# Synthesis and Crystal Structure of a Cocrystalline Compound of a Rare Earth Metalloporphyrin with Fullerene $\{[TPPYb(\mu\text{-}OH)_2Yb(THF)TPP]\cdot C_{60}\}_n$

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The reaction of $YbI_2(THF)_2$ with $TPPLi_2$ (TPP = 5,10,15,20-tetraphenylporphyrin) in THF, and then with 0.5 equiv. of $C_{60}$, which was solvated in toluene beforehand, gave the title compound $\{[TPPYb(\mu\text{-}OH)_2Yb(THF)TPP]\cdot C_{60}\}_n$, which is the first example of a rare earth metallofullerene cocrystal compound. X-ray structural analyses indicate that this compound displays a complicated supramolecular structure, which contains some unique noncovalent interactionsbetween $C_{60}$ and the rare earth metalloporphyrin units.



## Introduction

The fullerene ($C_{60}$) molecule has attracted much current attention due to its chemical properties, and uniform, spherical, and nanoscale physical structure, and its potential application in optical and electronic materials, superconductors, and sensors.[1] The organometallic chemistry of fullerene is becoming a flourishing subdiscipline of fullerene research.[2,3] However, research efforts are primarily focused on organotransition metal fullerene complexes in which the fullerene essentially behaves as a weak electron-deficient alkene ligand.[4] In the field of lanthanofullerene chemistry, only the chemistry of endohedral complexes with encapsulated metal atoms, $Ln@C_{2n}$ has been investigated.[5] These species are prepared by the arc vaporization of a mixture of graphite and lanthanoid oxide or carbide under helium.[6] Owing to the high electron-deficient character of lanthanide metal centers, the synthesis of exohedral lanthanide fullerene complexes poses a fundamental problem. The chemistry of exohedral lanthanide fullerene complexes has remained relatively unexplored.[2,7]

On the other hand, the weak noncovalent interactions of curved/flat or curved/curved molecular surfaces have recently attracted much attention in supramolecular chemistry and crystal engineering.[8] The curved π surface of $C_{60}$ shows a tendency to interact with other molecules, making it an interesting candidate for engineering supramolecular arrays. It has been confirmed that the ball-shaped $C_{60}$ molecule can cocrystallize with planar molecules such as porphyrins or metalloporphyrins through the interaction of the curved π surface of the fullerene with the planar π surface of the porphyrin, without the need to match convex surfaces with concave surfaces.[8] Many molecular complexes of fullerenes with transition metalloporphyrins have been obtained and structurally characterized.[9–11] However, no examples of cocrystals consisting of rare earth metalloporphyrins with fullerenes have been reported. In this contribution, we report the synthesis and structural characterization of a novel rare earth metalloporphyrin compound cocrystallized with $C_{60}$ molecules, $\{[TPPYb(\mu\text{-}OH)_2Yb(THF)TPP]\cdot C_{60}\}_n$ (**1**). The X-ray structural analysis of **1** provides some insight into the supramolecular assembly between the fullerenes and metalloporphyrins, which incorporates some unique supramolecular interactions.

## Results and Discussion

Bochkarev et al. synthesized the first fulleride complexes of low valence lanthanocene derivatives and confirmed the valence flexibility of $Ln^{II}$ ions in these charge-transfer compounds by temperature-dependent ESR spectroscopy.[7] When considering the noncovalent interactions between the porphyrin rings and the fullerene molecules, we anticipate that strong interactions will be observed between the low valence ytterbium porphyrins and the $C_{60}$ molecules. However, the reaction of $TPPYb^{II}$ with $C_{60}$ leads only to an oxidation product. The reactions of $TPPLi_2$ with $YbI_2(THF)_2$ in THF, and the subsequent reaction with 0.5 equiv. of $C_{60}$ which was solvated in toluene beforehand gave the ytterbium(III) porphyrinate complex cocrystallized with fullerene (**1**) [Equation (1)]. The oxidation of the $Yb^{II}$ units may be caused by trace amounts of oxygen gas and moisture in the inert atmosphere, as similarly observed for another rare earth metalloporphyrin.[12] To obtain a crystal of complex **1** suitable for X-ray diffraction analysis, the selection of an appropriate solvent may be important. Owing to

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$C_{60}$ being almost insoluble in THF, and the ytterbium complex of tetraphenylporphyrin being hardly soluble in toluene, we chose for our experiments a solvent mixture of THF and toluene (THF/toluene, 11:1.5). In fact, the final product **1** is also poorly soluble in THF and toluene. It should be noted that we could not obtain the analogous Samarofullerene compound under the same conditions.

$$H_2TPP \xrightarrow[2)\ YbI_2(THF)_2\ \ 3)\ C_{60}/\ toluene]{1)\ nBuLi} \underset{\mathbf{1}}{[TPPYb(OH)_2Yb(THF)TPP]\cdot C_{60}}$$

TPP = 5,10,15,20-tetraphenylporphyrin

(1)

Unambiguous structure determination of complex **1** was completed by X-ray crystallographic analysis of a single crystal, which had been obtained by the slow diffusion of *n*-hexane into the THF and toluene solution of **1**. The molecular structure of **1** is shown in Figure 1. Selected bond lengths and short contact distances are given in Table 1 and Table 2, respectively. The asymmetric unit of **1** consists of one $C_{60}$ molecule and one dinuclear ytterbium porphyrinate, in which the two ytterbium atoms are connected by two hydroxy-bridges. Compound **1** crystallizes in such a way that two dinuclear ytterboporphyrin units surround each fullerene. Within this unit the fullerene is positioned asymmetrically between the two [TPPYb(μ-OH)$_2$Yb(THF)-TPP] units. X-ray single crystal structure analysis reveals that supramolecular interactions between the curved/flat molecule interfaces exist. The most obvious noncovalent interaction is found between the planes of porphyrin rings and the curved surface of the fullerenes. The $C_{60}$ molecule is centered over the porphyrins giving two different short contact modes. In the first mode, one porphyrin plane interacts with the 5:6 ring-junction C–C bonds of $C_{60}$, and in the other mode, the porphyrin plane interacts with the 5:6 and 6:6 ring-junction C–C bonds of another $C_{60}$ molecule, as shown in Figure 2. This is significantly different form the results observed for most porphyrins or metalloporphyrins, which prefer to interact with the electron-rich 6:6 ring junction.[9,10] The mechanism of interaction of porphyrin with the 6:6 or 5:6 ring junctions of fullerene is unclear.[9g,10a] The N···C($C_{60}$) distances in **1** are in the range of 3.08–3.09 Å and lie at the lower end of the range of van der Waals contacts, and well below the "standard" contact distance (3.2–3.3 Å), and are similar to the corresponding distances in metal-free porphyrin fullerene complexes.[13] However, these distances are significantly longer than the corresponding distances in transition metalloporphyrin fullerene cocrystals.[9–11] This may be attributed to the electron-deficient character of rare earth metal ions, and the electron-acceptor nature of fullerene, resulting in weaker interactions between the metalated porphyrin units and the fullerenes.

Table 1. Selected bond lengths [Å] for the ytterbium porphyrin unit in **1**.

| | | | |
|---|---|---|---|
| Yb(1)–O(1) | 2.1819(9) | Yb(2)–O(1) | 2.2451(9) |
| Yb(1)–O(2) | 2.1893(9) | Yb(2)–O(2) | 2.2497(9) |
| Yb(1)–N(8) | 2.2935(10) | Yb(2)–N(2) | 2.3313(10) |
| Yb(1)–N(7) | 2.3090(9) | Yb(2)–N(1) | 2.3449(9) |
| Yb(1)–N(5) | 2.3166(9) | Yb(2)–N(4) | 2.3515(10) |
| Yb(1)–N(6) | 2.3323(11) | Yb(2)–N(3) | 2.3567(12) |
| Yb(1)–Yb(2) | 3.6237(2) | Yb(2)–O(3) | 2.3821(10) |

Table 2. Selected short contact distances [Å] in **1**.

| | | | |
|---|---|---|---|
| N(8)···C(128)$^{1}$ | 3.0861 | C(86)···C(132)$^{1\#}$ | 3.3524 |
| C(54)···C(149)$^{1}$ | 3.3941 | H(91A)···C(123)$^{2}$ | 2.8569 |
| C(55)···C(149)$^{1}$ | 3.3875 | Yb(1)···C(128)$^{1}$ | 4.0835 |
| C(58)···C(127)$^{1}$ | 3.3390 | Yb(1)···C(129)$^{1}$ | 3.8940 |
| N(1)···C(113)$^{2\#}$ | 3.0920 | Yb(2)$^{2\#}$···C(112) | 4.0517 |
| N(3)···C(112)$^{2\#}$ | 3.0881 | Yb(2)$^{2\#}$···C(113) | 3.9158 |
| C(6)···C(154)$^{2\#}$ | 3.3733 | | |

Symmetry transformations used to generate equivalent atoms: 1: *x*, *y*, *z*; 1#: –*x*, –*y*, –*z*; 2: 1/2 – *x*, 1/2 + *y*,1/2 – *z*; 2#: 1/2 + *x*, 1/2 – *y*, 1/2 + *z*.

As shown in Figure 3, the THF molecules may play a unique role in the crystal structure of **1**. This contrasts with other fullerene cocrystals of metalloporphyrins and metal-free porphyrins, in which the solvent molecules only exist in the crystal lattice.[9–11] Only one THF molecule in **1** is

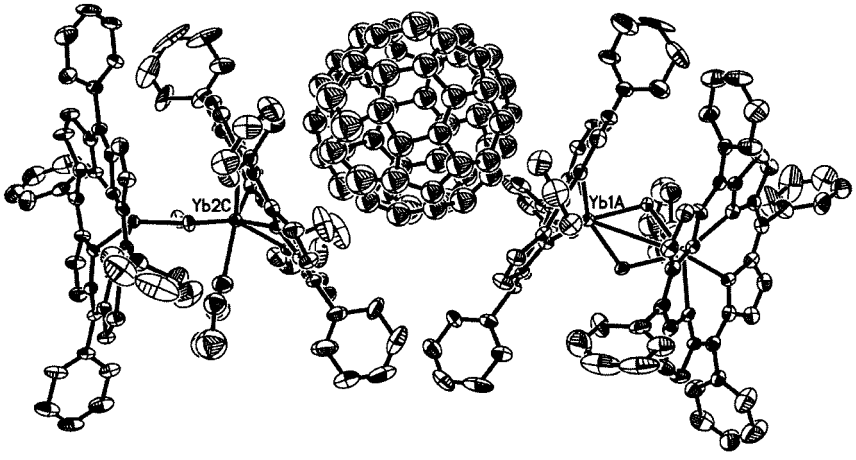


Figure 1. ORTEP diagram of the [TPPYb(μ-OH)$_2$Yb(THF)TPP]·$C_{60}$ unit with the thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

  

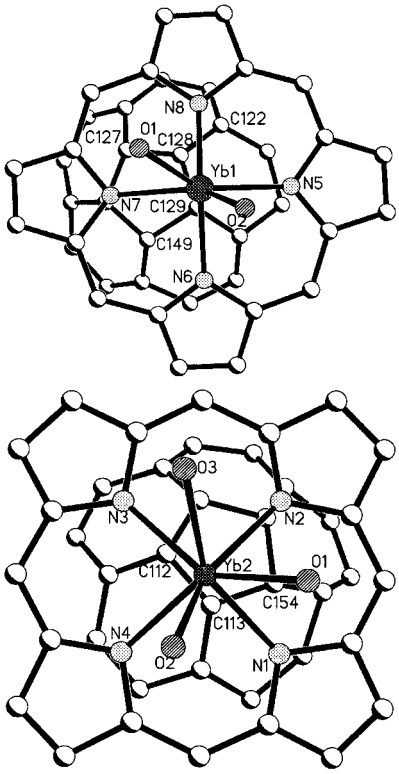


Figure 2. Orientation of $C_{60}$ with respect to the ytterboporphyrin plane, as seen in **1**.

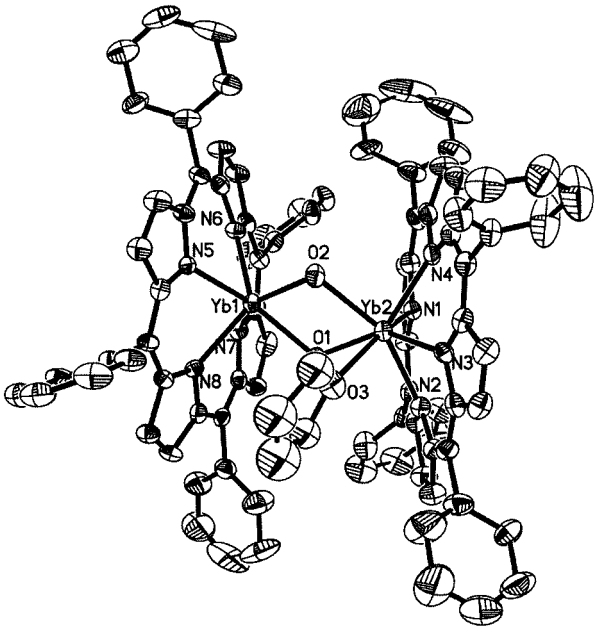


Figure 3. ORTEP diagram of the [TPPYb(μ-OH)$_2$Yb(THF)TPP] unit in **1** with the thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

coordinated to one $Yb^{3+}$ ion, and this results in different coordination environments around the metal centers, in that one $Yb^{3+}$ ion is seven-coordinate, while the other $Yb^{3+}$ ion is six-coordinate. This causes the two porphyrin rings in the dinuclear ytterbium porphyrin units to lie unparallel, the dihedral angle between them is 31.91(1)°. This angle is comparable to the corresponding values found in the unique example of [{$Yb^{III}$(TTP)}$_2$(μ-OH)(μ-$OCH_2CH_2OCH_3$)] where the dihedral angle between the two porphyrin ring planes is 30.5°.[12] The difference in the metal coordination environments also means that the average distance of Yb(1) to the nitrogen atoms of one porphyrin ring [3.313(1) Å] is significantly shorter than the average distance of Yb(2) to the nitrogen atoms of another porphyrin ring [3.346(1) Å]. Also, the Yb(1)–O(1) and Yb(1)–O(2) distances [2.1819(9) Å, 2.1893(9) Å] are significantly shorter than the Yb(2)–O(1) and Yb(2)–O(2) distances [2.2451(9) Å, 2.2497(9) Å]. It should be noted that dinuclear rare earth metalloporphyrin complexes containing such an unsymmetrical coordination mode are rarely reported,[12] and the unparallel arrangement of the porphyrin planes in the metalloporphyrin units may cause the differences in the short contacts between the two porphyrin rings and the $C_{60}$ molecule.

In **1**, the fullerene is too far from the ytterbium atoms for any covalent bond to form between them. The ytterbium atoms are displaced significantly out of the N4 planes of the porphyrins, in the direction opposite to that of the porphyrin-fullerene contacts, and as a result of this there is no possibility of a direct exohedral interaction forming between the ytterbium atoms and the fullerene molecules. This is significantly different from the results observed for the late transition metalloporphyrin fullerene cocrystals, in which strong noncovalent interactions exists between the metal centers and the fullerene molecules because of the electron-rich characters of these metal ions.[9,10] Interestingly, the fullerene is positioned so that the closest contact with the ytterbium atom involves 5:6 ring junctions, and it is significantly shorter than the van der Waals radii of the atoms involved. This may be attributed to the strong covalent interactions of the ytterbium atoms with the porphyrin rings through the hydroxyl bridges.

Within the cocrystal structures of metalloporphyrin with fullerene, there are two kinds of noncovalent interactions in the supramolecular assembly: one is the interaction of the planes of the porphyrin rings with the curved surfaces of the fullerenes, and the other is the porphyrin/porphyrin face-to-face contacts, which pair the porphyrin units. In the aryl-substituted metalloporphyrin fullerene cocrystalline complexes, the porphyrin/porphyrin contact is very weak due to the repulsive interactions of the terminal aryl substituents. Usually, in aryl-substituted porphyrin complexes only one metalloporphyrin unit interacts with two $C_{60}$ molecules.[10c] In complex **1**, in addition to the fullerene/porphyrin interactions, there are covalent interactions between the $Yb^{3+}$ ions and the two hydroxyl bridges between the two tetraphenyl-metalloporphyrins. This combination of covalent and noncovalent interactions produces helical ribbons that wind their way through the crystal (Figure 4).

Another feature of the structure of complex **1** is that there is a noncovalent interaction between the phenyl substituents of the porphyrin rings and the fullerene molecules. Although plenty of cocrystal complexes of fullerenes with

  

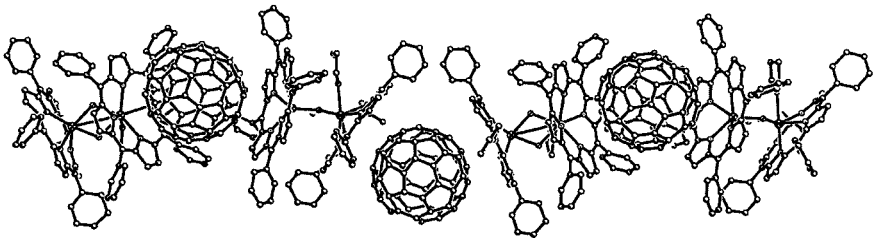

Figure 4. View of the helical chain in **1**.

transition metalloporphyrins have been obtained and structurally characterized, aryl-substituted metalloporphyrin fullerene cocrystalline complexes are very rare. Some researchers regard the modification of the structure of the terminal phenyl groups as very important in order to make the curved $C_{60}$ surface match the planar surface of the porphyrin to enable cocrystal growth.[10b] In complex **1**, one of the phenyl substituents of the dinuclear ytterboporphyrin units forms a contact with a third $C_{60}$ molecule, with the shortest C···C distance of 3.35 Å. To the best our knowledge, only one example of the phenyl substituents participating in noncovalent interactions has been reported, this previous example was of a metal-free porphyrin cocrystallized with $C_{60}$ molecules.[10c] In **1**, this interaction may be attributed to the unparallel arrangement of the porphyrin plane which allows the phenyl substituent to move closer to the $C_{60}$ molecules.

## Conclusions

In summary, in this paper we have reported the successful synthesis of the first crystallographically confirmed cocrystalline compound of a rare earth metalloporphyrin with fullerene. This compound displays a complicated supramolecular structure containing unique noncovalent interactions between the fullerene molecules and the dinuclear rare earth metalloporphyrin units.

## Experimental Section

**General Procedure:** All operations involving air- and moisture-sensitive compounds were carried out under purified argon or nitrogen using standard Schlenk techniques. The solvents THF, toluene, and *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. Tetraphenylporphyrin and *n*BuLi (2.0 M in cylcohexane) were purchased from Aldrich, and were used without further purification. Infrared spectra were obtained with a NICOLET FT-IR 360 spectrometer, with samples prepared as KBr pellets.

**Synthesis of 1:** *n*-Butyllithium (1.96 M, 120 μL in cyclohexane) was added dropwise to a solution of $H_2TPP$ (76 mg, 0.118 mmol) in THF (20 mL) at ambient temperature. After stirring for 12 h a THF solution of $YbI_2(THF)_2$ (68 mg, 0.118 mmol, 15 mL) was slowly added to the reaction mixture, which was then stirred for a further 12 h. Then a toluene solution of $C_{60}$ (42.6 mg, 0.59 mmol, 30 mL) was injected into the reaction solution. Towards the end of addition, brown solid precipitated from the dark purple solution. The reaction solution was stirred for 24 h at ambient temperature, and the precipitate was then filtered off. Crystallization by the slow diffusion of *n*-hexane into the pellucid dark purple solution yielded dark purple crystals of **1** after several months. IR (KBr): $\tilde{\nu}$ = 3436 (m), 1596 (m), 1477 (m), 1439 (s), 1330 (m), 1220 (m), 1182 (m), 1069 (s), 1006 (s), 990 (s), 798 (s), 751 (m), 722 (m), 700 (s), 656 (m), 632 (w), 577 (m), 527 (s) $cm^{-1}$.

**Crystallographic Data for 1:** Suitable single crystals of complex **1** for X-ray structural analysis were sealed under argon in Lindemann glass capillaries. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo-$K_\alpha$ ($\lambda$ = 0.71073 Å) radiation. During the collection of the intensity data, no significant decay was observed. Frames were integrated to the maximum $2\theta$ angle of 50.02° with the Siemens SAINT program to yield a total 44738 reflections, of which 18883 were independent ($R_{int}$ = 0.0795). The Laue symmetry indicated a monoclinic crystal system, and the final unit cell parameters were determined from the full-matrix least-squares refinement on $F^2$ employing the 18883 unique reflections. The intensities were corrected

Table 3. Crystal and data collection parameters for **1**.

| | **1** |
|---|---|
| Formula | $C_{152}H_{66}N_8O_3Yb_2$ |
| Molecular weight | 2398.21 |
| Crystal color | purple |
| Crystal dimensions [mm] | 0.20×0.15×0.10 |
| Crystal system | monoclinic |
| Space group | *P*21/*n* |
| *a* [Å] | 17.0274(14) |
| *b* [Å] | 29.097(2) |
| *c* [Å] | 22.6793(18) |
| *β* [°] | 107.150(1) |
| *V* [Å$^3$] | 10736.6(15) |
| *Z* | 4 |
| $D_{calcd.}$ [g cm$^{-3}$] | 1.484 |
| $\mu$ [mm$^{-1}$] | 1.797 |
| *F* (000) | 4792 |
| Radiation ($\lambda$ = 0.710730 Å) | Mo-$K_\alpha$ |
| Temperature [K] | 298(2) |
| Scan type | $\omega - 2\theta$ |
| $\theta$ range [°] | 1.17 to 25.01 |
| *h*,*k*,*l* range | $-15 \le h \le 20$, $-34 \le k \le 29$, $-26 \le l \le 26$ |
| No. of reflections measured | 44738 |
| No. of unique reflections | 18883 ($R_{int}$ = 0.0795) |
| Completeness to $\theta$ | 99.8% ($\theta$ = 25.01) |
| Max. and min. transmission | 0.8407 and 0.7151 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 18883/148/1166 |
| Goodness-of-fit on $F^2$ | 0.942 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1$ = 0.0732, $wR_2$ = 0.1900 |
| *R* indices (all data) | $R_1$ = 0.1454, $wR_2$ = 0.2173 |
| Largest diff. peak and hole [e Å$^{-3}$] | 1.831 and –0.989 |

  

for Lorentz-polarization effects and empirical absorption with the SADABS program.[14] The structure was solved by direct methods using the SHELXL-97 program.[15] All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included at calculated positions, with their isotropic thermal parameters related to those of the supporting carbon atoms, and were not included in the refinement. Further refinement led to the final $R$ indices [$I > 2\sigma(I)$] $R_1 = 0.0732$. All calculations were performed using the SHELXL-97 program. A summary of the crystallographic data is given in Table 3. CCDC-250532 (**1**) contains 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/data_request/cif.

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