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Transition from free rotation of C_{70} molecules to static disorder in the molecular C_{70} complex with covalently linked porphyrin dimers: $\{(Fe^{III}TPP)_2O\}\cdot C_{70}$

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ABSTRACT: Fullerene C_{70} and covalently linked porphyrin $(Fe^{III}TPP)_2O$ dimers (TPP: tetraphenylporphyrin) form molecular complex $\{(Fe^{III}TPP)_2O\}\cdot C_{70}$ (**1**). Each C_{70} molecule is sandwiched between two $(Fe^{III}TPP)_2O$ dimers and is surrounded by phenyl groups of four other porphyrin dimers. At 295 K, C_{70} molecules freely rotate about the short axis of the molecule in the *ab* plane. As a result, the disordered C_{70} molecules form spheroids flattened at the poles. The rotation of C_{70} stops near 100 K, resulting in the transition from a tetragonal to a monoclinic unit cell with a four-fold increase in the unit cell volume. In monoclinic phase the C_{70} molecules are located on the axis which coincides with the short axis of the molecule and passes through the midpoints of two oppositely located 6-6 bonds. Since this position has higher symmetry than the own symmetry of C_{70}, it results in statistic disorder of the C_{70} molecules between two orientations. It was shown that multiple Van der Waals contacts with a concave $Fe^{III}TPP$ macrocycle which appear below 100 K, play an important role in the ordering of C_{70}.

KEYWORDS: fullerene C_{70}, $(Fe^{III}TPP)_2O$ dimers, crystal structure, ordering transition.

INTRODUCTION

Fullerenes form a wide variety of donor-acceptor complexes [1–3], among which complexes with metalloporphyrins are of special interest [4–9]. These complexes manifest different crystal structures and charged states of fullerenes (zero [4–8], -1 [9, 10] and even -2 [11]). Metalloporphyrins also form complexes with endometallofullerenes, higher fullerenes and different fullerene derivatives. Thus, their molecular structures can be studied [12–15]. Some ionic fullerene complexes with metalloporphyrins show interesting magnetic transitions associated with the reversible formation of M-C coordination bonds [10]. Metalloporpohyrins with ethyl or phenyl substituents are mainly used for preparation of the complexes with fullerenes [4–11]. The nearly planar shape of porphyrin macrocycles provides close contacts between metal atoms of porphyrins and fullerenes which fix fullerene molecules in the ordered state. Another possibility is co-crystallization of fullerenes with five-coordinated porphyrins. Due to the coordination of an additional ligand to the metal center, a macrocycle in such porphyrins acquires a concave shape conforming well to a nearly spherical shape of fullerene molecules. However, the M(porphyrin)$\cdots$C(fullerene) distances are essentially increased in such complexes. Five-coordinated porphyrins are formed with monodentant, bidentant or tetradentant *N*-containing ligands. For example, zinc tetraphenylporphyrin (ZnTPP) forms monomers with pyridine and tetramethylethylenediamine; dimers with pyrazine, 4,4′-bipyridine (BPy) and *N,N′*-dimethylpyperazine (DMP); and pentamers with tetrapyridylporphyrin, which were further cocrystallized with C_{60} [16–18]. Zinc octaethylporphyrin $(ZnOEP)_2\cdot BPy$ dimers and (MOEP·DABCO) monomers (M: Zn and Co^{II}; DABCO: diazabicyclooctane) were also found to form ionic and molecular complexes with C_{60} [19, 20]. Fullerene complexes with five-coordinated porphyrins can be promising components in the design of photoactive materials since they show intense

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charge transfer (CT) bands in the visible range, indicating effective HOMO-LUMO overlapping of concave porphyrin surface and spherical C_{60} molecules. Fullerene complexes with four-coordinated porphyrins manifest weaker CT bands or they can be absent [6, 7, 10]. Additionally to coordinatively bound porphyrin assemblies, various covalently bonded dimers are known where bridging atoms can be O [21], N [22], C [23] and even two OH groups [24]. Some of these dimers form complexes with C_{60}: $(Fe^{III}OEP)_2O{\cdot}C_{60}{\cdot}C_6H_6$ [25], $\{(Fe^{III}TPP)_2O\}{\cdot}C_{60}$ [26] and $\{(Yb^{III}TPP{\cdot}OH)_2{\cdot}\,(THF)\}{\cdot}C_{60}$ [24].

However, complexes of fullerene C_{70} with either coordinatively or covalently linked porphyrin dimers are not known so far. In contrast to the spherical shape of C_{60}, C_{70} molecules have ellipsoidal shape and lower symmetry. In this work, for the first time, molecular complex of C_{70}: $\{(Fe^{III}TPP)_2O\}{\cdot}C_{70}$ (**1**) is obtained and its crystal structure is determined at room temperature (RT = 295(2) K) and 100(2) K. We found unusual rotation of the C_{70} molecules at RT and the transition from free rotation to statistic is disorder at 100 K, accompanied by changing of the unit cell from tetragonal to monoclinic and an increase in the unit cell volume. The effect of Van der Waals contacts between the $Fe^{III}TPP$ macrocycles and the C_{70} molecules to fix the free rotation of C_{70} molecules is discussed.

EXPERIMENTAL

Materials

$(Fe^{III}TPP)_2O$ was prepared according to reference 21. C_{70} of 99% purity was received from MTR Ltd. Solvents were purified in argon atmosphere. *o*-dichlorobenzene ($C_6H_4Cl_2$) was distilled over CaH_2 under reduced pressure and hexane was distilled over Na/benzophenone.

Synthesis

The crystals of **1** were obtained by diffusion. C_{70} (25 mg, 0.030 mmol) and one molar equivalent of $(Fe^{III}TPP)_2O$ were dissolved in 14 mL of $C_6H_4Cl_2$ under heating at 60 °C for two hours. The mixture was cooled, filtered in a 50 mL glass tube of 1.8 cm diameter with a ground glass plug, and 30 mL of hexane was layered over the solution. The diffusion was carried out for one month for the crystals of **1** to form on the wall of the tube. The solvent was decanted from the crystals, which were washed with hexane to give black prisms with a characteristic blue luster (up to $0.5 \times 0.5 \times 0.5$ mm^3 in size) in 40% yield. The composition of the complex was determined from X-ray diffraction on a single crystal: $\{(Fe^{III}TPP)_2O\}{\cdot}C_{70}$ (**1**). Several single crystals selected from the synthesis had the same unit cell parameters.

X-ray crystal structure determination

Crystal data of **1** at room temperature (295(2) K): $C_{158}H_{56}N_8Fe_2O$, M_r = 2193.81 mol^{-1}, black prisms, tetragonal, P 4/nnc, a = 16.9395(3), b = 16.9395(3), c = 17.3012 (5) Å, V = 4954.52(19) Å^3, Z = 2, d_{calc} = 1.468 g.cm^{-3}, μ = 0.363 mm^{-1}, F(000) = 2240, max. $2\theta_{max}$ = 56.56°, reflections measured 17890, unique reflections 2974, reflections with $I > 2\sigma(I)$ = 1932, parameters refined 287, R_1 = 0.0426, wR_2 = 0.1327, G.O.F. = 1.030. CCDC reference number is 731740.

Crystal data of **1** at 100(2) K: $C_{158}H_{56}N_8Fe_2O$, M_r = 2193.81 mol^{-1}, black prisms, monoclinic, I 1 1 2/b, a = 23.8192(8), b = 23.8192(8), c = 34.1855(11) Å, α = 90.00(2), β = 90.00(2), γ = 90.10(2)°, V = 19395.3(11) Å^3, Z = 8, d_{calc} = 1.503 g.cm^{-3}, μ = 0.372 mm^{-1}, F(000) = 8960, max. $2\theta_{max}$ = 57.40°, 92762 reflections measured, 24825 unique reflections, reflections with $I > 2\sigma(I)$ = 14034, 2157 refined parameters, 1785 restrains, R_1 = 0.0482, wR_2 = 0.1571, G.O.F. = 1.048. CCDC reference number is 731741.

The intensity data for the structural analysis were collected on an Oxford Diffraction Gemini-R CCD diffractometer with graphite monochromated MoK_α radiation using an Oxford Instrument Cryojet system. Raw data reduction to F^2 was carried out using CrysAlis Pro from Oxford Diffraction Ltd. The structures were solved by direct method and refined by the full-matrix least-squares method against F^2 using SHELX-97 [27]. Non-hydrogen atoms were refined in the anisotropic approximation for $(Fe^{III}TPP)_2O$ and isotropic approximation for the disordered C_{70} molecules. Positions of hydrogen atoms were calculated geometrically. Subsequently, the positions of H atoms were refined by the "riding" model with U_{iso} = 1.2 U_{eq} of the connected non-hydrogen atom.

RESULTS AND DISCUSSION

The crystals of $\{(Fe^{III}TPP)_2O\}{\cdot}C_{70}$ (**1**) were obtained by diffusion of hexane into *o*-dichlorobenzene solution containing C_{70} and $(Fe^{III}TPP)_2O$. After one month, the solvent was decanted and crystals were washed with hexane. The composition of **1** was determined from X-ray diffraction on a single crystal. Several single crystals tested from the synthesis had the same unit cell parameters.

Complex **1** at room temperature (RT) has a high-symmetry tetragonal unit cell (Fig. 1). C_{70} molecules are disordered and this disorder was approximated by 280 carbon atoms with the 0.25 occupancies. Disordered C_{70} reproduces rotating ellipsoid. Therefore, C_{70} molecules nearly freely rotate at room temperature. Phenyl substituents of $Fe^{III}TPP$ are statistically disordered between two orientations (only one orientation is shown in Fig. 1). The complex contains chains of alternating C_{70} molecules and $(Fe^{III}TPP)_2O$ dimers (Fig. 1a). Since $Fe^{III}TPP$ macrocycles have a concave shape, two of them form a cavity suitable for the accommodation of ellipsoidal C_{70}, and each C_{70} is sandwiched between two porphyrin dimers. There are only two Van der Waals contacts between the $Fe^{III}TPP$ macrocycle and C_{70}, whereas the $Fe{\cdots}C(C_{70})$ contacts are longer than 3.6 Å. Each C_{70} is surrounded by

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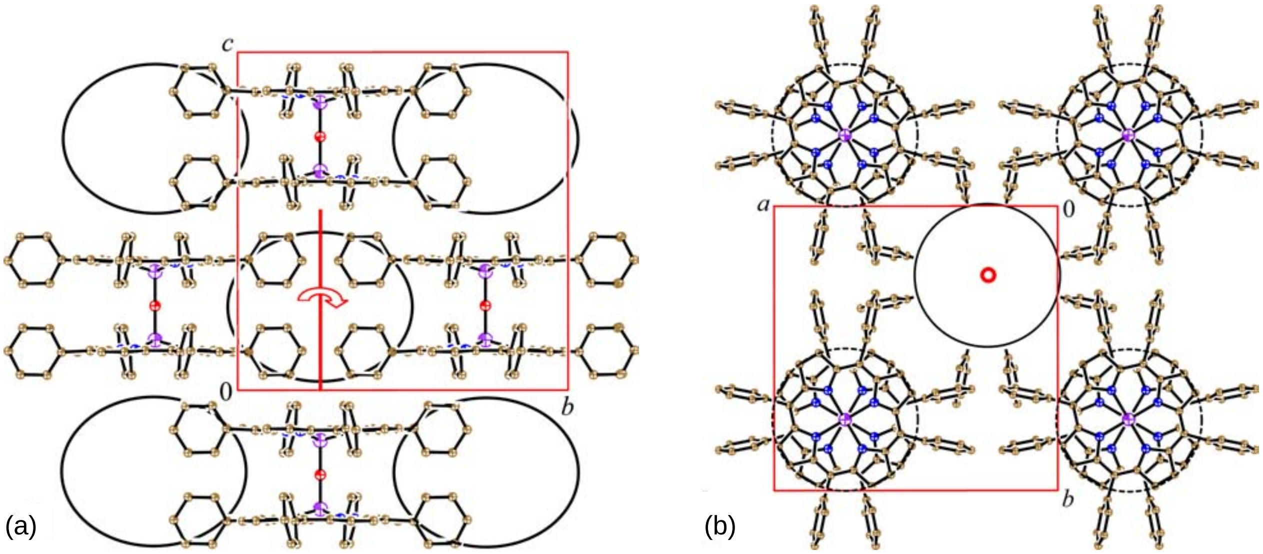

Fig. 1. View of the crystal structure of **1** along the crystallographic (a) *a*- and (b) *c*-axes at 295(2) K. Rotating C_{70} molecules are shown by ellipses and circles. The position of the axis about which the C_{70} molecules rotate is shown by line and circle

phenyl groups of four other $(Fe^{III}TPP)_2O$ dimers. Totally eight phenyl groups surround each C_{70} (Fig. 1b) and these phenyl groups form several Van der Waals C···C contacts with C_{70}. The cavities formed by the $(Fe^{III}TPP)_2O$ dimers are large and, due to a limited number of Van der Waals contacts with surrounding, C_{70} molecules freely rotate in the *ab* plane about the short axis of the molecule (Fig. 2a,b). Due to such unusual rotation, C_{70} forms large spheroid flattened at the poles. The side view on the spheroid is of an ellipse and the top view on the spheroid is of a circle of 7.96 Å in diameter (Figs 1 and 2a). C_{60} has a nearly spherical shape and can rotate in any direction in the complexes. As a result, different types of C_{60} disorder exist [7]. An ellipsoid-shaped C_{70} is generally disordered rotating about the long axis of the molecule [7], which is perpendicular to the short axis (Fig. 2b). For rotation about the short axis, larger space is needed than C_{70} occupies by itself. Close surrounding of C_{70} by donor and solvent molecules makes such rotation impossible in the complexes. Only in **1** the large cavity allows such type of rotation. Due to the ellipsoidal shape of C_{70} rotation about the short axis results in the location of its carbon atoms at different distances from the rotation axis (from 3.53 to 4.14 Å).

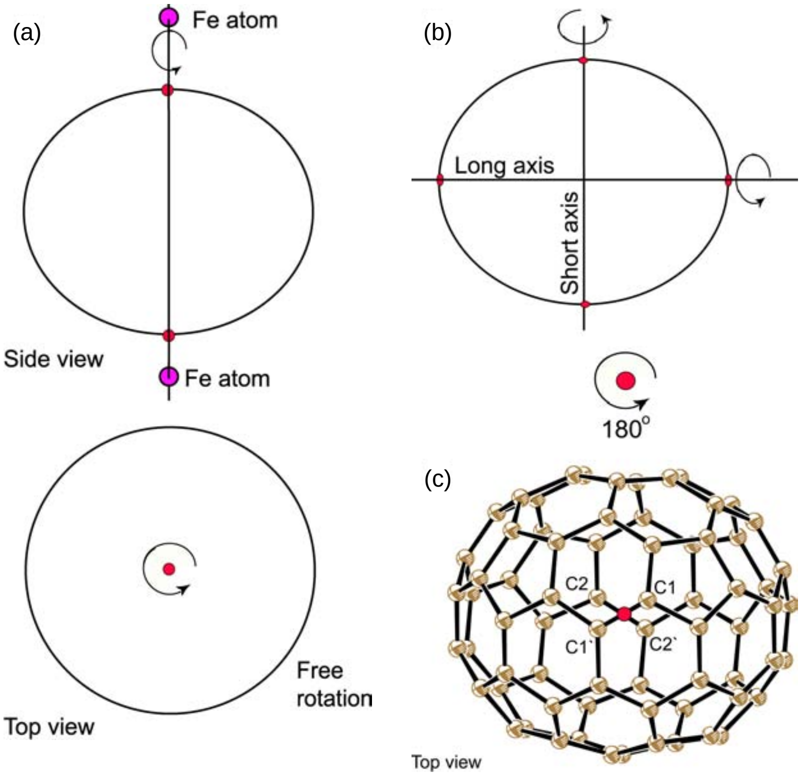

Fig. 2. Disorder of the C_{70} molecules in **1**. (a) Free rotation about the short axis at 295(2) K, (b) rotation about the short and long axes of the molecule, and (c) static disorder of the C_{70} molecule at 100(2) K. Spots show the points through which the rotation axis is passed

Crystal structure of a low-temperature phase was studied at 100(2) K. Free rotation of C_{70} stopped at this temperature. There is a transition from the tetragonal unit cell to the monoclinic one, with a four-fold increase in the unit cell volume. In the new structure, two crystallographically independent halves of C_{70} and $(Fe^{III}TPP)_2O$ moieties are present. Crystallographically independent C_{70} molecules are

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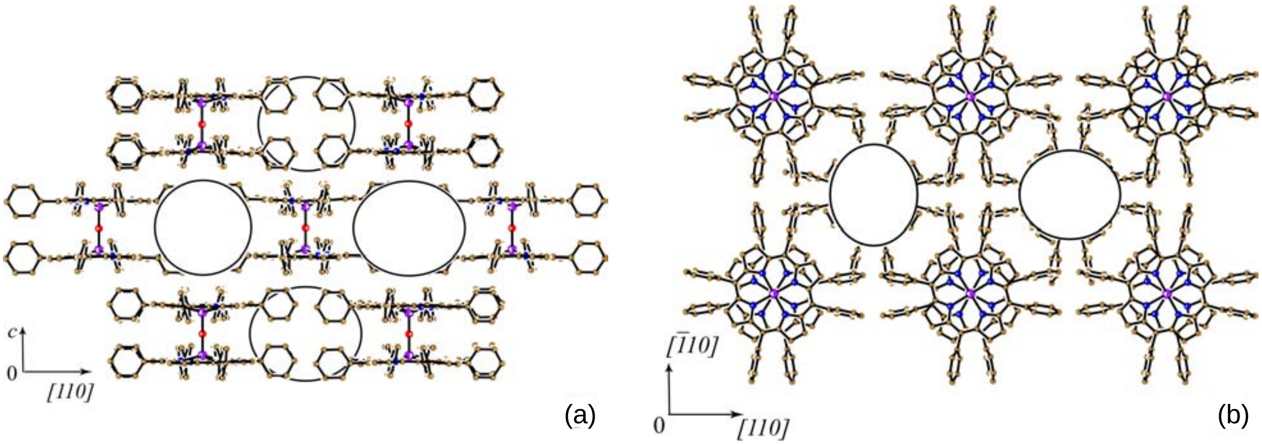

Fig. 3. View of the crystal structure of **1** (a) along the porphyrin macrocycles and (b) on the porphyrin macrocycles at 100(2) K. Disordered C_{70} molecules are shown by ellipses and circles

arranged perpendicular to each other in the cavities formed by $(Fe^{III}TPP)_2O$ (Fig. 3). The size of the cavities decreases at 100 K (the volumes of the cavities are 961 Å^3 at room temperature and 926 Å^3 and 936 Å^3 at 100 K) and provides the appearance of new Van der Waals contacts between Fe^{III}TPP macrocycle and C_{70}. The Fe···C(C_{70}) contacts of 3.31–3.32 Å are essentially shorter than those at 295 K. The N···C(C_{70}) and C···C(C_{70}) contacts are 3.085–3.119 and 3.296–3.396 Å, respectively, and several C(phenyl rings of Fe^{III}TPP)···C(C_{70}) contacts of 3.10–3.39 Å are formed. Most probably, the appearance of multiple Van der Waals contacts stops the rotation of C_{70}. The observed Fe···C(C_{70}) contacts in **1** at 100 K are close to the distances in the C_{60} complexes, with five-coordinated porphyrins: $(Fe^{III}TPP)_2O$, 3.23–3.51 Å [26] and Fe^{III}OEPCl, 3.20–3.37 Å [4]. These distances are essentially longer than those in the complexes with four-coordinared planar porphyrins: Fe^{III}TPP and Fe^{II}OEP, 2.57–3.41 Å [28, 20].

In spite of the absence of free rotation, the C_{70} molecules are still disordered at 100 K. However, this disorder is due to low symmetry of the molecule. The symmetry of the C_{70} position in **1** is higher than the own symmetry of the molecule; this results in statistic disorder between the two orientations (Fig. 2c). It should be noted that C_{60} molecules are located on the same high-symmetry position in $\{(Fe^{III}TPP)_2O\}\cdot C_{60}$ [26]. However, due to higher symmetry of the molecules, they are ordered at 90 K.

The geometry of the $(Fe^{III}TPP)_2O$ dimers changes insignificantly at complex formation with C_{70} (Table 1). A Fe-O-Fe bond angle in **1** is 180°, whereas such angles are 173–174° for $(Fe^{III}TPP)_2O$ in the complex with C_{60} and in individual state. The deviation of the Fe^{III} atoms from the mean plane of four nitrogen atoms decreases noticeably at complex formation with fullerenes (0.47–0.49 Å) in comparison with individual $(Fe^{III}TPP)_2O$ (0.54 Å). The Fe-N(TPP) distances are large (2.078–2.085(1) Å), indicating the high-spin (S = 5/2) state of Fe^{III}TPP and was proven by EPR measurements for $\{(Fe^{III}TPP)_2O\}\cdot C_{60}$ [26].

CONCLUSION

The C_{70} complex with covalently linked porphyrin dimers $(Fe^{III}TPP)_2O$ was obtained for the first time. The complex demonstrates new types of C_{70} disorder when it nearly freely rotates at 295 K about a short axis. As a result, a spheroidal top view of C_{70} and an ellipsoidal side view are observed. Free C_{70} rotation stops at 100 K

Table 1. Geometric parameters of individual $(Fe^{III}TPP)_2O$ dimers and the dimers in the complexes with C_{60} and C_{70}

Compound	Fe-N(TPP)$_{av}$	Fe-O$_{av}$	Fe···Fe	Fe-Ct, Å^a	Fe-O-Fe,°	Dehedral, N-Fe-Fe-N,°
$(Fe^{III}TPP)_2O$ [21]		1.763(1)	3.522	0.54	174.5(1)	35.4
$\{(Fe^{III}TPP)_2O\}\cdot C_{60}$	2.079(1)	1.745(1)	3.511	0.469 (0.509)	173.7(2)	29.7
90 K [26]	2.078(1)	1.771(1)		0.465 (0.505)		
$\{(Fe^{III}TPP)_2O\}\cdot C_{70}$	2.078(1)	1.755(1)	3.510	0.491 (0.548)	180.0(2)	29.0
295 K, this work						
$\{(Fe^{III}TPP)_2O\}\cdot C_{70}$	2.078(1)	1.757(1)	3.514	0.474 (0.519)	180.0(2)	29.3
100 K, this work	2.085(1)			0.478 (0.538)		

^{a} The deviation of the Fe^{III} atoms from the plane of four nitrogen atoms and the mean 24-atom plane (in brackets).

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and there is a transition from a tetragonal to a monoclinic unit cell accompanied by the four-fold increase in the unit cell volume. The disorder of C_{70} between two orientations exists even at 100 K. However, this disorder is associated with low symmetry of the C_{70} molecule since it is located in a high-symmetry position. The C_{60} molecules are located on the same high-symmetry position in $\{(Fe^{III}TPP)_2O\}\cdot C_{60}$ but are ordered at 90 K [26]. Rotation of C_{70} becomes possible due to large cavities formed by the $(Fe^{III}TPP)_2O$ dimers and the absence of Van der Waals contact with the environment. At low temperatures, the size of these vacancies decreases and additional Van der Waals contacts appear to stop free rotation of the C_{70} molecules.

Acknowledgements

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Supporting information

Crystallographic data in CIF format for complex **1** at 100(2) and 295(2) K is given in the supplementary material. This material is available free of charge at http://www.worldscinet.com/jpp/jpp.shtml. These data have been deposited at the CCDC (deposition numbers 731740 and 731741). Copies can be obtained on request, free of charge, *via* www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

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