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# New Molecular Complex of Fullerene $C_{60}$ with Porphyrin Dimer $[FeTPP]_2O$: Synthesis and Crystal Structure

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## ABSTRACT

New molecular complex of $C_{60}$ with covalently linked $(Fe^{III}TPP)_2O \cdot C_{60}$ dimer has been obtained. The complex has isolated packing of fullerenes in which fullerene molecule is embraced in a pocket built by porphyrins. $(Fe^{III}TPP)_2O$ preserves its initial geometry in the complex. The $Fe \cdots C(C_{60})$ contacts are in the 3.239–3.513 Å range indicating the

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absence of Fe–$C_{60}$ coordination. This results in the similarity of the EPR spectra of the complex and parent $(Fe^{III}TPP)_2O$.

*Key Words:* Fullerene $C_{60}$; Porphyrin; $(Fe^{III}TPP)_2O$; EPR spectra; Crystal structure.

## INTRODUCTION

Fullerenes form complexes with aromatic hydrocarbons, amines, substituted tetrathiafulvalenes, metallocenes, porphyrins, and metalloporphyrins.[1–3] The latter family of the complexes is of great interest because of their promising photoactive properties.[4] Among the fullerene complexes with tetraphenylmetalloporphyrins only two are known with $Fe^{III}$ containing porphyrins: $Fe^{III}ClTPP$[2] and $Fe^{III}TPP[B(C_6F_5)_4]$.[3] Additionally to chlorine, $Fe^{III}TPP$ interacts with other axial ligands, for example, it is covalently linked by oxygen atom to form $\mu$-oxo$(Fe^{III}TPP)_2O$ dimer.[5] It was shown that $(Fe^{III}TPP)_2O$ possesses photoactive properties.[6] The present work reports on the synthesis and crystal structure of the new $C_{60}$ complex with the $\mu$-oxo-*bis*[5,10,15,20-tetraphenylporphyrinatoiron (III)] $(Fe^{III}TPP)_2O$ dimer.

## RESULTS AND DISCUSSION

The crystals of $(Fe^{III}TPP)_2O \cdot C_{60}$ (**1**) were obtained by slow evaporation of toluene solution containing 20 mg of $C_{60}$ and 38 mg of $(Fe^{III}TPP)_2O$ (1 : 1 molar ratio) under argon during a week (yield 90%). The composition of **1** was determined from the X-ray diffraction on a single crystal.

The x-ray diffraction[7] shows that **1** has a 1 : 1 solid-state stoichiometry $((Fe^{III}TPP)_2O : C_{60})$. In the crystal, the $(Fe^{III}TPP)_2O$ and $C_{60}$ molecules alternate in chains along the crystallographic *c*-axis [Fig. 1(a)]. The chains are positioned so that each $C_{60}$ molecule is surrounded only by $(Fe^{III}TPP)_2O$ ones, and fullerenes do not make any shortened contacts to each other. As this takes place, $(Fe^{III}TPP)_2O$ forms a three-dimensional supramolecular network by the shortened $H(Ph) \cdots H'(Ph)$ (2.20–2.28 Å) and $H(Ph) \cdots C'(Ph)$ (2.72–2.86 Å) contacts. Each fullerene molecule is embraced in a pocket built by two porphyrin moieties from one chain and phenyl substituents of four porphyrins from the adjacent chains. The phenyl substituents form short van der Waals contacts with fullerenes with the $C(Ph) \cdots (C_{60})$ distances in the 3.235–3.358 Å range [Fig. 1(b)].

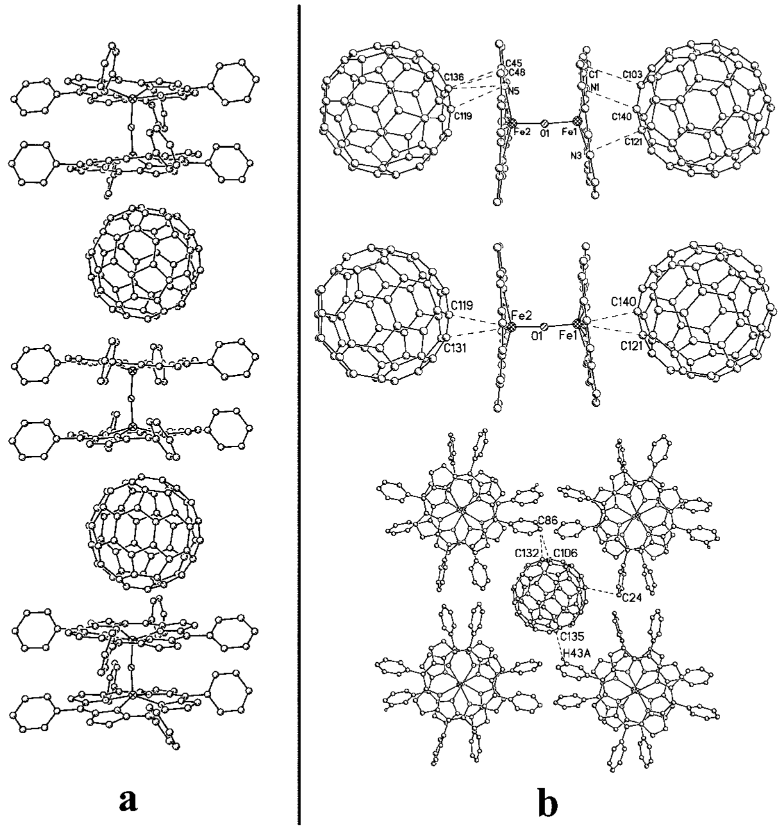

***Figure 1.*** The $(Fe^{III}TPP)_2O$ and $C_{60}$ chain of **1** (a) and a mutual arrangement of $(Fe^{III}TPP)_2O$ and $C_{60}$ molecules in **1** (b).

Iron atoms of $(Fe^{III}TPP)_2O$ are located on the other side of the porphyrin macrocycle relative to fullerene. Because of this, the $Fe \cdots C(C_{60})$ contacts of 3.239–3.513 Å are rather long as compared with those in fullerene complexes with other metal-containing porphyrins (2.57–3.12 Å[2,3,8]). In addition to the $Fe \cdots C_{60}$ contacts [Fig. 1(b)], porphyrins form shortened contacts with fullerenes by nitrogen [the $N(TPP) \cdots C(C_{60})$ contacts are 3.081–3.186 Å], and carbon atoms [the $C(TPP) \cdots C(C_{60})$ contacts are 3.244–3.425 Å]. For comparison, the sum of van der Waals radii of two C atoms is 3.42 Å and that of the C and N atoms is 3.21 Å.

The EPR behavior of **1** is close to that of parent $(Fe^{III}TPP)_2O$. For example, the EPR signals are not observed at room temperature (RT), while with the temperature decrease down to 77 K the EPR signals with $g = 5.7$ and $\Delta H_{pp} = 200$ G are observed for both compounds. The $g$-factor is characteristic of a square planar complex of $Fe^{III}$ with high-spin $3d^5$-configuration. A strong exchange interaction between $Fe^{III}$ in the dimer results in the absence of EPR signals at RT. However, the temperature decrease seems to cause the freezing of the state with the Fe1–O–Fe2 angle [173.7(2)°] slightly differing from 180° between the porphyrin planes and results in the appearance of a weak EPR signal.[9] The similarity of the EPR spectra of **1** and $(Fe^{III}TPP)_2O$ indicates the absence of $Fe^{III}$ coordination to fullerene and the changes in $(Fe^{III}TPP)_2O$ geometry in the complex with $C_{60}$ that is in agreement with the data of the x-ray analysis.

## ACKNOWLEDGMENTS

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