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# Syntheses and Physical Properties of Complexes of Fullerene with Magnetic Metal Porphyrins

Naoko Aizawa [a], Hatsune Hara [a], Tomohiko Ishii [a], Masahiro Yamashita [a], Hitoshi Miyasaka [a], Hiroyuki Matsuzaka [a], Takeshi Kodama [a], Kouichi Kikuchi [a] & Isao Ikemoto [a]

[a] Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo, 192-0397, Japan

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# Syntheses and Physical Properties of Complexes of Fullerene with Magnetic Metal Porphyrins

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*Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan*

Crystals containing $C_{60}$ and M(OEP) ($M^{2+}$ = Pd, Cu, Ag ; $OEP^{2-}$ = octaethylporphinato) were synthesized. From the X-ray analysis of the cocrystallites, it is revealed that the porphyrin molecules are still remaining their planar structures without deforming to the fit to the curved surface of fullerene.

*Keywords:* fullerene, metal porphyrin

## INTRODUCTION

For more than a decade $C_{60}$ has attracted much attention for the properties caused by its unique three-dimensional shape[1,2]. In the early structual chemistry of fullerenes, it has been reoprted that curved π-surfaces of fullerenes are not appropriate for cocrystallization with planar molecules, and curving of planar molecules might be necessary to fit the concave sutructures of fullerenes[3]. There have been a number of concave molecules based on cyclotriveratrylene, calix arene and tetrathiafulvalene have been reported to cocrystallize with fullerenes. Recently, Co(OEP), Zn(OEP) and Fe(OEP)Cl have been reported to form crystals with $C_{60}$ in remarkably close contact between the curved π surface of fullerene and the planar π surface of the porphyrin, without the need for matching convex with concave surfaces[4]. In addition, unique cocrystallites of $C_{60}$ and $C_{70}$ fullerenes with tetraphenylporphyrins have been reported[5]. Here we report on the first examples of *anti*-formed octaethylporphyrin cocrystallized with $C_{60}$.

## EXPERIMENTAL

The compounds reported here were obtained in a form suitable for single-crystal X-ray diffraction by slow evaporation of organic solvents solutions containing a 1:1 ratio of $C_{60}$ and a variety of metal octaethylporphyrins.

The X-ray diffraction measurement were performed on Rigaku RAXIS-RAPID 2 Imaging Plate diffractometer with

graphite monochromated Mo-Kα radiation. All calculations were performed using TEXSAN crystallographic software package.

Crystal data for Cu(OEP)·$C_{60}$·$2C_6H_6$ (**1**): P1, a = 14.3392(5)Å, b = 17.1603(7)Å, c = 14.1546(6)Å, α = 104.402(2)°, β = 104.378(1)°, γ = 87.379(2)°, V = 3267.4(2)Å$^3$, Z = 2. Ag(OEP)·$C_{60}$·$2C_6H_6$(**2**): P1, a = 14.4007(9)Å, b = 17.276(2)Å, c = 14.170(1)Å, α = 104.715(3)°, β = 104.128(1)°, γ = 87.445(4)°, V = 3306.0(5)Å$^3$, Z = 2. Pd(OEP)·$C_{60}$·$1.5C_6H_6$ (**3**): $P\bar{1}$, a = 14.3518(6)Å, b = 17.122(1)Å, c = 14.1949(4)Å, α = 104.377(4)°, β = 104.478(2)°, γ = 87.633(4)°, V = 3266.7(3)Å$^3$, Z = 2.

## RESULTS AND DISCUSSION

The structure of these compounds are isomorphous, except the space groups, acentric P1 for **1** and **2** and centric $P\bar{1}$ for **3**. Single crystal X-ray analysis revealed that the unit cell of these compounds consist of one $C_{60}$ molecule, one porphyrin and several molecules of benzene (Figures 1 and 2). In these compounds, the $C_{60}$ cage is fully orderd at 83 K. Each $C_{60}$ is positioned symmetrically between two porphyrin molecules. Fullerene is centered over the porphyin with 5:6 junction (pentagon-hexagon junction) in close approach to the metal atom on porphyrin, not with electron rich 6:6 ring juncture C=C bonds. The distances between the metel atom and adjacent carbon atoms of $C_{60}$ are in the range 3.01-3.10Å. They are shorter than normal van der Waals contact observed in a fcc packed $C_{60}$ (grater than 3.2Å)[6], though the metal atom

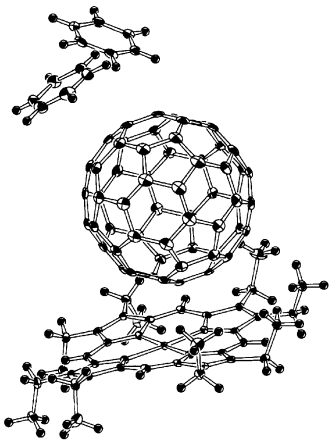

Figure 1. ORTEP drawing of **1** showing 50% thermal elliposoids

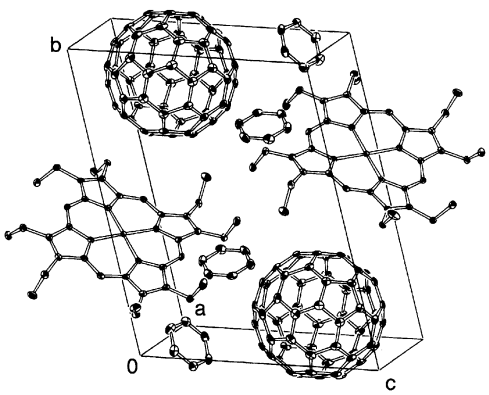


Figure 2. Stereoscopic packing diagram for **1**. The hydrogen atoms have omitted for clarity.

is not coordinated to any part of the fullerene. The structures of M(OEP) in cocrystallites with $C_{60}$ are observed to the anti- formed configuration, with the four ethyl groups of the octaethylporphyrin portions lying on either the same and

the opposite sides of the porphyrin plane toward the $C_{60}$. A variety of configrations of pristine octaethylporphyrins have been reported reflecting the structual flexibility of the terminal ethyl groups, but only compounds containing $C_{60}$ with *syn*-formed metal octaethylporphyrins have been found and reported up to now. In *syn*-formed octaethylporphyrin, the eight ethyl groups lie on the same side of the porphyrin plane. Therefore, the core molecular geometry of the metal octaethylporphyrin found in the cocrystallate with $C_{60}$ is not always similar to that found in the pristine metal octaethylporphyrin compound. Besides the fullerene-porphyrin interaction, there are porphyrin-porphyrin contacts with pairwise character. The shortest pairwise porphyrin-porphyrin distance is 3.18Å in the case of **1**, which is within van der Waals contact. The combination of fullerene-porphyrin and porphyrin-porphyrin contacts also produces a "soccer ball on stackable chairs"-like structure. The porphyrin molecules are still remaining their planer structure without deforming to fit to the curved surfaces of fullerene.

Table 1. Selected intramolecular distances (Å)

| | **1** | **2** | **3** |
|---|---|---|---|
| $C_{60}$···M distance | 3.01 | 3.07 | 3.01 |
| $C_{60}$···$C_{60}$ distance | 3.23 | 3.26 | 3.27 |
| M···M distance | 4.56 | 4.48 | 3.01 |
| Pophyrin···Pophyrin distance | 3.18 | 3.22 | 3.24 |

[a] Closest distance from metal to the C-C bond. [b] Closest carbon-carbon distance

## CONCLUSION

We synthesized new cocrystallites that contain $C_{60}$ and *anti*-formed metal complexes of octaethylporphyrin. The structures of all complexes are *anti*-formed configration, with four ethyl groups of the octaethylporphyrin portions lying on either the same and the opposite sides of the porphyrin plane toward the $C_{60}$. The fullerene is unusually located in the closest approach to the metal atom, involving 5:6 carbon ring junction of $C_{60}$.

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