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Fullerene Nanostructures: How the Oblong Shape of C₇₀ Forms a Cocrystal with an Enormous Asymmetric Unit and Related Cocrystals

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Cocrystallization of Ni^{II}(OEP) (where OEP is the dianion of octaethylporphyrin) with C₇₀ in *p*-xylene produces black plates of 12Ni^{II}(OEP)•12C₇₀•18*p*-xylene (**1**). Single crystal X-ray diffraction at 90 K reveals that the crystal contains 42 individual, well-ordered molecules in the asymmetric unit with distinctive interactions between each Ni^{II}(OEP)/C₇₀ pair and each pair of neighboring C₇₀ molecules. Warming the crystal to 186 K produces a phase change so that only four Ni^{II}(OEP)/C₇₀ sites and six *p*-xylene molecules are present. Under the same conditions Cu^{II}(OEP) cocrystallizes with C₇₀ to form Cu^{II}(OEP)•C₇₀•1.5*p*-xylene (**2**) with a much simpler structure consisting of one molecule of the porphyrin and the fullerene along with 1.5 molecules of *p*-xylene in the asymmetric unit. Crystallization of C₇₀ from toluene in the presence of Ni^{II}(Etioporphyrin-I) produces the black solvate 6C₇₀•6toluene (**3**). It seems that C₇₀ has a tendency to crystallize so that several orientations of the oblong molecule are present in the solid.

Introduction

Fullerenes, the unique molecular forms of carbon such as C₆₀ and C₇₀, come in a variety of sizes and shapes.^{1,2} Unlike other forms of carbon, fullerenes are soluble in a variety of organic solvents and are amenable to chemical manipulation using the tools of organic chemistry.^{3,4} Both C₆₀ and C₇₀ have become important components in the development of bulk heterojunction (BHJ) solar cells.⁵⁻⁸

The uniform outer surfaces of fullerenes, which consist of a combination of hexagonal and pentagonal rings, frequently produce crystals that are prone to disorder as is the case with C₆₀.⁹ Fortunately, fullerenes readily form cocrystals with a wide range of molecules and these cocrystals frequently have a high degree of internal order and are amenable to study by single-crystal X-ray diffraction. Such cocrystal-forming molecules include those with curved surfaces that complement the fullerene exterior.¹⁰⁻¹² However, molecules with flat surfaces such as porphyrins also cocrystallize with fullerenes.^{13,14} Indeed, cocrystallization with M^{II}(OEP) (OEP is octaethylporphyrin) has become a routine means of crystallizing fullerenes or endohedral fullerenes for structure determinations.¹⁵⁻²⁰

We have recently demonstrated that the metal ion in M^{II}(OEP) and the solvent used for crystallization play a

significant role in determining the intermolecular structure and the stoichiometry of cocrystals formed from the nearly spherical C₆₀ with *I_h* symmetry.^{21,22} Those results led to the question of determining the factors that would determine how the oblong C₇₀ molecule interacts with M^{II}(OEP) in various cocrystals. Additionally, C₇₀ is the simplest of a several fullerenes with a nano-tubular shape and provides a model for what to expect from such fullerenes. Other nano-tubular carbon cages with crystallographically determined structures include *D*_{5h}(1)-C₉₀,^{23,24} *D*_{3d}(3)-C₉₆,²⁵ La₂@*D*₅(450)-C₁₀₀,²⁶ and Sm₂@*D*_{3d}(822)-C₁₀₄.²⁷ Understanding the nature of the fullerene / M^{II}(OEP) interaction also provides molecular models for the non-covalent bonding of porphyrins to carbon nanotubes.²⁸⁻³⁰

The non-polar C₇₀ molecule with *D*_{5h} symmetry possesses a unique C₅ axis whose orientation is an excellent marker to identify the intermolecular interactions present in cocrystals. Previously, this laboratory demonstrated that C₇₀ cocrystallized with bis(ethylenedithio)tetrathiafulvalene (ET) so that two different alignments of the C₅ axis of the fullerene relative to the ET molecule were observed.³¹ There are two limiting orientations that the C₅ axis can have with the porphyrin plane. It may lie parallel to that plane, in which case we assign a tilt angle of 0° to the interaction. At the other extreme, the C₅ axis may be perpendicular to the porphyrin plane, in which case we assign a tilt angle of 90°. We anticipated that, by cocrystallization of C₇₀ with M^{II}(OEP) with a variety of metals and utilizing a variety of solvents, we would be able to obtain crystals that would have a range of intermolecular interactions between these components that could involve a range of tilt angles.

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To our surprise, we discovered that, in *p*-xylene, a remarkable cocrystal of C_{70} formed that displayed twelve different tilt angles with respect to $Ni^{II}(OEP)$ in a large asymmetric unit when examined by crystallography at 90 K. When the crystal was warmed to 186 K, the unit cell volume decreased to 1/3 of the original size accompanied by fullerene disorder. An intriguing discovery was that the similar crystal growing procedure with $Cu^{II}(OEP)$ yielded a basic unit cell containing only one formula unit of the cocrystal at 90 K and an ordered C_{70} . When C_{70} was crystallized with bis(ethylenedithio)tetrathiafulvalene (ET) in toluene as the solvent, no porphyrin co-crystals formed. Instead, a structure determination at 90 K revealed six formula units of C_{70} •toluene in the asymmetric unit.

Results and Discussion

Cocrystal Growth

Crystals of $12Ni^{II}(OEP) \cdot 12C_{70} \cdot 18p\text{-xylene}$ (**1**) and $Cu^{II}(OEP) \cdot C_{70} \cdot 1.5p\text{-xylene}$ (**2**) were prepared by layering equimolar solutions of C_{70} in *p*-xylene over a similar solution of the appropriate $M^{II}(OEP)$ in *p*-xylene. Crystals started appearing within 72 hours but they were allowed to grow for about four weeks to achieve the size satisfactory for data collection. Crystals of $6C_{70} \cdot 6\text{toluene}$ (**3**) were obtained by layering a solution of $Ni^{II}(\text{Etioporphyrin-I})$ in benzene solution over a solution of C_{70} in toluene. Crystallographic data are listed in the experimental section. Unit cell information can be found in the figure captions for the cocrystal structures drawings.

The structure of $12Ni^{II}(OEP) \cdot 12C_{70} \cdot 18p\text{-xylene}$ (1**) at 90 K.** The crystals form in the space group $P\bar{1}$ with twelve molecules of C_{70} , twelve molecules of $Ni^{II}(OEP)$ and eighteen molecules of *p*-xylene in general positions. A drawing of the asymmetric unit is shown in Figure 1. All molecules are ordered. Each fullerene molecule is cupped by one adjacent molecule of $Ni^{II}(OEP)$ with all eight ethyl groups embracing each fullerene. As is common with cocrystals of $Ni^{II}(OEP)$ and fullerenes, the $Ni^{II}(OEP)$ molecules make close face-to-face contact. In $12C_{70} \cdot 12Ni^{II}(OEP) \cdot 18p\text{-xylene}$ (**1**) columns containing fullerenes and porphyrins are formed with the solvate molecules arranged at the sides of these columns. As seen in Figure 1, the column bounded by fullerene 5 and fullerene 12 has a repeat length of 100 Å. There is a second column made up of fullerenes 1 to 4 with a shorter translational repeat. Within the columns there are close contacts between C_{70} molecules and the adjacent $Ni^{II}(OEP)$ molecules, between back-to-back $Ni^{II}(OEP)$ molecules and between two C_{70} molecules. The *p*-xylene molecules are arranged beside and between these columns.

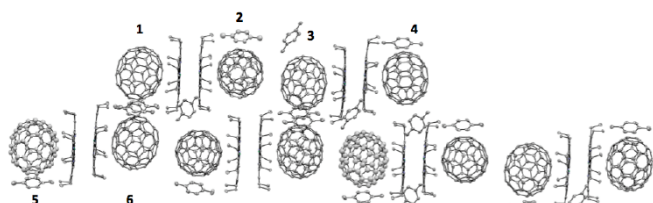


Figure 1. A view of the unit cell contents and their relative positions in $12C_{70} \cdot 12Ni^{II}(OEP) \cdot 18p\text{-xylene}$, (**1**). Crystal data are given in Table 2. Each of the twelve different C_{70} molecules is labelled **1** - **12** and that label also pertains to the $Ni^{II}(OEP)$ molecule that is adjacent to each fullerene. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 32% probability.

There are a number of differences between the relative orientations of fullerenes and porphyrins in this unusually large array of crystalline molecules. One difference involves the tilt angle between the C_5 axis of the C_{70} molecule and the plane of the porphyrin. If the C_5 axis is parallel to the porphyrin plane that angle would be 0° , but if the fullerene stood upright so that one of the pentagons along the C_5 axis faced the porphyrin plane, that angle would be 90° . Figure 2 shows drawings in which that angle is at a minimum (fullerene **2** with the tilt angle of only 0.3°) and at maximum (fullerene **1** with the tilt angle of 9.7°). The corresponding tilt angles of all of the 12 fullerenes are given in Table 1. For comparison, the tilt angles for other nano-tubular fullerenes are: 3.2° and 5.1° for the C_5 axis in $D_{5h}(1)\text{-}C_{90} \cdot Ni^{II}(OEP)^{23}$ and 8.7° for the C_3 axis in $D_{3d}(3)\text{-}C_{96} \cdot 2Ni^{II}(OEP) \cdot 2C_6H_6$.²⁵ For the endohedral fullerene in $La_2@D_5(450)\text{-}C_{100} \cdot 2Ni^{II}(OEP) \cdot 2(\text{toluene})$ the tilt angle for the C_5 axis is quite large, 73.6° .²⁶

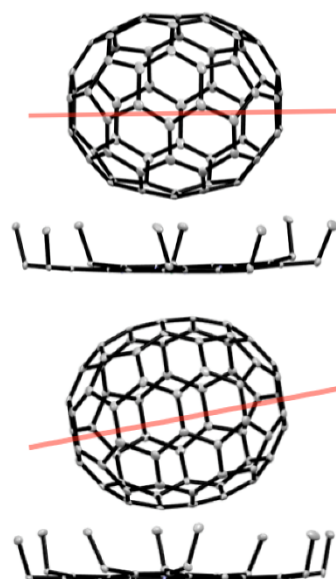


Figure 2. Extreme relative positions of the C_5 axis in red of the fullerene and the porphyrin plane in $12C_{70} \cdot 12Ni^{II}(OEP) \cdot 18p\text{-xylene}$, (**1**). Top; C_{70} **2** with the minimum angle, 0.3° , between the C_5 axis of the fullerene and the porphyrin plane. Bottom; C_{70} **1** with the maximum angle, 9.7° , between the C_5 axis of the fullerene and the porphyrin plane. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 32% probability level.

Table 1. Angles (deg.) regarding the position of the C_5 axis in $12C_{70} \cdot 12Ni^{II}(OEP) \cdot 18p$ -xylene, (**1**).

	Tilt Angle	Angle of C_5 axis relative to N-Ni-N line	Tilt Angle	Angle of C_5 axis relative to N-Ni-N line
C_{70} 1	9.7°	17.2°	C_{70} 7	8.9°
C_{70} 2	0.3°	18.0°	C_{70} 8	0.6°
C_{70} 3	0.9°	19.7°	C_{70} 9	0.6°
C_{70} 4	7.3°	20.1°	C_{70} 10	7.8°
C_{70} 5	1.9°	17.3°	C_{70} 11	8.8°
C_{70} 6	8.4°	16.0°	C_{70} 12	4.3°

A second difference involves the angle between the projection of the C_5 axis of the C_{70} molecule onto the adjacent $Ni^{II}(OEP)$ molecule and the angle that it makes from one of the N-Ni-N axes. The angle in question can take values from 0 to 45°. The angles all fall in the range 13.5 to 22.7° and are tabulated in Table 1.

Another difference involves the angle between the C_5 axes of two neighbouring C_{70} molecules. Figure 3 shows the two extreme situations. As seen in part A of the figure, fullerenes **8** and **9** are aligned nearly parallel to one another with an angle of only 0.2° between the C_5 axes of the fullerenes. However, as seen in part B, fullerenes **6** and **7** are arranged so that the angle between the two C_5 axes is 73.8°. The corresponding angles between the C_5 axes of all of pairs of neighbouring fullerenes are: **1** and **4**, 16.2°; **2** and **3**, 49.6°; **5** and **12**, 2.5°; **6** and **7**, 73.8°; **8** and **9**, 0.2°; **10** and **11**, 66.3°.

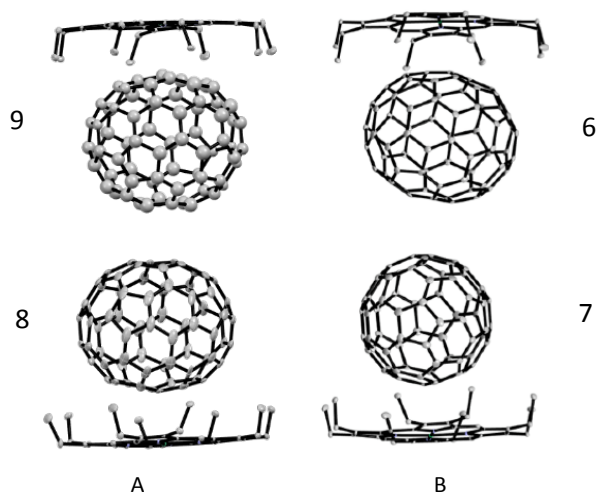


Figure 3. Extreme relative orientations of adjacent C_{70} molecules in $12C_{70} \cdot 12Ni^{II}(OEP) \cdot 18p$ -xylene, (**1**). **A**; C_{70} **8** and **9** with the minimum angle of 0.2° between the C_5 axes of the fullerenes. **B**; C_{70} **6** and **7** an angle of 73.8° between the two C_5 axes of the fullerenes. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 32% probability level.

As Figure 4 shows, in $12C_{70} \cdot 12Ni^{II}(OEP) \cdot 18p$ -xylene (**1**) the porphyrin rings are not entirely planar, but show varied distortions from planarity. In the chart below, the distances in Å of the core carbon and nitrogen atoms from the mean plane of the porphyrin are shown along the vertical axis while the individual atoms are shown in linear fashion along the horizontal axis. Such distortions of the porphyrin macrocycle have been classified as domed, saddled, ruffled, waved or pyrrole propellered.³² The most common form of distortion seen in $12C_{70} \cdot 12Ni^{II}(OEP) \cdot 18p$ -xylene (**1**) is a slight doming seen in all except for porphyrins **6**, **10** and **11**.

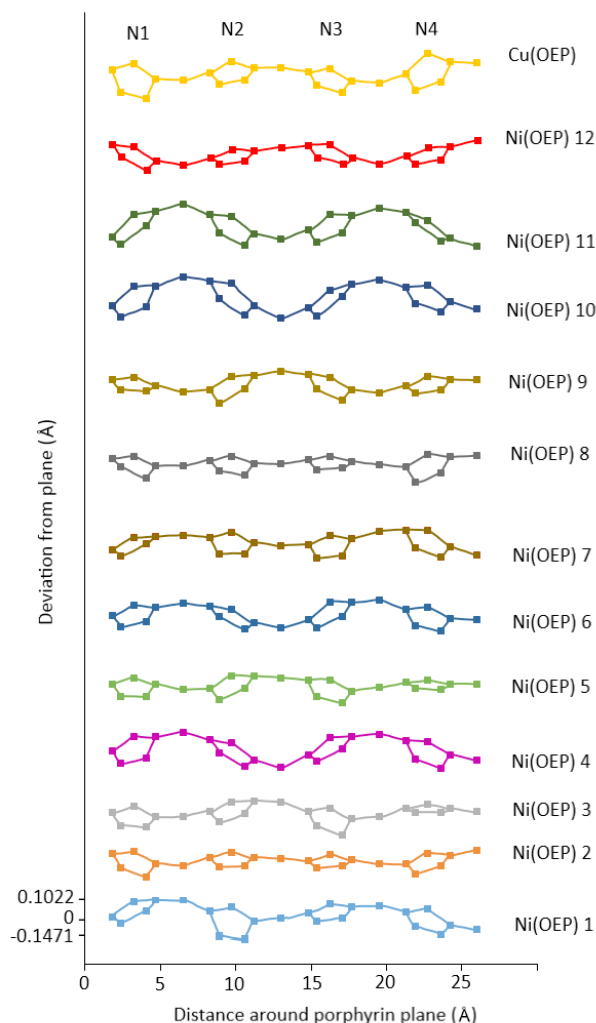


Figure 4. Comparison of the out-of-plane displacements of the porphyrin core atoms from the mean porphyrin plane as visualized in a linear fashion for the twelve $Ni^{II}(OEP)$ molecules in $12C_{70} \cdot 12Ni^{II}(OEP) \cdot 18p$ -xylene, (**1**) at 90 K and for $Cu^{II}(OEP)$ in $Cu^{II}(OEP) \cdot C_{70} \cdot 1.5p$ -xylene (**2**).

The transformation of $12Ni^{II}(OEP) \cdot 12C_{70} \cdot 18p$ -xylene (1**) at 186 K.** Upon warming, crystals of $12Ni^{II}(OEP) \cdot 12C_{70} \cdot 18p$ -

xylene (**1**) undergo a phase change. The structure of a crystal at 186 K has been determined by single crystal X-ray diffraction. At 186 K crystals are still triclinic with the same space group, $P\bar{1}$, but the lengths of a and b axes have decreased, and the unit cell volume has decreased by a factor of 33.7%. As shown in Figure 5, the unit cell now consists of four C_{70} molecules, four molecules of $Ni^{II}(\text{OEP})$ and six molecules of p -xylene. The porphyrin and p -xylene molecules are ordered, but each of the four sites for C_{70} molecules has a 50:50 occupation of two cage orientations.

The matrix for the low temperature \rightarrow high temperature phase transition is

$$\begin{pmatrix} -0.333 & 0 & 0.333 \\ 0.667 & 0 & 0.333 \\ 0 & 1 & 0 \end{pmatrix}$$

Thus, the b axis at low temperature becomes the c axis at high temperature. A set of three full occupancy C_{70} molecules in the structure at low temperature becomes a set of two of the half-occupancy C_{70} molecules at high temperature. It is possible to compute that the sets of C_{70} molecules (**2**, **7**, **10**); (**4**, **5**, **12**); (**1**, **8**, **9**) and (**3**, **6**, **11**) at low temperature become new C_{70} molecules (**1**, **2**); (**7**, **8**); (**5**, **6**) and (**3**, **4**), respectively, at higher temperature. Since both porphyrin and p -xylene species are ordered at both temperatures, it is obvious that the order-disorder phase change primarily involves reorientation of the C_{70} cages. A second crystal was mounted and the reversibility of the phase change was confirmed.

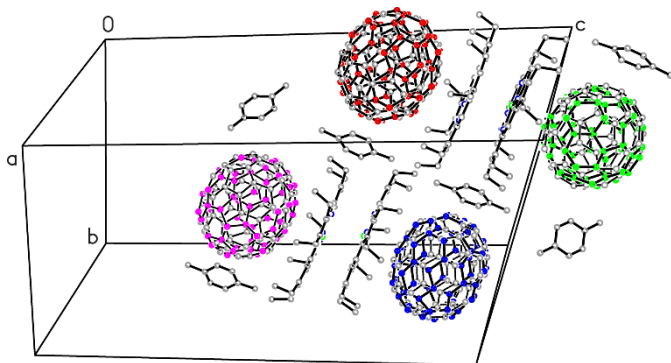


Figure 5. A view of the asymmetric unit in $12C_{70}\cdot 12Ni^{II}(\text{OEP})\cdot 18p\text{-xylene}$, (**1**) at 190 K. Crystal data are given in Table 2. Four ordered molecules of $Ni^{II}(\text{OEP})$ and six ordered molecules of p -xylene are present. Each of the four fullerene sites is occupied by two C_{70} molecules, one of which is shown as coloured spheres. The other C_{70} molecule at that site is represented by open circles. Hydrogen atoms have been omitted for clarity.

The structure of $Cu^{II}(\text{OEP})\cdot C_{70}\cdot 1.5p\text{-xylene}$ (2**).** Under the same conditions used to crystallize $12Ni^{II}(\text{OEP})\cdot 12C_{70}\cdot 18p\text{-xylene}$ (**1**) but substituting $Cu^{II}(\text{OEP})$ for $Ni^{II}(\text{OEP})$ produces $Cu^{II}(\text{OEP})\cdot C_{70}\cdot 1.5p\text{-xylene}$ (**2**), which has a rather simple structure. $Cu^{II}(\text{OEP})\cdot C_{70}\cdot 1.5p\text{-xylene}$ (**2**) crystallizes in the triclinic space group $P\bar{1}$ with just one molecule of $Cu^{II}(\text{OEP})$,

one molecule of C_{70} , and 1.5 molecules of p -xylene in the asymmetric unit. Figure 6 shows the interrelationship between the porphyrin and the fullerene. As usual, all eight ethyl groups surround the fullerene. The copper ion protrudes slightly on the side of the porphyrin that is away from the fullerene. The tilt angle of the C_5 axis relative to the porphyrin plane is 5.1° . Figure 7 shows the unit cell and the packing of the molecules. Two $Cu^{II}(\text{OEP})$ molecules come together in a back-to-back fashion, similar to the situation in $12Ni^{II}(\text{OEP})\cdot 12C_{70}\cdot 18p\text{-xylene}$ (**1**). Notice that the $12Ni^{II}(\text{OEP})\cdot 12C_{70}\cdot 18p\text{-xylene}$ (**1**) crystal and the $Cu^{II}(\text{OEP})\cdot C_{70}\cdot 1.5p\text{-xylene}$ (**2**) crystal form with the same ratios of components but the former has twelve independent versions of the three component molecules while the latter has just one.

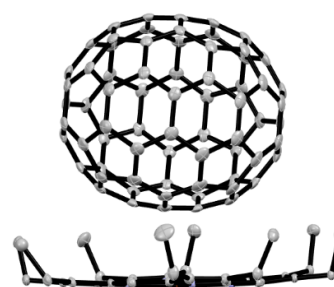


Figure 6. The relationship between the porphyrin and the fullerene in $Cu^{II}(\text{OEP})\cdot C_{70}\cdot 1.5p\text{-xylene}$ (**2**). Crystal data are given in Table 2. The solvate molecules, hydrogen atoms and minor disorder in one of the ethyl groups have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

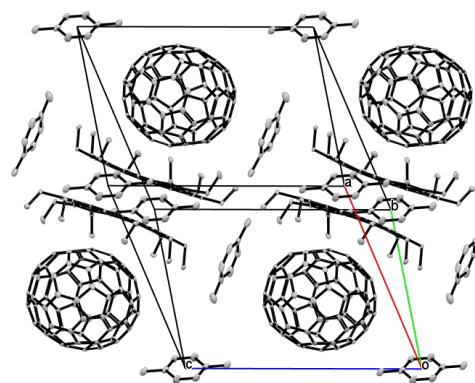


Figure 7. The molecular packing in $Cu^{II}(\text{OEP})\cdot C_{70}\cdot 1.5p\text{-xylene}$ (**2**). Disordered solvent and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Origin of the Structural Complexity of $12\text{Ni}^{\text{II}}(\text{OEP})\cdot 12\text{C}_{70}\cdot 18p\text{-xylene}$ (1). What is the cause of what we are seeing in this very large structure of C_{70} -containing molecules? Evidently, there is a distribution of multiple shallow energy conformations that occur due to the non-covalent interactions between the species in this structure. At 90 K, we can clearly observe a range of tilt angles between the plane of the porphyrin and the 5-fold rotation axis of C_{70} . This suggests that the weak $\pi\cdots\pi$ interactions and weak electrostatic interactions between the Ni metal and the fullerene are of primary importance. At 186 K, the intermolecular forces are a continuous influence on the crystal structure. The tilt angles do not vary greatly amongst the partially occupied fullerenes, and do not exceed nor fall below the tilt angles of the 90 K structure. The sensitivity of these interactions in driving differences in the crystallization of fullerenes in fullerene/porphyrin co-crystals is well documented.²¹ Since C_{70} has a lower point group symmetry (D_{5h}) than C_{60} (I_h) we can expect a wider range of these interactions in C_{70} . In the case of $12\text{Ni}^{\text{II}}(\text{OEP})\cdot 12\text{C}_{70}\cdot 18p\text{-xylene}$ (1), there are 12 different arrangements that are not due to the inversion symmetry of the unit cell. They are distinguished according to their small intermolecular energy differences. This occurrence has been termed modulation^{33,34}, and it is far more common now than in earlier days of crystallography, no doubt because of the much more common use of low temperatures. The 90 K structure is said to have $Z' = 12$, the number of symmetry-independent formula units. At 186 K, $Z' = 4$ because the different energy sets have sorted into four groups of three. We might project that $Z' = 1$ at even higher temperatures, yielding a Ni^{II} mimic of the basic structure ($Z' = 1$) of $\text{Cu}^{\text{II}}(\text{OEP})\cdot \text{C}_{70}\cdot 1.5p\text{-xylene}$. The reason for the difference between the nickel and copper structures is not obvious, but it is known that very small changes are capable giving very different results in these structures.

The structure of the solvate, $6\text{C}_{70}\cdot 6\text{toluene}$ (3). This solvate crystallizes in the monoclinic space group $P2_1/c$. It contains six C_{70} molecules and six toluene molecules in the asymmetric unit. Figure 8 shows a view of the asymmetric unit. Notice that each oblong C_{70} molecule adopts a unique orientation within this unit. The six C_{70} molecules shown in Figure 8 lie in a plane with a layer of toluene molecules positioned below them. The molecular packing can be seen in Figure 9. Of the six independent C_{70} molecules, two have 80:20 disorder, only the major sites are shown in Figure 8. Figure 9 shows the disorder in two of the C_{70} sites.

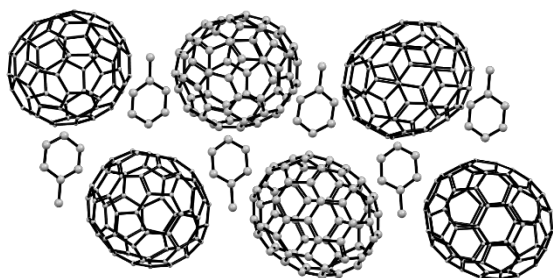


Figure 8. The asymmetric unit in the solvate, $6\text{C}_{70}\cdot 6\text{toluene}$ (3). The six fullerenes lie in a common plane with the toluene molecules in a layer below. Crystal data are given in Table 2. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 32% probability level.

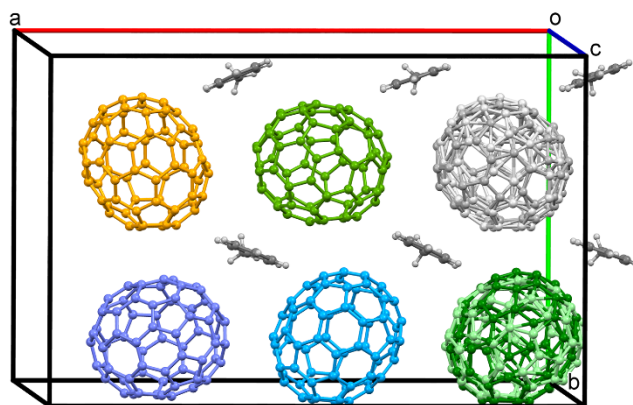


Figure 9. Molecular packing in the solvate, $6\text{C}_{70}\cdot 6\text{toluene}$ (3) looking down the c axis. Each distinct C_{70} is given a unique color, and the disorder in two of the C_{70} molecules is shown. Atoms are drawn as spheres with an arbitrary radius.

CONCLUSIONS

Two new cocrystals, $12\text{C}_{70}\cdot 12\text{Ni}^{\text{II}}(\text{OEP})\cdot 18p\text{-xylene}$ (1) and $6\text{C}_{70}\cdot 6\text{toluene}$ (3), have been discovered in which the oblong C_{70} molecule adopts several different orientations to produce remarkably complex solids. Somewhat surprisingly, these complex solids are formed from three relatively rigid molecules. C_{70} , $p\text{-xylene}$ and toluene have very well defined shapes and lack flexibility. $\text{Ni}^{\text{II}}(\text{OEP})$ has some degree of flexibility in that it can distort from planarity as is seen in the four polymorphs it forms.^{21,35-38} However as seen in Figure 4, each $\text{Ni}^{\text{II}}(\text{OEP})$ in $12\text{C}_{70}\cdot 12\text{Ni}^{\text{II}}(\text{OEP})\cdot 18p\text{-xylene}$ (1) is nearly planar and avoids the marked saddle distortion seen for the tetragonal polymorph.³³ The ethyl groups in $\text{Ni}^{\text{II}}(\text{OEP})$ do have the opportunity to adopt different orientations about the porphyrin plane. Nevertheless, in $12\text{C}_{70}\cdot 12\text{Ni}^{\text{II}}(\text{OEP})\cdot 18p\text{-xylene}$ (1) all ninety-six ethyl groups are positioned on one side of the porphyrin plane to embrace the adjacent C_{70} molecule. While such embraces are common in cocrystals of $\text{M}^{\text{II}}(\text{OEP})$ and various fullerenes,¹⁵⁻²⁰ there are many situations where some of the ethyl groups do not lie on the same side of the porphyrin and next to the fullerene. For example, in $\text{Ni}^{\text{II}}(\text{OEP})\cdot \text{C}_{60}\cdot 2\text{C}_6\text{H}_6$ only four of the ethyl groups surround the C_{60} molecule.³⁹ The other four lie on the opposite side of the

porphyrin plane and do not interact with a fullerene. In $6Zn^{II}(OEP) \cdot 5C_{60} \cdot 5CH_2Cl_2$ (**2**) of the twenty-four ethyl groups in the asymmetric unit, there is one that is turned away from embracing a C_{60} molecule.²¹ In $D_{5h}(1)-C_{90} \cdot Ni^{II}(OEP)$, one $Ni^{II}(OEP)$ molecule has four ethyl groups embracing a C_{90} molecule on one side and the other four embracing a C_{90} molecule on the opposite side. A second $Ni^{II}(OEP)$ has the ethyl arms arranged in a two up, one down, one up, two down, one up, one down fashion with each arm near a C_{90} molecule.²³

There are a few other cases where cocrystallization of a fullerene with $M^{II}(OEP)$ produces crystals with more than one molecule of the fullerene in the asymmetric unit. In $6Co^{II}(OEP) \cdot 5C_{60} \cdot 5CH_2Cl_2$ and $6Zn^{II}(OEP) \cdot 5C_{60} \cdot 5CH_2Cl_2$ there are three independent C_{60} molecules in the asymmetric unit.²¹ In $Sc_2(\mu_2-S)@C_3(6)-C_{82} \cdot Ni^{II}(OEP) \cdot 2C_6H_6$ there are two independent molecules of the endohedral fullerene present, one of which is fully ordered including the position of the $Sc_2(\mu_2-S)$ group inside.⁴⁰

It is fortunate that cocrystallization of fullerenes and $M^{II}(OEP)$ usually produces relatively straightforward structures like that of $Cu^{II}(OEP) \cdot C_{70} \cdot 1.5p$ -xylene (**2**) with only one fullerene site. Such relatively simple cocrystals allow the structure of a new fullerene component to be fully investigated and ascertained, as has been done repeatedly.¹⁵⁻²⁰

EXPERIMENTAL

Materials and General Consideration

$Ni^{II}(OEP)$ and $H_2(OEP)$ were purchased from Frontier Scientific. Metalation of $H_2(OEP)$ was accomplished by an established route.⁴¹ C_{70} was purchased from SES Research with 99% purity. Solvents were obtained commercially and used as received. Etioporphyrin-I was purchased from Frontier Scientific with 95% purity. $Ni^{II}(EtiO-I)$ was prepared according to literature methods by reacting the free-base etioporphyrin-I with nickel (II) acetate.^{42,43}

Crystal Growth

Procedure for $12Ni^{II}(OEP) \cdot 12C_{70} \cdot 18p$ -xylene (**1**) and $Cu^{II}(OEP) \cdot C_{70} \cdot 1.5p$ -xylene (**2**)

In a clean scintillation vial, a 0.00168 mmol solution of C_{70} in p -xylene was prepared by sonication for approximately 30 minutes. In a separate scintillation vial, an equal volume of a 0.00168 mmol solution of $M^{II}(OEP)$ in p -xylene was prepared. Cocrystallization was conducted in sterile, thick-walled glass tubes with an approximate inner volume of 2.0 mL. A 1.0 mL portion of the $M^{II}(OEP)$ solution in p -xylene was slowly pipetted into the tube through a filter-pipet. Next, 1.0 mL of the C_{70} solution in p -xylene was carefully layered over the $M^{II}(OEP)$ solution through a fresh filter pipet. The crystal tubes were capped with a rubber septum and left undisturbed in a dark cabinet until suitable crystal growth occurred. Crystal

growth occurred in as little as 72 hours but crystals were allowed to grow for up to three months before they were harvested for data collection.

Procedure for $6C_{70} \cdot 6$ toluene (**3**)

In a clean scintillation vial, a 0.017 mmol solution of C_{70} in toluene was prepared by sonication for approximately 30 minutes. In a separate scintillation vial, an equal volume of 0.0868 mmol solution of nickel etioporphyrin(I) in toluene was prepared by sonication for 30 minutes. Cocrystallization was conducted in sterile, thick-walled glass tubes with an approximate inner volume of 2.0 mL. A 1.0 mL portion of the C_{70} solution in toluene was slowly pipetted into the tube through a filter-pipet. Next, 1.0 mL of the etioporphyrin-1 nickel solution in toluene was slowly pipetted into the tube through a fresh filter pipet. The crystal tubes were capped with a rubber septum and left undisturbed in a dark cabinet. Suitable crystals for data collection formed after eight months of growth.

Crystal Structure Determination

A black plate of $12Ni^{II}(OEP) \cdot 12C_{70} \cdot 18p$ -xylene (**1**) was mounted in the 90 K nitrogen cold stream provided by a CRYO Industries low-temperature apparatus on a Bruker D8 DUO instrument equipped with a molybdenum microsource ($\lambda = 0.71073 \text{ \AA}$). A different crystal of (**1**) was mounted in a 186 K nitrogen cold stream on the same instrument. To determine the topotactic transformation previously discussed, the crystal of (**1**) run at 186 K was cooled to 90 K following the higher temperature run. Data for $Cu^{II}(OEP) \cdot C_{70} \cdot 1.5p$ -xylene (**2**) (black plate) were obtained similarly. A black block of $6C_{70} \cdot 6$ toluene (**3**) was mounted on a Bruker Apex II diffractometer employing a fine-focus Mo sealed tube, ($\lambda = 0.71073 \text{ \AA}$). All data sets were reduced with the use of Bruker SAINT,⁴⁴ and a multi-scan absorption correction was applied with the use of SADABS. Structure solutions and refinements were conducted with SHELXT-2015⁴⁵ and SHELXL-2018,⁴⁶ respectively. Crystallographic data are reported in Supporting Information and in Table 2 below.

Table 2. Cocrystal Data.

	$12Ni^{II}(OEP) \cdot 12C_{70} \cdot 18p$ -xylene (1) at 90 K	$4Ni^{II}(OEP) \cdot 4C_{70} \cdot 6p$ -xylene (1) at 186 K
chemical formula	$C_{118}H_{59}N_4Ni$	$C_{118}H_{59}N_4Ni$
formula weight	1591.40	1591.40
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
T (K)	90 (2)	186 (2)
a (Å)	35.187 (4)	17.1062 (10)

Journal Name			ARTICLE		
b (Å)	35.564 (4)	25.9900 (15)	reflections	111006	398191
c (Å)	35.852 (4)	35.865 (2)	collected		
α (deg)	102.301 (2)	107.0885 (11)	data/parameters/	16311/1113/0	81001/2904/1488
β (deg)	92.802 (2)	90.3877 (11)	restraints		
γ (deg)	101.834 (2)	108.0069 (10)	R(int)	0.0607	0.1452
V (Å³)	42702 (8)	14410.9 (14)	R₁ [data with I >	0.0427 [14011]	0.0861 [60597]
Z	24	8	2σ(I)]		
reflections			wR₂ (all data)	0.1108	0.2956
collected	522801	116981			
data/parameters/	176272/11934/31	74615/5053/50			
restraints	86	40			
R(int)	0.1029	0.0406			
R₁ [data with I >	0.1084 [80841]	0.1186 [46461]			
2σ(I)]					
wR₂ (all data)	0.3642	0.3438			

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

Conflicts of interest

The authors have no conflicts of interest to declare.

Supporting Information

Crystallographic data in CIF Format. CCDC 2018102-2018105 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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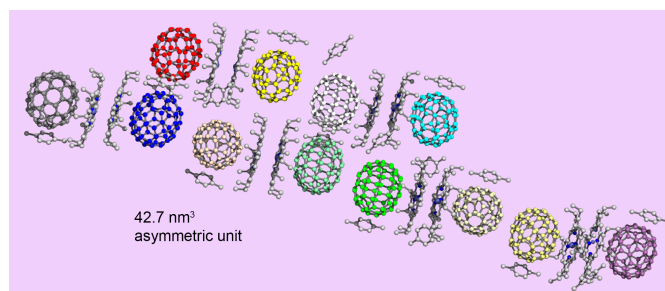
	Cu ^{II} (OEP)•C ₇₀ •1.5p-xylene (2) at 90 K	6C ₇₀ •6toluene (3) at 90 K
chemical formula	C ₁₁₈ H ₄₄ N ₄ Cu	C ₇₇ H ₈₈
formula weight	1598.06	932.83
crystal system	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
T (K)	90 (2)	90 (2)
a (Å)	15.2358 (4)	32.398 (6)
b (Å)	15.8431 (4)	21.103 (4)
c (Å)	16.7025 (4)	32.293 (6)
α (deg)	76.7210 (10)	90
β (deg)	72.5020 (10)	90.006 (3)
γ (deg)	68.6150 (10)	90
V (Å³)	3548.20 (16)	22079
Z	2	24

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Graphical Abstract Caption:

A cocrystal with an asymmetric unit of 12 C₇₀ • 12 Ni^{II}(OEP) • 18 p-xylene, with a 10 nm translation and a volume of 42.7 nm³.



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