

Synthesis, Crystal Structure, and Optical Properties of a New Molecular Complex of C₆₀ with a Covalently Linked (Fe^{III}TPP)₂O Dimer

Aleksey L. Litvinov,^[a] Dmitri V. Konarev,^[a] Andrey Yu. Kovalevsky,^[b]
Alexander N. Lapshin,^[a] Evgeniya I. Yudanov,^[a] Natalia V. Drichko,^[c] Philip Coppens,^[b]
and Rimma N. Lyubovskaya*^[a]

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A new molecular complex of C₆₀ with covalently linked μ -oxo dimer (Fe^{III}TPP)₂O are (TPP = tetraphenylporphyrin) was obtained. The complex has a neutral ground state and is formed mainly by van der Waals forces. The X-ray analysis of the crystal structure of the complex showed it to have

isolated packing of fullerenes in which each fullerene molecule is embraced in a pocket built by porphyrins. Optical properties and EPR behavior of the complex are described. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Fullerenes form complexes with aromatic hydrocarbons, amines, substituted tetrathiafulvalenes, metallocenes, porphyrins, and metalloporphyrins.^[1–6] The latter family of complexes is of great interest because of their promising photoactive properties.^[7] Metalloporphyrins can be used to develop neutral and ionic multi-component systems^[8,9] and to determine the molecular structure of endohedral^[10] and chemically modified fullerenes.^[6] Different chemically modified porphyrins in which two porphyrin moieties bonded by one (“jaw” porphyrins^[11]) or two bridged chains (cyclic dimers^[12]) have been used to prepare complexes with fullerenes. These molecules have a high affinity for fullerenes.^[11,12]

Additionally to monomeric and chemically modified porphyrins, covalently linked dimers of metal-containing porphyrins with different bridging atoms (O,^[13] N,^[14] and C^[15]) are also promising components for the development of photoactive complexes with fullerenes. It has been shown that, on photoexcitation with a 441.6 nm laser, (Fe^{III}TPP)₂O undergoes photodisproportionation to the oxoferryl species

Fe^{IV}=O(TPP) and five-coordinate, high-spin Fe^{II}-TPP(L).^[16]

The present work reports for the first time the synthesis, crystal structure, and optical properties of the C₆₀ complex, (Fe^{III}TPP)₂O·C₆₀ (**1**), with a covalently linked μ -oxo-bis[5,10,15,20-tetraphenylporphyrinatoiron(III)] dimer.

Results and Discussion

X-ray diffraction^[17] shows that **1** has a 1:1 solid-state stoichiometry [(Fe^{III}TPP)₂O:C₆₀]. The crystal is a racemic twin with two equal components [the Flack parameter^[18] is 0.50(2)].

In the crystal, the (Fe^{III}TPP)₂O and C₆₀ molecules alternate in chains along the crystallographic *c* axis (Figure 1, a). The chains are positioned so that each C₆₀ molecule is surrounded only by (Fe^{III}TPP)₂O moieties; their are no inter-fullerene contacts. Because of this, (Fe^{III}TPP)₂O forms a three-dimensional supramolecular network (Figure 1, b) through shortened H(Ph)⋯H'(Ph) (2.20–2.28 Å) and H(Ph)⋯C'(Ph) (2.72–2.86 Å) contacts. Each fullerene molecule is found in a pocket built by two porphyrin moieties from one chain and the phenyl substituents of four porphyrins from the adjacent chains. The phenyl substituents form short van der Waals contacts with fullerenes, with C(Ph)⋯C(C₆₀) distances in the 3.235–3.358 Å range.

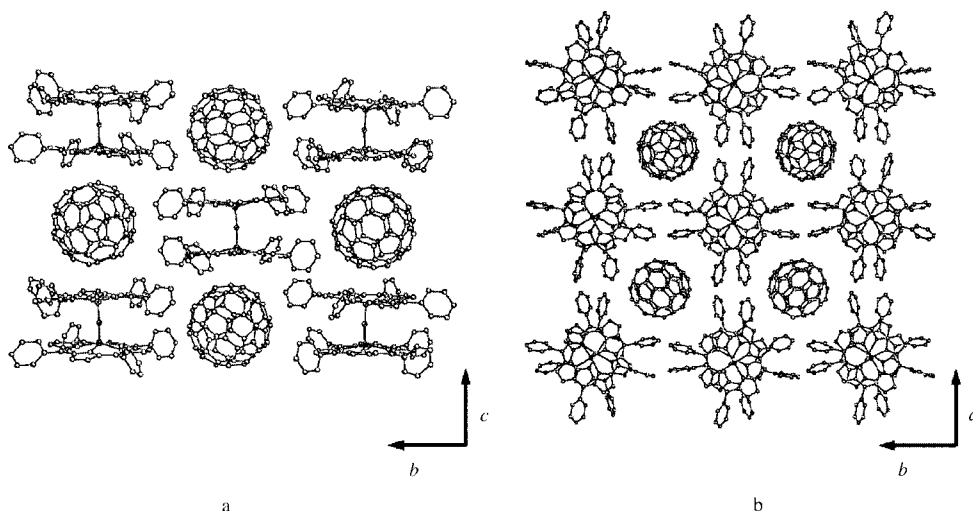
The bond lengths and angles of (Fe^{III}TPP)₂O in **1** are similar to those of the parent compound^[13] (Table 1). The Fe–O–Fe moiety is bent, with an Fe1–O–Fe2 bond angle of 173.7(2)°. Four nitrogen atoms form an almost perfect plane. The Fe1 and Fe2 atoms are displaced from their planes by 0.46 and 0.47 Å, respectively, in the direction of the μ -oxo group. The porphyrin rings are strongly distorted and have a saddle-like conformation. Moreover, the por-

^[a] Institute of Problems of Chemical Physics RAS, Chernogolovka, Moscow region 142432, Russia
Fax: (internat.) +7-096-5155420
E-mail: lyurn@icp.ac.ru

^[b] Department of Chemistry, State University of New York at Buffalo, Buffalo, New York, 14214, USA
Fax: (internat.) +1-716-6456948
E-mail: ayk@buffalo.edu

^[c] A.F. Ioffe Physical-Technical Institute, St.-Petersburg, 194021, Russia,
Fax: (internat.) +7-0812-5156747
E-mail: natalia.drachko@mail.ioffe.ru

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Figure 1. Projections of the crystal structure of **1** along the bc (a) and ab (b) planesTable 1. Bond lengths and angles for parent $(Fe^{III}TPP)_2O$ and for the $(Fe^{III}TPP)_2O$ moieties in **1**

Compound	Fe1–O	Fe2–O	Fe1–Fe2	Fe1–Ct	Fe2–Ct	Fe1–O–Fe2	Torsion angle $N-Fe-Fe'-N'$
$[Fe^{III}TPP]_2O^{[13]}$	1.763	1.763	3.522	0.54	0.54	$174.5(1)^\circ$	35.4°
$[Fe^{III}TPP]_2O \cdot C_{60}$	1.745	1.771	3.511	0.47	0.46	$173.7(2)^\circ$	29.7°

pyrrole rings are rotated about the $Fe-O-Fe$ moiety (the least torsion angle $N-Fe-Fe'-N'$ is 29.7°).

The iron atoms of $(Fe^{III}TPP)_2O$ are located on the other side of the porphyrin macrocycle from the fullerene. Because of this the $Fe \cdots C(C_{60})$ contacts of 3.239–3.513 Å are rather long compared to those in fullerene complexes with other metal-containing porphyrins (2.57–3.12 Å^[5,6,8,19]). In addition to the $Fe \cdots C_{60}$ contacts (Figure 2), the porphyrins form shortened contacts with fullerenes through 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 the van der Waals radii of two C atoms is 3.42 Å and that of a C and an N atom is 3.21 Å.^[20]

Two complexes of C_{60} with Fe^{III} porphyrinates have been structurally characterized (Table 2). Provided the absence of an axial ligand at $Fe^{III}TPP$, a shortened $Fe \cdots C(C_{60})$ contact

of 2.56 Å is observed in $Fe^{III}TPP \cdot [B(C_6F_5)_4] \cdot C_{60} \cdot 2.5C_6H_4Cl_2$ ($C_6H_4Cl_2 = 1,2$ -dichlorobenzene),^[19] while because of the presence of chlorine in octaethylporphyrinatoiron(III) chloride ($Fe^{III}ClOEP$), these contacts are much longer (3.20 Å^[6]) in $Fe^{III}ClOEP \cdot C_{60} \cdot CHCl_3$. In **1** the $Fe \cdots C_{60}$ contacts are close to those in the C_{60} complex with $Fe^{III}ClOEP$. The van der Waals $N(TPP) \cdots C(C_{60})$ and $C(TPP) \cdots C(C_{60})$ contacts have similar values in all three complexes (Table 2). It should be noted that the C_{60} molecules in **1** and in the C_{60} complex with $Fe^{III}TPP \cdot [B(C_6F_5)_4]$ ^[19] are isolated, while in the C_{60} complex with $Fe^{III}ClOEP$ one observes one-dimensional zig-zag chains from C_{60} .^[6]

The IR spectrum of **1** is a superposition of those of the individual components, namely C_{60} and $(Fe^{III}TPP)_2O$. The band for the $F_{1u}(4)$ vibration of C_{60} , which is most sensitive to charge transfer to the C_{60} molecule, is observed at 1427

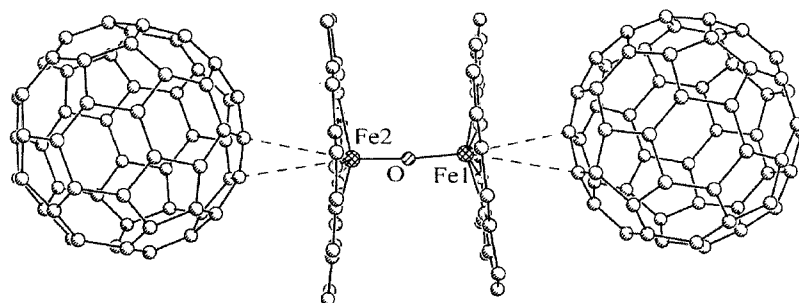
Figure 2. Mutual arrangement of $(Fe^{III}TPP)_2O$ and C_{60} molecules in **1**; phenyl substituents of $(Fe^{III}TPP)_2O$ are not shown

Table 2. Structural data for C₆₀ complexes with Fe^{III}-containing porphyrins

Complex	C ₆₀ order	C ₆₀ ...C ₆₀ centre to center	Fe...Fe	Fe...C(C ₆₀)	N...C(C ₆₀)	C(porphyrin)...C(C ₆₀)
Fe ^{III} CIOEP·C ₆₀ ·CHCl ₃ ^[6]	—	9.94	8.079	3.204–3.371	3.020–3.208	3.237–3.336
Fe ^{III} TPP·[B(C ₆ F ₅) ₄]·C ₆₀ ·2.5C ₆ H ₄ Cl ₂ ^[19]	—	14.43	11.684	2.570–3.413	3.018–3.448	3.263–3.421
(Fe ^{III} TPP) ₂ O·C ₆₀	+	14.20	3.511	3.239–3.513	3.090–3.247	3.245

cm⁻¹ in **1**, and is similar to that in the parent fullerene (1429 cm⁻¹), indicating no noticeable charge transfer. The absorption bands of (Fe^{III}TPP)₂O are slightly shifted in **1** (up to 4 cm⁻¹) relative to the parent porphyrin.

The Vis-NIR reflectance spectra of a single crystal of **1** were measured in two perpendicular polarizations with maximal anisotropy of reflectivity from the most developed face of the crystal (*E*||*c* and *E*⊥*c*). The corresponding absorption spectra in both polarizations (Figure 3) show strong bands attributed to the dipole-allowed electronic transitions in the fullerene: *h_u*→*h_g* and *g_g*,*h_g*→*t_{1u}* at 270 and 343 nm for *E*⊥*c*, and 272 and 335 nm for *E*||*c*. The *E*⊥*c* spectrum also shows strong bands attributed to the absorption of (Fe^{III}TPP)₂O, at 417 and 579 nm, with a shoulder at 615 nm. These bands are red shifted (up to 10 nm) relative to the parent metalloporphyrin indicating a slight change in its initial geometry. In the structure of **1** the (Fe^{II}-TPP)₂O and fullerene molecules alternate in the stacks directed parallel to the crystallographic *c* axis, the planes of the porphyrin macrocycles of (Fe^{III}TPP)₂O being perpendicular to the *c* axis. Consequently, with polarization perpendicular to the porphyrin planes (*E*||*c*), the absorption bands of (Fe^{III}TPP)₂O are absent. A similar anisotropy was observed in the spectrum of Co^{II}TPP·C₆₀·0.5CS₂.^[5] Thus, the absorption spectrum of the complex is a superposition of those of the parent molecules, indicating a neutral ground state in **1**.

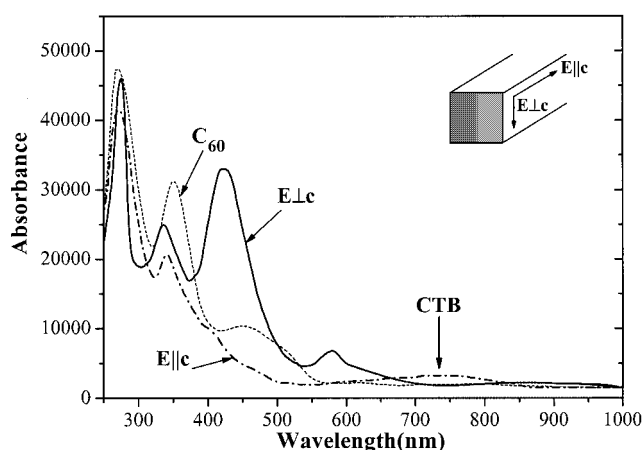


Figure 3. The UV/Visible absorption spectra of a single crystal of **1** for two polarizations of light (*E*||*c* and *E*⊥*c*)

It should be noted that the bands of dipole-allowed transitions of the fullerene (*h_u*→*h_g* and *g_g*,*h_g*→*t_{1u}*) in the spectrum of the complex are narrower than those in the spectrum of a pure fullerene crystal and are shifted to higher

frequencies. In *E*||*c* polarization, the position of the band *g_g*,*h_g*→*t_{1u}* is close to that of the parent C₆₀ molecule (335 nm). The absorption band of C₆₀ at 450 nm is also absent in the spectrum of the complex (Figure 3). Previously,^[21] this band was attributed to intermolecular electron transfer between the adjacent C₆₀ molecules. Indeed, the isolation of fullerene molecules from each other by the (Fe^{III}TPP)₂O ones in **1** results in the absence of the band at 450 nm.

An additional weak absorption is observed in the visible range with a maximum at 720 nm in *E*⊥*c* polarization. This band is also present in the isotropic spectrum of **1** in a KBr matrix and could be evidence of photoinduced charge transfer from (Fe^{III}TPP)₂O to C₆₀. The position of this band is close to that in C₆₀ complexes with (tetraphenylporphyrin)cobalt(II): Co^{II}TPP·C₆₀·0.5CS₂ (750 nm)^[5] and tetrakis(*p*-methoxyphenyl)porphyrincobalt(II): Co^{II}TMPP·(C₆₀)₂·3C₇H₈ (820 nm).^[8] The position of a charge-transfer band (CTB) in a series of complexes with one acceptor is dependent on the ionization potentials of the donors. The ionization potential of (Fe^{III}TPP)₂O is not known. However, metal-containing tetraphenylporphyrins have similar ionization potentials (Fe^{III}TPP·Cl: 6.1±0.2 eV; Co^{II}TPP: 6.1±0.2 eV; Cu^{II}TPP: 6.2±0.2 eV; Mn^{III}TPP: 6.0±0.2 eV^[22]) that can be evidence of a close position of CTB in the complexes with C₆₀.

The EPR behavior of **1** is close to that of parent (Fe^{III}TPP)₂O. EPR signals were not observed at room temperature, whereas upon lowering the temperature down to 77 K, EPR signals with *g* = 5.7 and Δ*H*_{pp} = 200 G appeared in both compounds. The *g* factor of the signal is characteristic of a square-planar complex of Fe^{III} with a high-spin 3d⁵ configuration. A strong exchange interaction between Fe^{III} in the dimer results in the absence of EPR signals at room temperature. However, the temperature decrease seems to cause a freezing of the state with the dihedral N–Fe–Fe'–N angle differing slightly from 180° between the porphyrin planes and results in the appearance of a weak EPR signal.^[23] 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 C₆₀, in agreement with the data of the X-ray analysis. A similar phenomenon was observed earlier for a C₆₀ complex of Fe^{III}CITPP, which also has an EPR spectrum similar to that of starting Fe^{III}CITPP.^[5] It seems that Fe^{III} is shifted from the porphyrin plane to oxygen in **1** as well as to chlorine in Fe^{III}CITPP that hinders the Fe^{III} coordination to C₆₀.

Conclusion

A new complex of C₆₀ with (Fe^{III}TPP)₂O has been synthesized. The complex has a neutral ground state and is formed mainly by van der Waals forces. The neutral ground state and the occurrence of a charge-transfer band in **1** provides for possible photoinduced charge transfer in the complex.

Experimental Section

General Remarks: The IR spectra of the powdered samples pressed in KBr pellets (1:400) were registered with a Perkin–Elmer 1725X spectrophotometer in the 400–7000 cm^{−1} range. Electronic absorption spectra were registered with a Perkin–Elmer Lambda 19 UV/Vis-NIR spectrophotometer in the 220–3000 nm range (KBr pellet, 1:2000). Polarized reflectance spectra of the single crystals were recorded with a microspectroreflectometer equipped with a UV/Vis microscope in the 260–1000 nm range at room temperature. The spectra were measured from one crystal face in two orthogonal directions with the maximal reflectance anisotropy, their orientation relative to the crystal axis was done based on the positions of the polarized absorption bands of the (Fe^{III}TPP)₂O molecule. The absorption spectra were derived from the reflectance ones by the Kramers–Kronig transformation. EPR spectra were registered with a Radiopan SE/X 2547 spectrometer.

(Fe^{III}TPP)₂O·C₆₀ (1**):** Crystals of **1** were obtained by slow evaporation of the solvent from a toluene solution containing 20 mg of C₆₀ and 38 mg of (Fe^{III}TPP)₂O^[24] (1:1 molar ratio) under argon during a week (yield 18 mg, 90%). The composition of the complex was determined by X-ray diffraction on a single crystal.

X-ray Crystallographic Study: X-ray diffraction data for **1**^[17] were collected at 90(1) K using a Bruker SMART1000 CCD diffractometer with a rotating anode source (Mo-K_α radiation, λ = 0.71073 Å), and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. The data were collected by the rotation method with a 0.3° frame-width (ω scan) and 40 sec exposure time per frame. Four sets of data (600 frames in each set) were collected, nominally covering half of the reciprocal space. The data were integrated, scaled, sorted and averaged using the SMART software package.^[25] The structure was solved by the Patterson method using SHELXTL NT Version 5.10.^[26] The structure was refined by full-matrix least-squares against F².

Non-hydrogen atoms were refined in the anisotropic approximation. Anisotropic thermal parameters of several carbon atoms were restrained to behave isotropically. Positions of hydrogen atoms were refined using the “riding” model with U_{iso} = 1.2U_{eq}.

Acknowledgments

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^[17] Crystallographic data for **1**: C₁₄₈H₅₆Fe₂N₈O, M_r = 2073.71 g·mol^{−1}, black parallelepipeds, tetragonal, P-4₂/c, a = 33.1647(9), b = 33.1647(9), c = 16.8998(7) Å, γ = 90°, V = 18588(1) Å³, Z = 8, ρ_{calcd.} = 1.482 g·cm^{−3}, μ = 0.383 mm^{−1}, T = 90(1) K, max. 2θ = 49.7°, R_{int} = 15033 (0.102), Reflections I > 2σ(I) = 10476, R[I > 2σ(I)] = 0.052, wR₂ = 0.162, G.O.F. = 1.095. CCDC-209328 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
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