Crystallographic characterization and identification of a minor isomer of C_{84} fullerene†

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We report the synthesis and single crystal X-ray analysis of C_{84} (14)·AgTPP (Ag tetraphenylporphyrin) cocrystal—the first ordered crystal structure containing a pristine higher fullerene.

Since higher fullerenes were discovered,[1–3] it has been shown that the existence of several structural isomers significantly complicates their investigation as well as their structure determination. C_{84} has 24 possible isomers obeying the isolated pentagon rule (IPR),[4] ten of which have been isolated to date. The two most abundant are C_{84}-D_{2d} and C_{84}-D_2. C_{84}-D_{2d} possesses a unique ^{13}C NMR pattern and was determined as isomer **23** (the numbering of isomers is according to ref. 4).[5–8] C_{84}-D_2 was identified as isomer **22** according to a 2D-NMR measurement.[9] Two minor isomers C_{84}-D_{3d} and C_{84}-D_{6h} were obtained employing the arc-discharge technique using Gd as a catalyst and identified as **24** and **19** according to their distinctive NMR patterns.[10] One of the five possible C_{84}-C_2 isomers was obtained using Dy as a catalyst, however its structure remained unexplored.[11] The isolation of five other minor isomers was achieved using multistage recycling HPLC.[12] From these five species only D_{2d} has been unambiguously identified as isomer **4**, whereas the others (C_2, D_2, and two C_s) were only ascribed to point group symmetries. NMR analyses of the two C_s isomers indicate that they correspond to isomers **14** and **16** (Fig. 1). Since a strict assignment cannot be made on the basis of one-dimensional ^{13}C NMR data, the two discovered C_s isomers were provisionally assigned as C_s(a) and C_s(b).[12] Subsequent confirmation of their structures was made on the basis of electrochemical properties together with density functional theory (DFT) calculations.[13] The calculated energy levels were found to be in a good agreement with the experimentally determined redox potentials, which made it possible to assign C_{84}-C_s(b) to **16**, and C_{84}-C_s(a) to **14**. On the other hand, a detailed analysis of experimental and theoretically predicted ^{13}C-NMR spectra, has lead to the opposite assignment for the C_s isomers (C_s(a) – **16**, C_s(b) – **14**).[14] The theoretical calculations of the relative stabilities additionally confirm this assignment since isomer **16** is more stable than isomer **14**, and therefore represents the more abundant fullerene.[15–17]

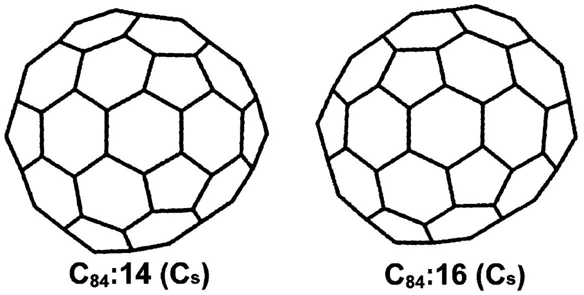
C_{84}:14 (C_s) C_{84}:16 (C_s)

Fig. 1 Two IPR isomers of C_{84} (C_s) fullerene having the same NMR pattern (2 × 1, 41 × 2). Isomer numbering follows ref. 4.

Since both indirect approaches have given contradictory results, the structures of C_s(a) and C_s(b) isomers remain unsettled. A direct method of structure determination, such as X-ray crystallography, is envisaged to solve the query of a single isomer recognition. However, owing to the virtually spherical shape of all fullerenes and their high mobility in the crystal lattice, the quality of fullerene crystals is generally poor. As a result, no ordered crystal structures of pristine fullerenes, except C_{60} and C_{70}, have been reported up to now.[18] Recently, we have shown that the temperature difference technique (TDT)[19–21] is a convenient and effective method for the growth of fullerene–metalloporphyrine cocrystals suitable for single crystal X-ray measurements even from small amounts of starting material.[22] Herein we report the synthesis and single crystal X-ray analysis of C_{84}-C_s(b) fullerene with AgTPP, which represents the first fully ordered crystal structure of a pristine higher fullerene. The X-ray data analysis allowed us to determine the connectivity pattern of C_{84}-C_s(b) and unambiguously identify this isomer.

Fullerene soot was produced along the RF-furnace route.[23,24] The isolation of the pure C_{84}-C_s(b) isomer was achieved by multistage HPLC. In the first step, a fraction containing different C_{84} fullerenes was obtained using Buckyprep column and toluene as a mobile phase. In the second step, recycling using 5PYE column and toluene as a mobile phase gave pure C_{84}-C_s isomer which was assigned to C_{84}-C_s(b), according to a previous work.[12] The fullerene co-crystal was obtained from the mixture of C_{84}-C_s(b) (*ca.* 0.1 mg in 0.1 ml of benzene) and 2 ml of saturated solution of AgTPP in benzene using the TDT. AgTPP was synthesized from

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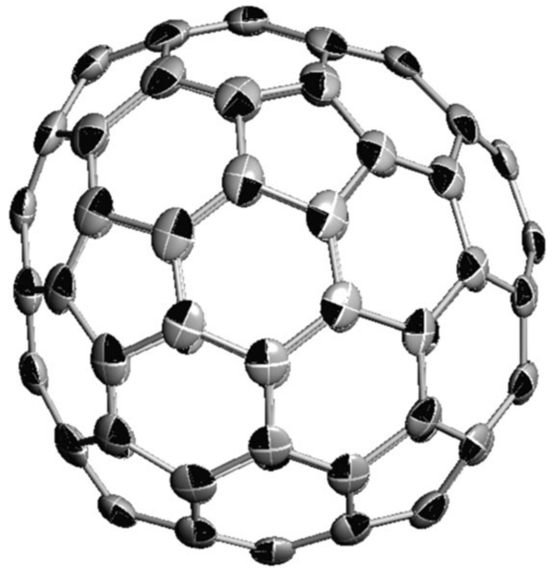

Fig. 2 ORTEP projection of the molecular structure of C_{84}(**14**) in the crystal. Thermal ellipsoids are drawn at 50% probability level.

tetraphenylporphyrin according to the known procedure.[25] X-ray diffraction data were collected using a Bruker three circle diffractometer SMART 6000 CCD, detector Osmic "blue" mirror CMF12-38Cu6, MacScience rotating anode ($Cu_{k\alpha}$ radiation λ = 1.54178 Å).‡ The crystal structure was solved and all atoms refined in the anisotropic approximation using SHELXTL.[26] Quantum chemical calculations were performed using the DFT method of B3LYP/6-31G with Gaussian 03.[27]

Under TDT crystallization conditions, the C_{84}-C_s(b) fullerene forms black pseudo-tetragonal crystals (C_{84}-C_s·AgTPP·C_6H_6) in the triclinic space group $P\bar{1}$. Analysis of the crystal structure precisely attributes C_s(b) fullerene to isomer **14**. According to the ORTEP projection of C_{84} (Fig. 2), the carbon atoms are characterized by rather small thermal ellipsoids which reflect the high efficiency of fullerene fixation in the crystal lattice.

The resolution achieved is good enough not only to identify precisely the connectivity pattern of the fullerene cage, but also to extract bond length data with high accuracy. As can be seen from Fig. 3, the bond length distribution shows a good correlation with the one predicted by DFT calculations. Some deviation is observed only for the short C–C bonds, for which the values are even smaller than the predicted ones and almost reach 1.34 Å, typical for common double bonds. The C–C bond lengths in C_{84}(**14**) depend on the type of fragment in which they are incorporated. In first approximation, four different fragments can be recognized as presented in Fig. 3. The shortest bonds (1.34–1.38 Å) correspond to the bonds between two pentagons in the pyracylene fragments, the longest ones (1.46–1.48 Å) are involved in pyrene fragments. Interestingly, decreasing the number of pentagons in the fragments leads to significant elongation of the corresponding bond in comparison with the aromatic bond length (1.40 Å), despite the geometry in these fragments being more suitable for effective conjugation.

The molecular packing in the cocrystal shows a remarkably high degree of π-stacking interactions. The fullerene cage forms a sandwich complex with two AgTPPs with short Ag–fullerene distances of 2.96 Å and 3.07 Å. This indicates a significant interaction between the π-systems of fullerenes and porphyrin moieties. At the same time, each porphyrin is involved in contacts with two fullerene molecules. Such a coordination leads to the formation of fullerene porphyrin chains extending along [011] (Fig. 4). On the other hand, the fullerenes are aligned in double columnar arrays along [100] (Fig. 4), a very rare structural motif.[28,29] The intermolecular distances between fullerene molecules are short enough (2.95 Å and 3.40 Å) to conclude that an efficient overlapping of the p-orbitals takes place. Thus, all fullerene molecules, as well as all porphyrins, interact with one another and appear to form a common 3-dimensional π-system covering the whole crystal. Such crystal packing is interesting not only from the theoretical point of view but is also prospective for various applications. As an example, this geometry is very promising for the construction of organic single crystal field-effect transistors (FETs), since the 3-dimensional π-stacking can solve the problem of injection of charge carriers into the conducting channel of the FET.[30–32] In contrast, in materials commonly used for the fabrication of FETs, the π–π stacking of the molecules only extends in one direction. Since the injection of carriers into the crystal usually takes place perpendicular to this direction, sizeable power is lost (*i.e.* there is a high contact resistance) due to the lack of three dimensional π–π stacking.[30]

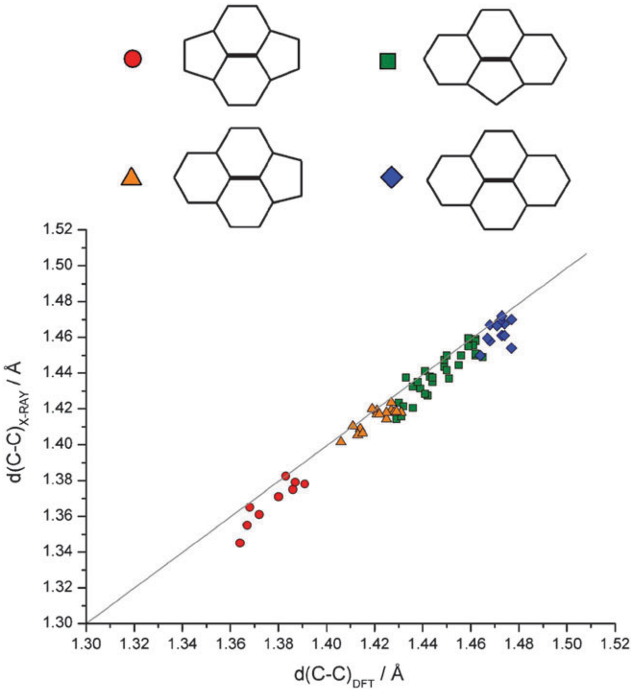

Fig. 3 Correlation between the experimentally obtained and the DFT calculated C–C bond distances in C_{84}(**14**). Correlation between the C–C bond length and the type of fragment in which the corresponding bonds are involved (the bonds under consideration are shown in bold).

In summary, a fully ordered crystal structure containing a pristine higher fullerene was obtained for the first time. The carbon connectivity pattern of the C_{84}-C_s(b) isomer has been unambiguously determined by means of single crystal X-ray analysis and has provided the possibility to attribute this molecule to C_{84}(**14**). Accordingly, the previously separated

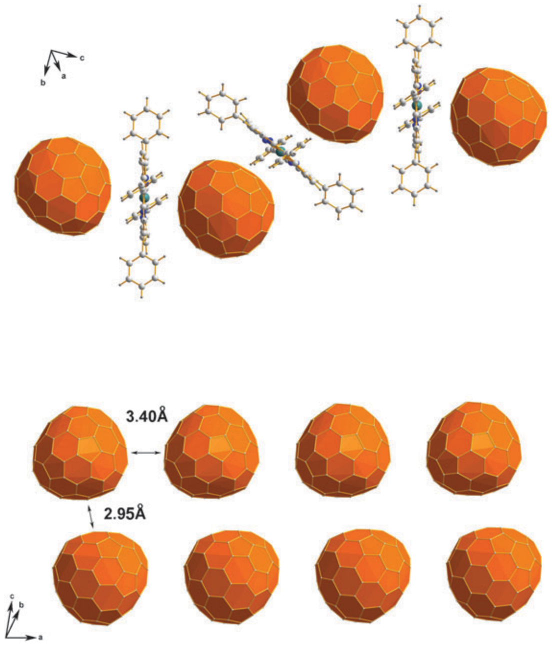

Fig. 4 Extended π–π stacking within C_{84}(**14**)·AgTPP·C_6H_6 crystal. The fullerene porphyrin chains along [011] (top) and columnar arrangement of C_{84}(**14**) along [100] with short intermolecular C···C contacts (bottom).

isomer, C_{84}-C_s(a), has to be addressed as isomer **16**. The results obtained confirm an earlier isomer assignment made on the base of comparison of the experimentally obtained chemical shifts with DFT-calculated ones,[14] and corroborated the effectiveness of this approach for recognition of higher fullerene isomers. Since metalloporphyrins appear to be universal co-crystallization agents capable to form crystals of good quality with higher pristine fullerenes, we are optimistic, that the proposed crystallization technique would provide the possibility to obtain good quality crystals and to characterize other higher fullerenes which are available thus far only in very small amounts.

Notes and references

‡ Crystal data. C_{84}·AgTPP·C_6H_6, $M = 1807.52$, triclinic, space group $P\bar{1}$, $a = 11.9115(11)$, $b = 14.4879(14)$, $c = 22.244(2)$ Å; $\alpha = 81.668(6)$, $\beta = 80.692(5)$, $\gamma = 77.854(5)°$, $U = 3678.9(6)$ Å^3, $Z = 2$, $T = 100(2)$ K, $2\theta_{max} = 137.86°$; $-14 < h < 14$, $-17 < k < 17$, $-26 < l < 26$, $\lambda = 1.54178$ Å, 54 440 reflections measured, 12 983 unique ($R_{int} = 0.052$), 10 576 reflections observed, 1225 parameters, $R_1 = 0.040$ (observed data), $wR_2 = 0.107$ (all data). CCDC 684824.†

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