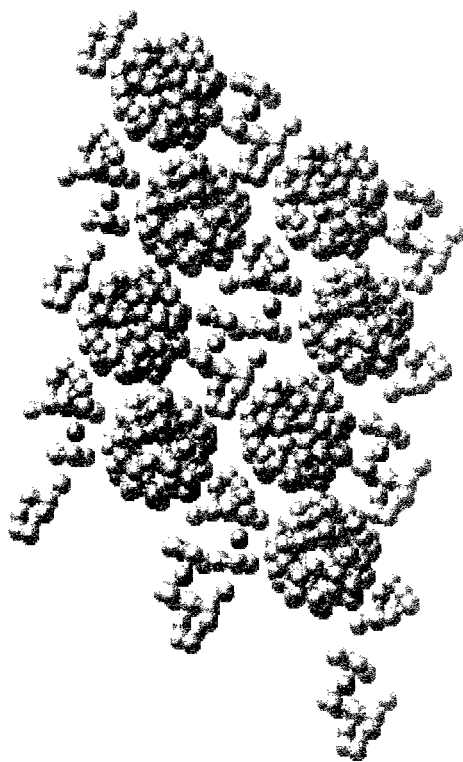


Figure 4. A view of the structure of $(\text{biFc})\cdot 2\text{C}_{60}\cdot 2\text{C}_6\text{H}_5\text{CH}_3$.

3. EXPERIMENTAL SESSION

3.1 Preparation of Crystals

$(\text{biFc})\cdot 2\text{C}_{60}\cdot 2\text{C}_6\text{H}_5\text{CH}_3$. Biferrocene complex (biFc) was synthesized according to the method described elsewhere [10]. A 0.040 g (0.056 mmol) sample of C_{60} was dissolved in 50 ml of

toluene. The solution was filtered and then mixed with a filtered solution of 0.010 g (0.028 mmol) of biFc dissolved in 50 ml of toluene. The resultant mixture was allowed to stand for 5-8 days, during which dark crystals were formed. These were collected by decanting the solvent to yield 0.018 g (50 %) of product.

3.2 X-ray DATA Collection

The black platelet crystals having approximate dimensions of $0.10 \times 0.10 \times 0.10$ mm were coated with a light hydrocarbon oil and mounted on a glass fiber. Data for $(\text{biFc})\cdot 2\text{C}_{60}\cdot 2\text{C}_6\text{H}_5\text{CH}_3$ was collected on a Rigaku RAXIS-RAPID 2 Imaging Plate diffractometer with graphite monochromated Mo-K α radiation. Data were processed by a PROCESS-AUTO [12,13] program package. A symmetry-related absorption correction using the program ABSCOR [14] was applied. The data were corrected for Lorentz and polarization effects. Check reflections were stable throughout data collection. The crystal data are summarized in Table 1.

The structure was solved by direct methods [15] and expanded using Fourier techniques [16]. The non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber [17]. The values for the mass attenuation coefficients are those of Creagh and Hubbel [18]. All calculations were performed using the teXsan [19] crystallographic software package.

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