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First syntheses of cocrystallites consisting of *anti*-formed metal octaethylporphyrins with fullerene C_{60}

Tomohiko Ishii,[a] Naoko Aizawa,[a] Masahiro Yamashita,[a] Hiroyuki Matsuzaka,[a] Takeshi Kodama,[a] Koichi Kikuchi,[a] Isao Ikemoto[a] and Yoshihiro Iwasa[b]

[a] *Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University and PRESTO (JST), 1-1, Minamiohsawa, Hachioji, Tokyo 192-0397, Japan. E-mail: mail@tishii.com*
[b] *Department of Physical Materials Science, School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1, Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan*

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The first examples of crystals that contain C_{60} with *anti*-formed metal complexes of octaethylporphyrin (OEP) have been obtained. In the structures of $Pd^{II}(OEP)\cdot C_{60}\cdot 1.5C_6H_6$ and $Cu^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$, four ethyl groups of the metal octaethylporphyrin portions lie on one side and the other four on the opposite side of the porphyrin plane toward the C_{60}. The fullerene is peculiarly positioned in its closest approach to the metal atom, involving the 5:6 ring junctions. There is the possibility of a strong interaction between the metal octaethylporphyrin and C_{60}. On the other hand, *syn*-formed metal octaethylporphyrins are observed in the cases of $Ru^{II}(CO)(OEP)\cdot C_{60}\cdot 2C_6H_5CH_3$ and $2Zn^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$, suggesting that there is a face-to-face interaction between two adjacent octaethylporphyrins. The intermolecular interactions of the *anti*- and *syn*-formed metal octaethylporphyrins in the cocrystallites containing C_{60} are also described.

Introduction

For more than 10 years the syntheses and physical properties of C_{60} have been investigated extensively for the unique properties caused by its three-dimensional shape.[1,2] The facile electron-accepting ability it possesses is one of the most remarkable points. Considering that C_{60} has a first reduction potential similar to that of an electron acceptor in photosynthetic models, C_{60} itself is predicted to be an electron acceptor by the artificial photosynthetic model. However, very few compounds that consist of charge transferred C_{60} have been reported up to now. The $TDAE^+C_{60}^-$ (TDAE = tetrakis(dimethylamino)ethylene) compound[3] is the most famous example in which the charge has transferred from the TDAE molecule to C_{60}, but the mechanism of the charge transfer and the origin of the ferromagnetic interaction between radical spins on $TDAE^+C_{60}^-$ have not fully been explained so far.

It has been reported that ball-shaped fullerenes such as C_{60} and C_{70} are not appropriate to cocrystallize with planar molecules, and curving of the latter to match the concave structure is required in order to fit to the fullerenes.[4,5] There have been several reports of researchers obtaining curved surfaces that are able to encircle a fullerene by building complex structures from planar aromatic hydrocarbon units and other flat moieties. A number of concave molecules based on cyclotriveratrylene,[6] bis(ethylenedithio)tetrathiafulvalene[7] and tetramethylenedithiodimethyltetrathiafulvalene[8] have been reported to form cocrystallites with C_{60}. Concerning macrocyclic metal compounds, concave structures based on planar molecules such as Ni(OMTAA),[9] Ni(TMTAA)[10] and Cu(TMTAA)[11] have also been required in order to form cocrystallites with C_{60}. Recently, complexes of Co, Zn and Fe with 2,3,7,8,12,13,17,18-octaethylporphyrin (H_2OEP) have been reported[12] to form solids with C_{60} in remarkably close contact, that is an interaction takes place between the curved π surface of the fullerene with the planar π surface of the porphyrin, without the need for matching convex with concave surfaces.[13] In addition, unique cocrystallites of C_{60} and C_{70} fullerenes with tetraphenylporphyrins have been reported.[14]

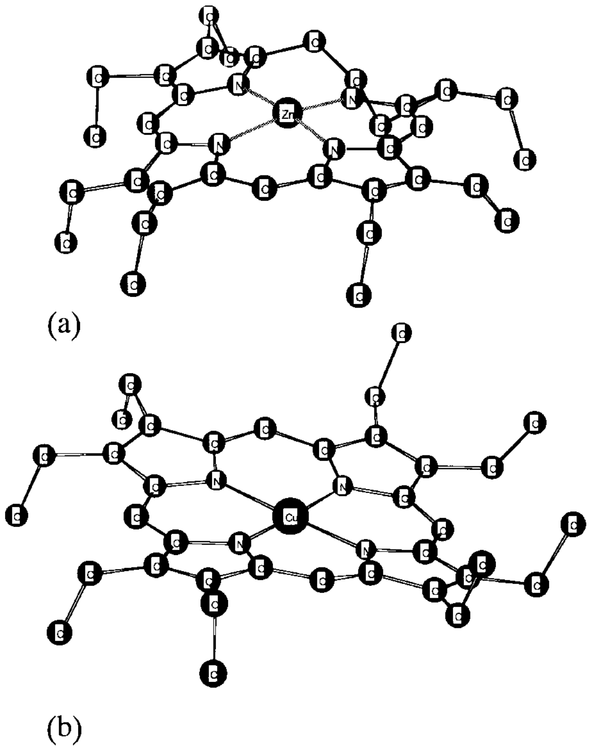

Fig. 1 Configurations of metal octaethylporphyrins observed in cocrystallites with C_{60}: (a) *syn*-formed $Zn^{II}(OEP)$ in $2Zn^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$ and (b) *anti*-formed $Cu^{II}(OEP)$ in $Cu^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$.

Here we report on the first examples of metal complexes of *anti*-formed[15] octaethylporphyrin (Fig. 1) cocrystallized with C_{60}. The orientation of the eight terminal ethyl groups on the metal octaethylporphyrin is supposed to be very important in order to make cocrystalline the curved surfaced C_{60} with the planar surfaced porphyrin. Syntheses and crystal structural analyses of cocrystallites of C_{60} with several kinds of metal

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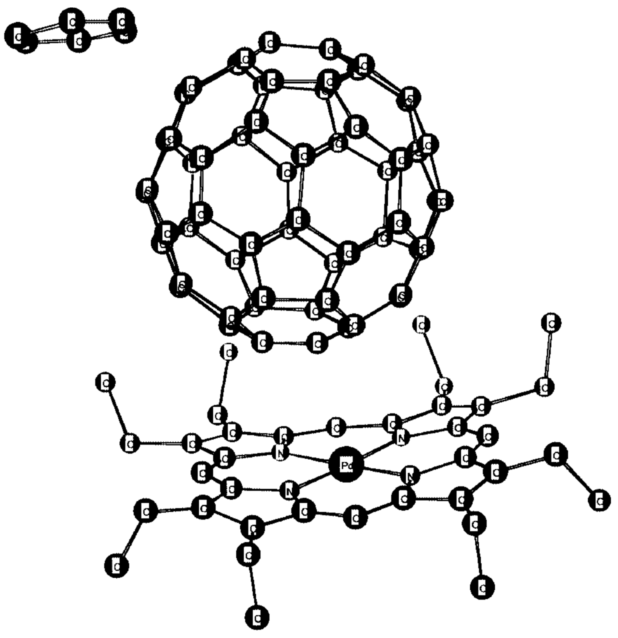

Fig. 2 Molecular packing in $Pd^{II}(OEP)\cdot C_{60}\cdot 1.5C_6H_6$.

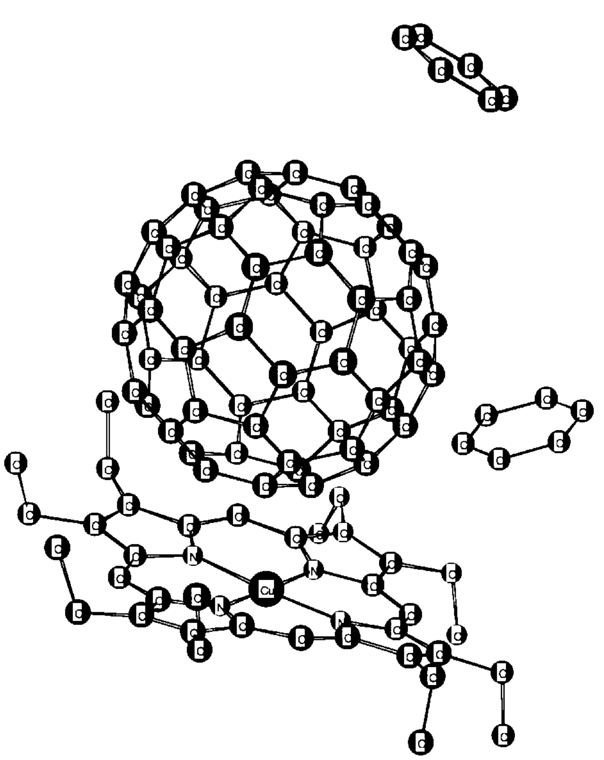

Fig. 3 Molecular packing in $Cu^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$.

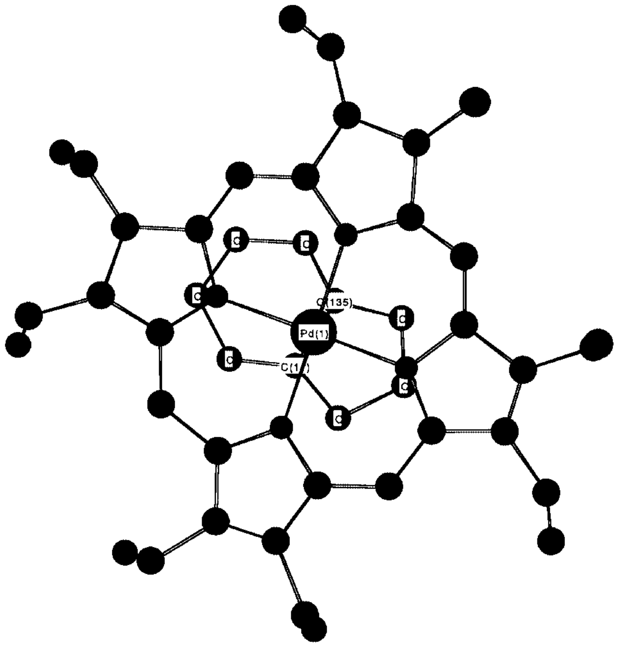

Fig. 4 The 5:6 carbon ring junction in the closest approach to the palladium atom in $Pd^{II}(OEP)\cdot C_{60}\cdot 1.5C_6H_6$ shown from the opposite side to the fullerene. The carbon atoms of fullerene except the (C labeled) ones involving the 5:6 ring junction are omitted.

complexes involving *anti*-formed octaethylporphyrins have been carried out. We also describe the relationship between configuration and physical properties in comparison with those of *syn*-formed metal octaethylporphyrins.

Results

The compounds reported here were obtained in a form suitable for single-crystal X-ray diffraction by diffusion of a solution of the fullerene in benzene into a solution of the metal octaethylporphyrin in toluene.

The first *anti*-formed metal octaethylporphyrin series, $Pd^{II}(OEP)\cdot C_{60}\cdot 1.5C_6H_6$ and $Cu^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$

These two new compounds are almost isomorphous structures, only the space groups being different, acentric $P1$ and centric $P\bar{1}$ for palladium and copper respectively. The unit cell in each compound consists of a C_{60} molecule, one metal octaethylporphyrin and several molecules of benzene, as shown in Figs. 2 and 3 for $Pd^{II}(OEP)\cdot C_{60}\cdot 1.5C_6H_6$ and $Cu^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$, respectively. In each compound the C_{60} cage is fully ordered at 83 K. Within the unit cell the fullerene is positioned symmetrically between two $Pd^{II}(OEP)$ units, and is too far from the atoms of the $Pd^{II}(OEP)$ for any covalent bonding between them. The planar structure of the metal porphyrin still remains in the cocrystallite with C_{60}; in contrast, M(TMTAA) and M(OMTAA) macrocyclic complexes with C_{60} have been reported to possess saddle shaped structures. It is suggested that interaction takes place between the curved π surface of the fullerene with the planar π surface of the porphyrin, without the need for matching convex with concave surfaces. In general, it has been thought that C_{60} is centered over the metal atom of complexes with electron-rich 6:6 ring-juncture C–C bonds, which is provided by filled h_u orbitals, in close approach to the plane of the metal complex core. On the other hand, the fullerene is peculiarly positioned in the closest approach to the palladium atom involving the 5:6 ring junction, which indicates π antibonding between the carbon atoms (*i.e.* the Pd(1)··· [C(11)–C(135) bond] in Fig. 4). The shortest distance from the palladium atoms to the C–C bond is 3.01–3.04 Å. In general, the closest contacts between C_{60} and the central metal atom in cocrystallites with M(TMTAA) is 3.18–3.37 Å. On the other hand, the corresponding value for the copper compound is 3.007 Å (Cu(1)···[C(27)–C(85)]). The Pd–C and Cu–C distances are Pd(1)···C(11), 3.10(1); Pd(1)···C(135), 3.17(1); Cu(1)···C(27), 3.024(2); Cu(1)···C(85), 3.212(2) Å. While these distances are too long for co-ordination, they are shorter than the normal van der Waals contacts seen between neighboring fullerenes (greater than 3.2 Å).[16]

The most characteristic feature is that these cocrystallites consist of the *anti*-formed metal octaethylporphyrins and C_{60}, that is the four ethyl groups of both metal octaethylporphyrin portions lie on the same side of the porphyrin toward the fullerene, and the other four ethyl groups lie on the opposite side of the porphyrin from the fullerene. The distances from the fullerene to the ethyl hydrogen atoms span the range 2.5–

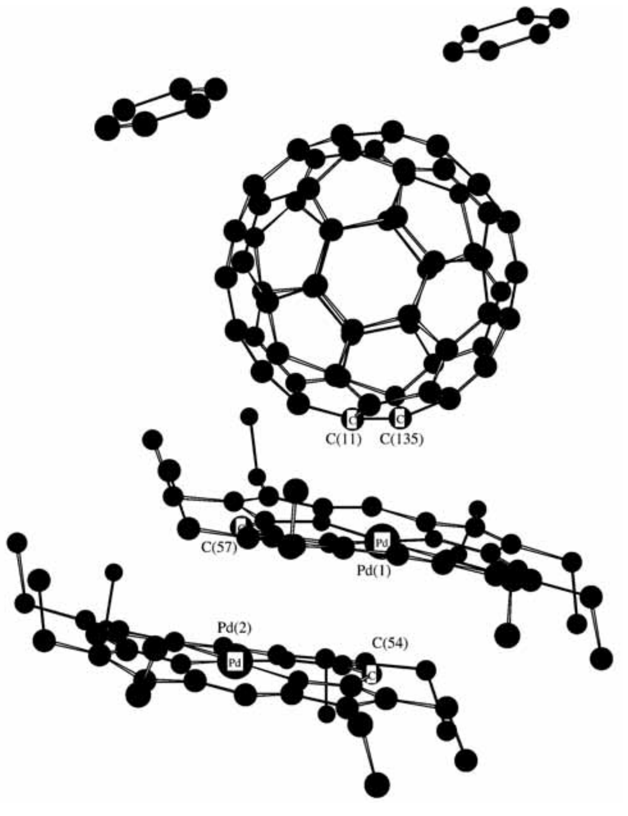

Fig. 5 A view of the fullerene/porphyrin units in $Pd^{II}(OEP)\cdot C_{60}\cdot 1.5C_6H_6$ with 50% thermal ellipsoids.

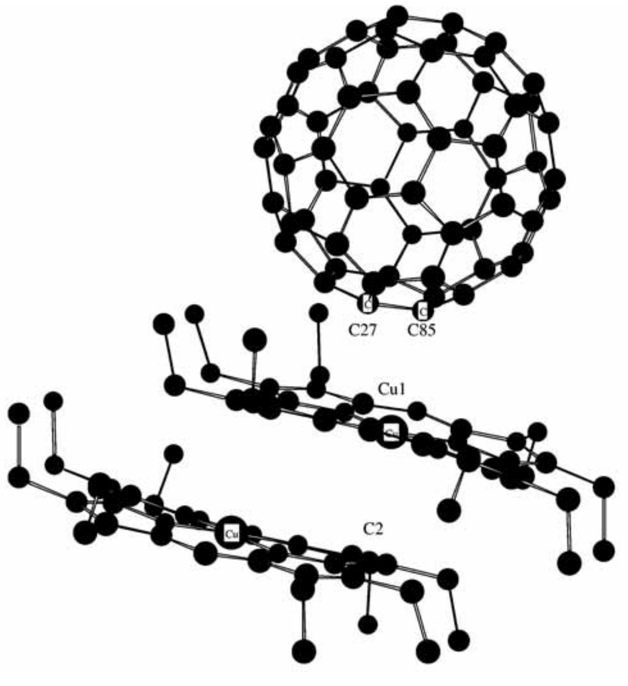

Fig. 6 A view of the fullerene/porphyrin units in $Cu^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$ with 50% thermal ellipsoids.

2.7 Å. Figs. 5 and 6 show drawings of the molecular packing that make clear the fullerene near the four ethyl groups of $Pd^{II}(OEP)\cdot C_{60}\cdot 1.5C_6H_6$ and $Cu^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$, respectively.

In addition to these fullerene/porphyrin interactions, there are significant *anti*-formed porphyrin/porphyrin contacts with pairwise character. This combination of fullerene/porphyrin and porphyrin/porphyrin contacts produces a "soccer ball on stackable chairs-like" structure. The pairwise porphyrin–porphyrin distances are Pd(1)···C(54), 3.30(1); Pd(2)···C(57), 3.23(2) Å. The porphyrin–porphyrin distance of the copper compound is shorter still, that is Cu(1)···C(2), 3.177(2) Å. Thus, the two porphyrin planes are within van der Waals contact of each other.

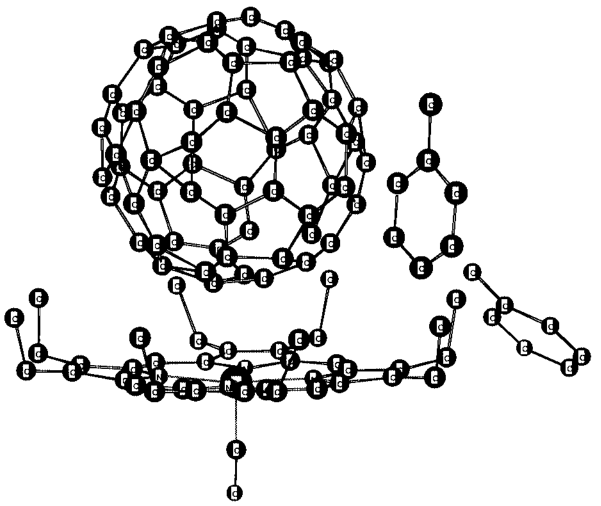

Fig. 7 Molecular packing in $Ru^{II}(CO)(OEP)\cdot C_{60}\cdot 2C_6H_5CH_3$.

The core molecular geometries of the metal octaethylporphyrin in $Pd^{II}(OEP)\cdot C_{60}\cdot 1.5C_6H_6$ and $Cu^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$ are very similar to those found in pristine $Pd^{II}(OEP)$ and $Cu^{II}(OEP)$ compounds.[17,18] Notice from these results that the pairwise porphyrin/porphyrin contacts are greater in the fullerene cocrystallites than they are in pristine $Pd^{II}(OEP)$ and $Cu^{II}(OEP)$ compounds.

The *syn*-formed ruthenium octaethylporphyrin complex, $Ru^{II}(CO)(OEP)\cdot C_{60}\cdot 2C_6H_5CH_3$

We have also obtained a new compound consisting of C_{60} with ruthenium carbonyl octaethylporphyrin. The centric unit cell of *Pnma* space group in the compound consists of a C_{60} molecule, one ruthenium carbonyl octaethylporphyrin and two solvent molecules of toluene, as shown in Fig. 7. Unfortunately, the C_{60} cage is disordered even at 83 K in this compound. Within this unit cell the fullerene is positioned symmetrically between two $Ru^{II}(CO)(OEP)$ units. It is also peculiarly positioned in the closest approach to the ruthenium atom involving 5:6 ring junctions. The distance from the ruthenium atom to this C–C bond is 2.75 Å. The Ru–C distances are Ru(1)···C(52), 2.83(3); Ru(1)···C(92), 2.86(3) Å. These are short enough for interaction between neighboring fullerenes.

The most important difference from the above palladium and copper compounds is that the cocrystallite consists of the *syn*-formed octaethylporphyrin and C_{60}. The eight ethyl groups of the ruthenium carbonyl octaethylporphyrin portion lie on the same side of the porphyrin, toward the fullerene. A carbonyl ligand is located on the opposite side of the planar porphyrin from the eight ethyl groups. This structural feature is very similar to that reported for $Fe^{III}Cl(OEP)\cdot C_{60}\cdot 2CHCl_3$.[12] Fig. 8 shows a drawing of the molecular packing that makes clear the fullerene near the eight ethyl groups of these ruthenium carbonyl octaethylporphyrin molecules.

In addition to these fullerene/porphyrin interactions, there are significant porphyrin/porphyrin contacts with either pairwise or face-to-face contact. Combination of fullerene/porphyrin and porphyrin/porphyrin contacts produces a "two slipped potlids-like" structure. The two slipped potlids arrangement is facilitated by the positioning of the ethyl groups on the same side of the porphyrin.

The *syn*-formed zinc octaethylporphyrin complex, $2Zn^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$

The asymmetric unit cell of $P2_12_12_1$ space group in the compound consists of a C_{60} molecule, two zinc octaethylporphyrins

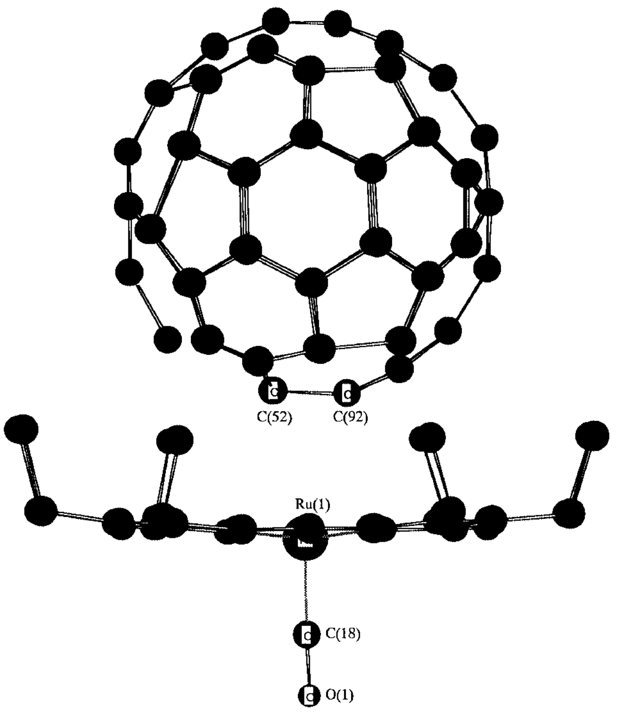

Fig. 8 A view of the fullerene/porphyrin units in $Ru^{II}(CO)(OEP)\cdot C_{60}\cdot 2C_6H_5CH_3$ with 50% thermal ellipsoids.

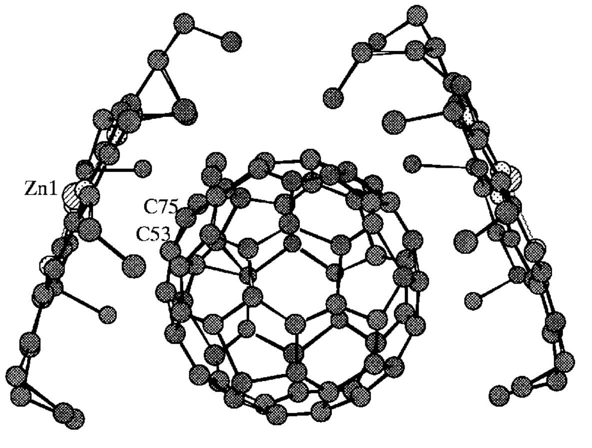

Fig. 9 A view of the fullerene/porphyrin units in $2Zn^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$. The benzene molecules are omitted.

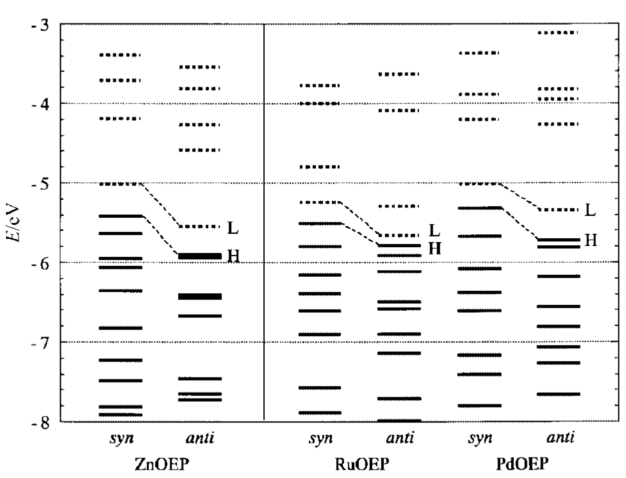

Fig. 10 DV-Xα calculated for electronic structures of *syn*- and *anti*-formed Zn(OEP), Ru(OEP) and Pd(OEP). Solid and dashed lines indicate the occupied and unoccupied energy levels, respectively. "H" and "L" denote the HOMO and LUMO energy levels, respectively. The basis functions of the metal were up to the 4p orbital for Zn(OEP) and the 5p orbital for Pd(OEP) and Ru(OEP).

and two solvent molecules of benzene, as shown in Fig. 9. In the same way as the $Ru^{II}(CO)(OEP)\cdot C_{60}\cdot 2C_6H_5CH_3$ mentioned above, the C_{60} cage is disordered at 83 K in this compound. Within the unit cell the fullerene is positioned symmetrically between two $Zn^{II}(OEP)$ units. The closest approach to the zinc atom involves the 5:6 ring junctions, as in all these new compounds. The distance from the zinc atom to this C–C bond is 2.97 Å. The Zn–C distances are Zn(1)···C(53), 3.20(4); Zn(1)···C(75), 3.19(5); Zn(1)···C(189), 2.98(3) Å. This structural feature is very similar to that reported in $2Zn^{II}(OEP)\cdot C_{60}\cdot 2CH_2Cl_2$.[12]

A minor difference from the previous zinc compound[12] is the presence of two solvent molecules of benzene instead of chloroform. In this complex all of the ethyl groups on the zinc octaethylporphyrin portion lie on the same side of the porphyrin toward the fullerene, the so-called *syn*-formed octaethylporphyrin. Fig. 9 also shows a drawing of the molecular packing that makes clear the fullerene near the eight ethyl groups of these zinc octaethylporphyrin molecules. In addition to these fullerene/porphyrin interactions, there are significant porphyrin/porphyrin contacts with pairwise or face-to-face contact. It is expected that the face-to-face porphyrin/porphyrin contact is greater in the fullerene cocrystallites than it is in the pristine $Zn^{II}(OEP)$ compound.[19,20]

Discussion

In this work four new crystals containing C_{60} molecules with different kinds of metal complexes of octaethylporphyrin were synthesized. The *anti*-formed configuration with four ethyl groups on one side of the porphyrin plane and four on the opposite side is observed for the first time in the cases of $Pd^{II}(OEP)\cdot C_{60}\cdot 1.5C_6H_6$ and $Cu^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$. A variety of configurations of pristine octaethylporphyrins have been reported reflecting the structural 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. Therefore, the core molecular geometry of the metal octaethylporphyrin found in the cocrystallite with C_{60} is not always similar to that found in the pristine metal octaethylporphyrin compound. It is very important to discuss the difference of the stability between the *anti*- and the *syn*-formed metal octaethylporphyrins in the cocrystallites with C_{60}. In addition, we need to examine the strength of the intermolecular interaction and the charge transfer between the fullerene and the metal octaethylporphyrins.

In order to discuss the stability of these complexes the electronic structures of *syn*- and *anti*-formed $Zn^{II}(OEP)$, $Ru^{II}(OEP)$ and $Pd^{II}(OEP)$ molecules were calculated. The structural models for the DV-Xα molecular orbital calculation[21] for the *syn*-formed $Zn^{II}(OEP)$, $Ru^{II}(OEP)$ and *anti*-formed $Pd^{II}(OEP)$ are derived from the results of the X-ray structural analyses, though the *syn*-formed $Pd^{II}(OEP)$ and *anti*-formed $Zn^{II}(OEP)$ and $Ru^{II}(OEP)$ were calculated by means of the MM2 method. The results are summarized in Fig. 10. From this calculation the energy levels of the *anti*-formed configurations are more stable in all cases than those of the *syn*-formed configurations. This is consistent with the fact that the *anti*-formed configurations are observed in the pristine metal octaethylporphyrins. In the $Zn^{II}(OEP)\cdot C_{60}\cdot 2C_6H_6$ and $Ru^{II}(CO)(OEP)\cdot C_{60}\cdot 2C_6H_5CH_3$ compounds there is the possibility of the existence of a strong face-to-face interaction between two adjacent metal octaethylporphyrins, resulting in the *syn*-formed octaethylporphyrins being transformed from the energetically stable *anti*-formed configuration. This situation is very similar to the reasoning for the change from the *anti*-formed metal octaethylporphyrin to the *syn*-formed one in the case of $Co(OEP)\cdot C_{60}\cdot 2CHCl_3$.[12] The distances between two adjacent porphyrin planes in the

Table 1 Summary of crystallographic data for the complexes

	$\mathrm{Pd^{II}(OEP){\cdot}C_{60}{\cdot}1.5C_6H_6}$	$\mathrm{Cu^{II}(OEP){\cdot}C_{60}{\cdot}2C_6H_6}$	$\mathrm{Ru^{II}(CO)(OEP){\cdot}C_{60}{\cdot}2C_6H_5CH_3}$	$\mathrm{2Zn^{II}(OEP){\cdot}C_{60}{\cdot}2C_6H_6}$
Chemical formula	$\mathrm{C_{105}H_{53}N_4Pd}$	$\mathrm{C_{108}H_{56}CuN_4}$	$\mathrm{C_{111}H_{60}N_4ORu}$	$\mathrm{C_{144}H_{100}N_8Zn_2}$
Formula weight	1477.00	1473.20	1566.79	2073.19
Crystal system	Triclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	$P1$ (no. 1)	$P\bar{1}$ (no. 2)	*Pnma* (no. 62)	$P2_12_12_1$ (no. 19)
a/Å	14.3518(6)	14.3392(5)	26.019(3)	20.9675(6)
b/Å	17.122(1)	17.1603(7)	15.838(2)	29.5204(9)
c/Å	14.1949(4)	14.1546(6)	16.805(2)	14.7971(4)
α/°	104.377(4)	104.402(2)		
β/°	104.748(2)	104.378(1)		
γ/°	87.633(4)	87.379(2)		
V/Å^3	3266.7(3)	3267.4(2)	6925(2)	9158.9(5)
T/K	83	83	83	83
Z	2	2	4	4
μ/mm^{-1}	0.348	0.400	0.293	0.594
No. of reflections measured (total, unique)	26754, 13393	30839, 14695	31815, 6903	56838, 11253
Observed reflects ($I > 3\sigma(I)$)	11321	11225	3145	3940
$R1$ (obs. data)	0.079	0.037	0.095	0.167
$wR2$	0.090	0.073	0.219	0.193

syn-formed $\mathrm{Zn^{II}(OEP){\cdot}C_{60}{\cdot}2C_6H_6}$ and $\mathrm{Ru^{II}(CO)(OEP){\cdot}C_{60}{\cdot}2C_6H_5CH_3}$ compounds are shorter than those in the *anti*-formed $\mathrm{Pd^{II}(OEP){\cdot}C_{60}{\cdot}1.5C_6H_6}$ and $\mathrm{Cu^{II}(OEP){\cdot}C_{60}{\cdot}2C_6H_6}$ compounds. This is the reason why the *syn*-formed configurations are observed in the cases of $\mathrm{Zn^{II}(OEP){\cdot}C_{60}{\cdot}2C_6H_6}$ and $\mathrm{Ru^{II}(CO)(OEP){\cdot}C_{60}{\cdot}2C_6H_5CH_3}$. In contrast, in $\mathrm{Pd^{II}(OEP){\cdot}C_{60}{\cdot}1.5C_6H_6}$ and $\mathrm{Cu^{II}(OEP){\cdot}C_{60}{\cdot}2C_6H_6}$ there is the possibility of the existence of strong interaction between $\mathrm{C_{60}}$ and the metal atoms.

In $\mathrm{Ru^{II}(CO)(OEP){\cdot}C_{60}{\cdot}2C_6H_5CH_3}$ the *syn*-formed configuration contrasts the *anti*-formed configurations reported in several Ru(OEP) compounds.[22,23] In this compound a carbonyl ligand is located at the opposite side of the porphyrin plane from the eight ethyl groups. The face-to-face interaction between adjacent porphyrins is strengthened by these two carbonyl ligands, with the result that the *syn*-formed configuration of the octaethylporphyrin in a "two slipped podlids-like" structure is observed.

Conclusion

We can obtain complexes of $\mathrm{C_{60}}$ with several metal octaethylporphyrins. Not only the *syn*-formed but also the *anti*-formed configuration have been observed in these cocrystallites. In $\mathrm{Zn^{II}(OEP){\cdot}C_{60}{\cdot}2C_6H_6}$ and $\mathrm{Ru^{II}(CO)(OEP){\cdot}C_{60}{\cdot}2C_6H_5CH_3}$ the *syn*-formed configurations have been explained by the strong face-to-face interaction between two adjacent octaethylporphyrins. On the other hand, the *anti*-formed configuration seen in the pristine metal octaethylporphyrins has also been observed in $\mathrm{Pd^{II}(OEP){\cdot}C_{60}{\cdot}1.5C_6H_6}$ and $\mathrm{Cu^{II}(OEP){\cdot}C_{60}{\cdot}2C_6H_6}$ compounds for the first time. This implies that the existence of charge transfer from the metal octaethylporphyrin to the $\mathrm{C_{60}}$ fullerene is caused by the strong interaction between them.

Experimental

Preparation of crystals

A 0.020 g (0.028 mmol) sample of $\mathrm{C_{60}}$ was dissolved in 50 ml of benzene, the solution filtered and then mixed with a filtered solution of 0.018 g (0.028 mmol) of $\mathrm{Pd^{II}(OEP){\cdot}C_{60}}$ dissolved in 50 ml of benzene. The resultant mixture was allowed to stand for 5–8 days, and dark crystals were formed. These were collected by decanting the solvent to yield 0.020 g (50%) of product. The other cocrystallized samples $\mathrm{Cu^{II}(OEP){\cdot}C_{60}{\cdot}2C_6H_6}$, $\mathrm{Ru^{II}(CO)(OEP){\cdot}C_{60}{\cdot}2C_6H_5CH_3}$ (using toluene instead of benzene) and $\mathrm{2Zn^{II}(OEP){\cdot}C_{60}{\cdot}2C_6H_6}$ were prepared by a similar procedure from their respective components.

X-Ray data collection

All black block and platelet crystals having approximate dimensions of 0.25 × 0.20 × 0.10 mm were coated with a light hydrocarbon oil and mounted on glass fibers. Data for $\mathrm{Pd^{II}(OEP){\cdot}C_{60}{\cdot}1.5C_6H_6}$, $\mathrm{Cu^{II}(OEP){\cdot}C_{60}{\cdot}2C_6H_6}$, $\mathrm{Ru^{II}(CO)(OEP){\cdot}2C_{60}{\cdot}C_6H_5CH_3}$ and $\mathrm{2Zn^{II}(OEP){\cdot}C_{60}{\cdot}2C_6H_6}$ were collected on a Rigaku RAXIS-RAPID 2 Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. Data were processed by a PROCESS-AUTO program package. A symmetry-related absorption correction using the program ABSCOR[24] 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 structures were solved by direct methods[25] and expanded using Fourier techniques.[26] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms isotropically. Hydrogen atoms were included through the use of a riding model. Neutral atom scattering factors were taken from Cromer and Waber.[27] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[28] All calculations were performed using the TEXSAN[29] crystallographic software package.

CCDC reference number 186/2211.

See http://www.rsc.org/suppdata/dt/b0/b006593p/ for crystallographic files in .cif format.

DV-Xα Molecular orbital computational method

Non-relativistic DV-Xα calculations[30] were performed with the Slater exchange parameter, α, of 0.7 for all atoms and with 5000 DV sampling points, which provided a precision of less than 0.1 eV for valence electron energy eigenvalues. We employed basis functions for the metal atoms up to the 4p orbitals for Cu and Zn and the 5p orbitals for Pd and Ru, while for nitrogen, carbon and oxygen atoms the functions were up to the 2p orbitals. The calculations were carried out self-consistently until the difference in orbital populations between the initial and final states of the iteration was less than 0.01 electron per orbital. The computation details of the non-relativistic (DV-HFS) method used have been described elsewhere.[31,32]

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